CHEMICAL THERMODYNAMICS

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CHEMICAL THERMODYNAMICS OF IRON

Part 1

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BETTER POLICIES FOR BETTER LIVES

TΔB
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NEA
NUCLEAR ENERGY AGENCY

CHEMICAL THERMODYNAMICS OF IRON

PART 1

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Vol. 12. Chemical Thermodynamics of Tin, OECD Nuclear Energy Agency Data Bank, Eds., OECD Publications, Paris, France, (2012).

Preface

Volume 13a of the “Chemical Thermodynamics” (TDB) series, edited by the OECD Nuclear Energy Agency (NEA), is the first of two volumes describing the selection of chemical thermodynamic data for species of iron. After an initiation report for iron was presented to the NEA in late 2004, it was decided (and confirmed in 2008) that because of the voluminous information in the literature, it would be more efficient to prepare the review in two (unequal) parts. This larger first part contains assessments of data for the metal, simple ions, aqueous hydroxido, chlorido, sulfido, sulfato and carbonato complexes, and for solid oxides and hydroxides, halides, sulfates, carbonates and simple silicates. As this volume goes to press, work is well underway on the second part of the review, which will provide assessments of data for other aqueous halido species, sulfide solids, and solid and solution species with nitrate, phosphate and arsenate, as well as address some aspects of solid solutions in iron-oxide and iron-sulfide systems.

Originally the iron Review Team included Urs Berner, Robert Lemire (chairperson), Claude Musikas, Donald Palmer, Nobuaki Sato and Peter Taylor, with Kastriot Spahiu as the NEA TDB Executive Group Liaison. A first meeting of the Review Team was held at the NEA offices in Issy-les-Moulineaux, France in February 2005. Subsequent meetings were held in Toronto, Canada in December 2005, and again in Issy-les-Moulineaux in July 2006 and February 2007. In mid-2007, time constraints and the pressure of other commitments forced Nobuaki Sato to resign from the Review Team, and Osamu Tochiyama joined as a new member. A final sub-group meeting was held at Issy-les-Moulineaux in February 2008. Editorial work was done in late 2008 and through 2009, and the draft was submitted for peer review in January 2010. By the time the peer review comments were received and addressed, several of the members of the iron Review Team were already involved in new NEA reviews or had other commitments. Also, resources at the NEA have been limited. Therefore, it has taken considerable time to put this volume into its final form. The co-ordination of the iron project at the NEA was initially done by Federico Mompean, and between 2008 and 2010 by Mireille Defranceschi. Since then, Jane Perrone has taken on the duties of co-ordinator, and from the beginning of the project in 2005 she also carried out the arduous task of incorporating the drafts submitted by the iron team into the full manuscript. Without her persistence, it is doubtful whether this work would have been published.

Although almost all of the final Review Team members contributed text and comments to several of the chapters, primary responsibility for the different chapters was divided as follows: Peter Taylor for the section on oxides, Urs Berner for the sections on iron(II) complexes with chloride, fluoride, sulfate and carbonate, Osamu Tochiyama for the section on iron sulfide complexes, Claude Musikas for the sections on the electrochemistry of the aquo ions and the iron(III) complexes with chloride, sulfate and carbonate, Donald Palmer for the sections on hydrolysis and, with the chairman, for other sections on the aquo ions. The chairman took the lead for the sections on iron metal and the halide, sulfate, carbonate and silicate solids, and also was the main author for the section on resolution of inconsistent values from different chemical thermodynamic cycles.

As is the case with databases for many other elements, “key” iron-species values are often based on very limited experimental values. For example, careful studies of the Fe(III)/Fe(II) couple as a function of ionic medium are surprisingly sparse, and most are rather dated. A further complication has been that many of the experimentally determined thermodynamic quantities for different iron species are related. To maintain database consistency it was necessary to consider many of these quantities together as part of the related chemical thermodynamic cycles (*cf*. Chapter XI). After an initial consistency calculation, three of the experimental results were reassessed, and minor adjustments were made to four other assessed uncertainties to generate a final set of selected values. These selected values are consistent with the input experimental quantities within the stated uncertainties.

Any chemical thermodynamic database does no more than represent a survey of what is known at a particular time. The time required to carefully compile and consider data dictates that any database is at least slightly “out-of-date” when it appears in print. The current version is no exception. Although an arbitrary cut-off date of 2008 was set for papers used in this review, a few later papers have been included. Unfortunately, despite extensive literature searches, it is likely that a few significant earlier papers have been missed; some of these may be reviewed in TDB Iron Part 2.

Deep River, Canada, March 2013 Robert J. Lemire, Chairman

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The authors wish to thank the TDB III Management Board, Executive Committee and the staff at the OECD Nuclear Energy Agency Data Bank for shepherding this volume to completion. In particular we are grateful for the assistance of Jane Perrone, who has worked with us throughout the iron review, initially as volume editor and finally as series editor and project co-ordinator.

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The entire manuscript has undergone a peer review by an independent, international group of reviewers, according to the procedures in the TDB-6 Guidelines, available from the NEA. The peer reviewers have 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 NEA. The peer reviewers were Professor Juraj Majzlan (Institute of Earth Sciences, Jena, Germany), Dr. Valérie Moulin (CEA, Saclay, France), and Professor R. Fernández-Prini (University of Buenos Aires, Argentina). Their valuable contributions to this review are gratefully acknowledged.

Editor's note

This is the 13th volume of a series of expert reviews of the chemical thermodynamics of key chemical elements in nuclear technology and waste management. This volume is the first part of a review devoted to the inorganic species and compounds of Iron. 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 is available at www.oecd-nea.org. Selected data and computer programs, as well as many documents in electronic format, can also be found on the NEA website.

To contact the TDB Project co-ordinator or the authors of the review reports, send comments on the TDB reviews or request further information, please send e-mails to tdb@oecd-nea.org or write to:

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Part 1

Introductory material

Chapter I

Introduction

I.1 Background

In the field of radioactive waste management, the hazardous material consists to a large extent of actinides, fission products and activation 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 to establish a reliable thermochemical database that fulfils the requirements for proper modelling of the behaviour of actinides and fission products in the environment.

Between 1963 and 1967, the International Atomic Energy Agency (IAEA) in Vienna published three technical reports with thermochemical assessments of the nuclear fuel systems: U-C and Pu-C [1963IAE], UO_2 and related phases [1965IAE], and Pu-O and U-Pu-O [1967IAE]. These reports were followed by nine special issues of Atomic Energy Review with compilations of physicochemical properties of compounds and alloys of elements important in reactor technology: Pu, Nb, Ta, Be, Th, Zr, Mo, Hf and Ti. In 1976, the IAEA also started publication of the series “The Chemical Thermodynamics of Actinide Elements and Compounds”, oriented towards nuclear engineers and scientists. This international effort resulted in the publication of ten volumes, each concerning the thermodynamic properties of a given type of compounds for the entire actinide series. These reviews cover the literature up to about 1984, although the last volume published in this series, Part 12: The Actinide Aqueous Inorganic Complexes [1992FUG/KHO], did not appear until 1992. Unfortunately, four of the reviews planned for inclusion in the IAEA series, reviews of importance for radioactive waste management, were never published (for example, Part 10: The Actinide Oxides and Part 14: Aqueous Organic Complexes).

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

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

In 2003 TDB-III, the third phase of the Project, began, and it was organized in a way similar to that used for TDB-II. An expert group was constituted to prepare a state-of-the-art report on the chemical thermodynamics of solid solutions of interest in radioactive waste management. That report [2007BRU/BOS] was published as volume 10 of the Chemical Thermodynamics Series. Also, three Review Teams were established to focus on the elements thorium, tin and iron. The volumes devoted to inorganic species and compounds of thorium [2008RAN/FUG] and tin [2012GAM/GAJ] have been published as volumes 11 and 12 of the Chemical Thermodynamics Series. However, it was recognized early in Phase III that assessment of the chemical thermodynamics of inorganic species and complexes of iron was too large an endeavour for a single book. Therefore, in 2008 the NEA RWMC and the Executive Group endorsed deferral of the assessment of data for some iron species to Phase IV of the Project. The present volume, the thirteenth in the Chemical Thermodynamics Series, is the first of two volumes on iron species and compounds, and is the final deliverable from TDB-III. The second iron volume is being prepared and will be published as part of Phase IV.

The earlier twelve volumes of the series are listed in the frontispiece of this volume; it may be noted that first two volumes [1992GRE/FUG], [1995SIL/BID] and the companion volume on the modelling of aqueous solutions [1997ALL/BAN], are available without charge from the NEA.

Simultaneously with the NEA TDB project, other reviews on the physical and chemical properties of actinides have appeared, including the book by Cordfunke *et al.* [1990COR/KON], the series edited by Freeman *et al.* [1984FRE/LAN], [1985FRE/LAN], [1985FRE/KEL], [1986FRE/KEL], [1987FRE/LAN], and [1991FRE/KEL], Part 12 of the IAEA review series by Fuger *et al.* [1992FUG/KHO] mentioned above and the two comprehensive books by Katz *et al.* [1986KAT/SEA] and Morss *et al.* [2006MOR/EDE] (particularly Chapter 19 [2006KON/MOR]). All the compilations mentioned, although much less detailed than the NEA reviews (particularly with regard to documentation and discussion of published data), are important sources of information, and complement the thermodynamic data contained in the TDB volumes (though only with due regard to consistency).

I.2 Focus of the review

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

As outlined in the previous section, the focus of the critical review presented in this book is on the thermodynamic data of iron relevant to the safety assessment of radioactive waste repositories in the geosphere. This includes the release of waste components from the repository into the geosphere (*i.e.*, its interaction with the waste container and the other near-field materials) and their migration through the geological formations and the various compartments of the biosphere. As ground waters and pore waters are the transport media for the waste components, the knowledge of the thermodynamics of the corresponding elements in waters of various compositions is of fundamental importance. Iron is a structural material that may be used during repository construction, but also is a component of minerals that might be expected to have a substantial role in conditioning ground water that will come in contact with waste.

The present review therefore puts much weight on the assessment of the thermodynamics of iron in aqueous solution at ambient temperatures, and makes independent analyses of the available literature in this area. Appendix B describes in detail the Specific Ion Interaction Treatment that is the model selected for use in the NEA TDB review series to describe ionic interactions between components in aqueous solutions. This allows the general and consistent use of the selected data for modelling purposes, regardless of the type and composition of the ground water.

The interactions between solid compounds and aqueous solutions are as important as the interactions within the aqueous solution, because the solid materials in the geosphere control the chemistry of the ground water, and also contribute to the overall solubilities of key elements. The present review therefore also considers the thermodynamic data of many solid iron compounds.

This book contains a summary and critical reviews of the thermodynamic data on compounds and complexes containing iron, as reported in the available chemical literature up to the end of 2008, but a few more recent references also are included. A large number of primary references are discussed separately in Appendix A.

Although the focus of this review is on iron, it is necessary to use data on a number of other species during the evaluation process that lead to the recommended data. These auxiliary data are taken both from the publication of CODATA Key Values [1989COX/WAG] and from the evaluation of additional auxiliary data in the other volumes of this series detailed above, and their use is recommended by this review. Care has been taken that all the selected thermodynamic data at standard conditions (*cf.* Section II.3) and 298.15 K are internally consistent. For this purpose, special software has been developed at the NEA Data Bank that is operational in conjunction with the NEA TDB database system, *cf.* Section II.6. To maintain consistency in the application of the values selected by this review, it is essential to use these auxiliary data when calculating equilibrium constants involving iron compounds and complexes.

The present review is only the first of two NEA TDB volumes for iron, and deals with data for the metal, simple ions, aqueous hydroxido, chlorido, sulfido, sulfato and carbonato complexes, and for solid oxides and hydroxides, halides, sulfates, carbonates and simple silicates. Several key sections relevant to the safety assessment of radioactive waste repositories have been deferred to the second volume. Neither volume will include data for species containing organic ligands or species in non-aqueous solvents.

I.3 Review procedure and results

The objective of the present review is to present an assessment of the sources of published thermodynamic data in order to decide on the most reliable values and their uncertainties that can be recommended for modelling purposes. Experimental measurements published in the scientific literature are the main source for the selection of recommended data. Previous reviews are not neglected, since they form a valuable source of critical information on the quality of primary publications. When necessary, experimental source data are re-evaluated by using chemical models which are either found to be more realistic than those used by the original author, or are consistent with subsequent experimental information. For example, data on solubilities might need to be re-interpreted to take into account the crystal structure and particle size of the phases actually investigated.

Re-evaluation of literature values might be also necessary to correct for known systematic errors (for example, if complex formation was neglected in the original publication) or to make extrapolations to standard state conditions (I = 0) by using the specific ion interaction (SIT) equations (*cf.* Appendix B). For convenience, these SIT equations are referred to in some places in the text as “the SIT”. To ensure that consistent procedures are used for the evaluation of primary data, a number of guidelines have been developed. They have been updated and improved since 1987, and their most recent versions are available at the NEA [1999WAN], [1999WAN/OST], [2000GRE/WAN], [2000OST/WAN], [2000WAN/OST]. Some of the procedures also are outlined in this volume, *cf.* Chapter II, Appendix B, and Appendix C. Parts of these sections were recently revised in the thorium [2008RAN/FUG] and tin [2012GAM/GAJ] reviews. Further minor changes were made in this review, including corrections to a very few entries in the Tables of Appendix B.

Once the critical review process for each volume in the NEA TDB project is completed, the resulting manuscript is reviewed independently by qualified experts nominated by the NEA. The independent peer review is performed according to the procedures outlined in the TDB-6 guideline [1999WAN]. The purpose of the additional peer review is to obtain an independent view of the judgements and assessments made by the primary reviewers, to verify assumptions, results and conclusions, and to check whether the relevant literature has been exhaustively considered. The independent peer review is performed by scientists having technical expertise in the subject matter to be reviewed.

The thermodynamic data selected in the present review (see Chapter III) refer to the reference temperature of 298.15 K and to standard conditions, *cf.* Section II.3. For the modelling of real systems it is, in general, necessary to recalculate the standard thermodynamic data to non-standard state conditions. For aqueous species a procedure for the calculation of the activity factors is required. As noted earlier, this review uses an approximate specific ion interaction treatment (SIT) for the extrapolation of experimental data to the standard state in the data evaluation process, and in some cases this requires the re-evaluation of original experimental values (solubilities, cell-potential data, *etc.*). For maximum consistency, the selected data presented in this review must always be used in conjunction with this method as described in Appendix B. The thermodynamic data selected in this review are provided with uncertainties representing the 95% confidence level. As discussed in Appendix C, there is no unique way to assign uncertainties, and the assignments made in this review are to a large extent based on the subjective choices of the reviewers, supported by their scientific and technical experience in the corresponding area.

The quality of thermodynamic models cannot be better than the quality of the data on which they are based. The quality aspect includes both the numerical values of the thermodynamic data used in the model and the “completeness” of the chemical model used, *e.g.,* the inclusion of all the relevant dissolved chemical species and solid phases. For the user it is important to note that the selected data set presented in this review (Chapter III) is certainly *not* “complete” with respect to all the conceivable systems and conditions; there are gaps in the information. The gaps are pointed out in the main text (Chapters V to XI), and this information may be used as a basis for the assignment of future research priorities. Addition of thermodynamic values from other sources for modelling purposes without proper consideration of compatibility with the values in Chapters III and IV may lead to incorrect results.

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
E_{cell}	Potential difference of an electrochemical cell

(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
isop	Isopiestic
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	E_{cell} with redox electrode
SEM	Scanning Electron Microscopy
sp	Spectrophotometry
sol	Solubility
TC	Transient Conductivity
TEM	Transmission Electron Microscopy
TGA	Thermo Gravimetric Analysis
TLS	Thermal Lensing Spectrophotometry
Tj	Temperature jump
TRLFS	Time Resolved Laser Fluorescence Spectroscopy
UV	Ultraviolet
vlt	Voltammetry
XANES	X-ray Absorption Near Edge Structure
XRD	X-ray Diffraction
?	Method unknown to the reviewers

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

II.1.2 Symbols and terminology

The symbols for physical and chemical quantities used in the TDB review follow the recommendations of the International Union of Pure and Applied Chemistry, IUPAC [1979WHI], [1993MIL/CVI], [2007COH/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
relative atomic mass	A_r
molar mass	M
density (mass divided by volume)	ρ
molar surface area	$\mathcal{A}$
time	t
frequency	ν
wavelength	λ
internal transmittance (transmittance of the medium itself, disregarding boundary or container influence)	T
internal transmission density, (decadic absorbance): $\log_{10}(1/T_\mathrm{i})$	A
molar (decadic) absorption coefficient: $A / c_\mathrm{B} l$	ε
relaxation time	τ
Avogadro constant	N_A
relative molecular mass of a substance$^{(a)}$	M_r
thermodynamic temperature, absolute temperature	T
Celsius temperature	t
(molar) gas constant	R
Boltzmann constant	k_B
Faraday constant	F
(molar) entropy	S_m
(molar) heat capacity at constant pressure	$C_{p,\mathrm{m}}$
(molar) enthalpy	H_m
(molar) Gibbs energy	G_m
chemical potential of substance B	μ_B
pressure	p
partial pressure of substance B: $x_\mathrm{B}\,p$	p_B
fugacity of substance B	f_B

(Continued next page)

Table II-2 (continued)

Symbols and terminology	
fugacity coefficient: f_B/p_B	γ_{f_B}
amount of substance[b]	n
mole fraction of substance B:	x_B
molarity or concentration of a solute substance B (amount of B divided by the volume of the solution) [c]	c_B, [B]
molality of a solute substance B (amount of B divided by the mass of the solvent) [d]	m_B
factor for the conversion of molarity to molality of a solution: m_B / c_B	ξ
mean ionic molality [e], $m_\pm^{(\nu_+ + \nu_-)} = m_+^{\nu_+} m_-^{\nu_-}$	$m_\pm$
activity of substance B [*]	a_B
activity coefficient, molality basis: a_B / m_B	γ_B
activity coefficient, concentration basis: a_B / c_B	y_B
mean ionic activity [e], $a_\pm^{(\nu_+ + \nu_-)} = a_B = a_+^{\nu_+} a_-^{\nu_-}$	$a_\pm$
mean ionic activity coefficient [e], $\gamma_\pm^{(\nu_+ + \nu_-)} = \gamma_+^{\nu_+} \gamma_-^{\nu_-}$	$y_\pm$
osmotic coefficient, molality basis	ϕ
ionic strength: $I_m = ½\sum_i m_i z_i^2$ or $I_c = ½\sum_i c_i z_i^2$	I
SIT ion interaction coefficient between substance B_1 and substance B_2)	$\varepsilon(B_1, B_2)$
stoichiometric coefficient of substance B (negative for reactants, positive for products	ν_B
general equation for a chemical reaction	$0 = \sum_B \nu_B B$
equilibrium constant [f]	K
charge number of an ion B (positive for cations, negative for anions)	z_B
charge number of a cell reaction	n
Potential difference of an electrochemical cell	E
$pH = -\log_{10}[a_{H^+} / (mol \cdot kg^{-1})]$	pH
molar conductivity	Λ
molar conductivity at $I = 0$	Λ_0
superscript for standard state [g]	$^\circ$

a: Ratio of the average mass per formula unit of a substance to $\frac{1}{12}$ of the mass of an atom of nuclide ^{12}C.

b: *cf.* sections 1.2 and 3.6 of the IUPAC manual [1979WHI].

c: This quantity is called "amount–of–substance concentration" in the IUPAC manual [1979WHI]. A solution with a concentration equal to 0.1 $mol \cdot dm^{-3}$ is called a 0.1 molar solution or a 0.1 M solution.

d: A solution having a molality equal to 0.1 moles of solute per kg solvent is called a 0.1 molal solution or a 0.1 m solution.

e: For an electrolyte $N_{\nu_+}X_{\nu_-}$ which dissociates into $\nu_\pm$ $(= \nu_+ + \nu_-)$ ions, in an aqueous solution with molality *m*, the individual cationic molality and activity coefficient are $m_+ (= \nu_+ m)$ and $\gamma_+ (= a_+ / m_+)$. A similar definition is used for the anionic symbols. Electrical neutrality requires that $\nu_+ z_+ = \nu_- z_-$.

f: Special notations for equilibrium constants are outlined in Section II.1.7. In some cases, K_c is used to indicate a concentration constant in molar units, and K_m a constant in molal units.

g: See Section II.3.1.

*: In many places in this volume a_W has been used as synonym for a_{H_2O}.

II.1.3 Chemical formulae and nomenclature

This review follows the recommendations made by IUPAC [1971JEN], [1977FER], [1990LEI] on the nomenclature of inorganic compounds and complexes, except for the following items:

- The formulae of co-ordination compounds and complexes are not enclosed in square brackets [1971JEN] (Rule 7.21). Exceptions are made in cases where square brackets are required to distinguish between co-ordinated and unco-ordinated ligands.
- The prefixes "oxy-" and "hydroxy-" are retained if used in a general way, *e.g.*, "gaseous uranium oxyfluorides". For specific formula names, however, the IUPAC recommended citation [1971JEN] (Rule 6.42) is used, *e.g.*, "uranium(IV) difluoride oxide" for $UF_2O(cr)$.

An IUPAC rule that is often not followed by many authors [1971JEN] (Rules 2.163 and 7.21) is recalled here: the order of arranging ligands in co-ordination compounds and complexes is the following: central atom first, followed by ionic ligands and then by the neutral ligands. If there is more than one ionic or neutral ligand, the alphabetical order of the symbols of the ligands determines the sequence of the ligands. For example, $(UO_2)_2CO_3(OH)_3^-$ is standard, $(UO_2)_2(OH)_3CO_3^-$ is not recommended.

It is convenient to have a shorthand method of referring to an a ionic medium where the anion concentration is kept constant, but the cation concentrations vary, since such solutions are often used to minimise changes in interionic attractions. For this we enclose the major cation in parentheses. For example, a solution described as "3.00 M $(Na)ClO_4$" could be a mixture of 0.01 M $Th(ClO_4)_4$ and 2.96 M $NaClO_4$ with a total perchlorate concentration of 3.00 M.

Abbreviations of names for organic ligands appear sometimes in formulae. Following the recommendations by IUPAC, lower case letters are used, and if necessary, the ligand abbreviation is enclosed within parentheses. Hydrogen atoms that can be replaced by the metal atom are shown in the abbreviation with an upper case "H", for example: H_3edta^-, Am(Hedta)(s) (where edta stands for ethylenediaminetetraacetate).

II.1.4 Phase designators

Chemical formulae may refer to different chemical species and are often required to be specified more clearly in order to avoid ambiguities. For example, UF_4 occurs as a gas, a solid, and an aqueous complex. The distinction between the different phases is made by phase designators that immediately follow the chemical formula and appear in parentheses. The only formulae that are not provided with a phase designator are aqueous ions. They are the only charged species in this review since charged gases are not considered. The use of the phase designators is described below.

- The designator (l) is used for pure liquid substances, *e.g.*, $H_2O(l)$.
- The designator (aq) is used for undissociated, uncharged aqueous species, *e.g.*, $U(OH)_4(aq)$, $CO_2(aq)$. Since ionic gases are not considered in this review, all ions may be assumed to be aqueous and are not designed with (aq). If a chemical reaction refers to a medium other than H_2O (*e.g.*, D_2O, 90% ethanol/10% H_2O), then (aq) is replaced by a more explicit designator, *e.g.*, "(in D_2O)" or "(sln)". In the case of (sln), the composition of the solution is described in the text.
- The designator (sln) is used for substances in solution without specifying the actual equilibrium composition of the substance in the solution. Note the difference in the designation of H_2O in Eqs. (II.2) and (II.3). $H_2O(l)$ in Reaction (II.2) indicates that H_2O is present as a pure liquid, *i.e.*, no solutes are present, whereas Reaction (II.3) involves an HCl solution, in which the thermodynamic properties of $H_2O(sln)$ may not be the same as those of the pure liquid $H_2O(l)$. In dilute solutions, however, this difference in the thermodynamic properties of H_2O can be neglected, and $H_2O(sln)$ may be regarded as pure $H_2O(l)$.

  Example:

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

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

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

- The designators (cr), (am), (vit), and (s) are used for solid substances. (cr) is used when it is known that the compound is crystalline, (am) when it is known that it is amorphous, and (vit) for glassy substances. Otherwise, (s) is used.
- In some cases, more than one crystalline form of the same chemical composition may exist. In such a case, the different forms are distinguished by separate designators that describe the forms more precisely. If the crystal has a mineral name, the designator (cr) is replaced by the first four characters of the mineral name in parentheses, *e.g.*, $SiO_2(quar)$ for quartz and $SiO_2(chal)$ for chalcedony. If there is no mineral name, the designator (cr) is replaced by a Greek letter preceding the formula and indicating the structural phase, *e.g.*, α-UF_5, β-UF_5.

Phase designators are also used in conjunction with thermodynamic symbols to define the state of aggregation of a compound to which a thermodynamic quantity refers. The notation is in this case the same as outlined above. In an extended notation (*cf.* [1982LAF]) the reference temperature is usually given in addition to the state of aggregation of the composition of a mixture.

Example:

$\Delta_f G_m^o(\text{Na}^+, 298.15\ \text{K})$	standard molar Gibbs energy of formation of aqueous Na^+ at 298.15 K
$S_m^o(\text{UO}_2(\text{SO}_4)\cdot 2.5\text{H}_2\text{O, cr, } 298.15\ \text{K})$	standard molar entropy of $\text{UO}_2(\text{SO}_4)\cdot 2.5\text{H}_2\text{O(cr)}$ at 298.15 K
$C_{p,m}^o(\text{UO}_3, \alpha, 298.15\ \text{K})$	standard molar heat capacity of α-UO_3 at 298.15 K
$\Delta_f H_m(\text{HF, sln, HF}\cdot 7.8\text{H}_2\text{O})$	enthalpy of formation of HF diluted 1:7.8 with water.

II.1.5 Processes

Chemical processes are denoted by the operator Δ, written before the symbol for a property, as recommended by IUPAC [1982LAF]. An exception to this rule is the equilibrium constant, *cf.* Section II.1.7. The nature of the process is denoted by annotation of the Δ, *e.g.*, the Gibbs energy of formation, $\Delta_f G_m$, the enthalpy of sublimation, $\Delta_{sub} H_m$, *etc.* The abbreviations of chemical processes are summarised in Table II-3.

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

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

The most frequently used symbols for processes are $\Delta_f G$ 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 Nomenclature in log terms

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

II.1.7 Equilibrium constants

IUPAC has not explicitly defined the symbols and terminology for equilibrium constants of reactions in aqueous solution. The NEA TDB Project has therefore adopted the conventions that have been used in the work *Stability Constants of Metal Ion Complexes* by Sillén and Martell [1964SIL/MAR], [1971SIL/MAR]. An outline is given in the paragraphs below. Note that, for some simple reactions, there may be different correct ways to index an equilibrium constant. It may sometimes be preferable to indicate the number of the reaction to which the data refer, especially in cases where several ligands are discussed that might be confused. For example, for the equilibrium:

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

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

The expressions in sub-Sections II.1.7.1.1 through II.1.7.1.4 are expressed in terms of (amount substance) concentrations (*i.e.*, $[\mathrm{X}] \equiv c_\mathrm{X}$ and the constants are K_c; *cf.* footnote *f* to Table II-2), but parallel nomenclature has been used in the rest of the review for equilibria expressed using molalities (K_m) or using activities in thermodynamic equilibrium constants (K°). The units here for

$$K_c = \prod_\mathrm{B} c^{\nu_\mathrm{B}}$$

are $(\mathrm{mol{\cdot}dm^{-3}})^{\Sigma_\mathrm{B}\nu_\mathrm{B}}$.

II.1.7.1 Protonation of a ligand

$$\mathrm{H^+} + \mathrm{H}_{r-1}\mathrm{L} \rightleftharpoons \mathrm{H}_r\mathrm{L} \qquad K_{1,r} = \frac{[\mathrm{H}_r\mathrm{L}]}{[\mathrm{H^+}][\mathrm{H}_{r-1}\mathrm{L}]} \qquad \text{(II.5)}$$

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

This notation has been proposed and used by Sillén and Martell [1964SIL/MAR], but it has been simplified later by the same authors [1971SIL/MAR] from $K_{1,r}$ to K_r.

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

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

Eq. (II.8) refers to the overall formation constant of the species H_rL_q.

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

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

Example:

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

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

II.1.7.2 Formation of metal complexes

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

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

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

$$M + M_{m-1}L \rightleftharpoons M_mL \qquad K_{1,m} = \frac{[M_mL]}{[M][M_{m-1}L]} \qquad \text{(II.11)}$$

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

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

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

It has sometimes been customary to use negative values for the indices of the protons to indicate complexation with hydroxide ions, OH^-. This practice is not adopted in this review. If OH^- occurs as a reactant in the notation of the equilibrium, it is treated like a normal ligand L, but in general formulae the index variable n is used instead of q. If H_2O occurs as a reactant to form hydroxide complexes, H_2O is considered as a protonated ligand, HL, so that the reaction is treated as described below in Eqs. (II.13) to (II.15) using n as the index variable. For convenience, no general form is used for the stepwise constants for the formation of the complex $M_mL_qH_r$. In many experiments, the formation constants of metal ion complexes are determined by adding 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.

$$\mathrm{ML}_{q-1} + \mathrm{HL} \rightleftharpoons \mathrm{ML}_q + \mathrm{H}^+ \qquad {}^*K_q = \frac{[\mathrm{ML}_q][\mathrm{H}^+]}{[\mathrm{ML}_{q-1}][\mathrm{HL}]} \tag{II.13}$$

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

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

Example:

$$\mathrm{UO}_2^{2+} + \mathrm{HF(aq)} \rightleftharpoons \mathrm{UO_2F}^+ + \mathrm{H}^+ \qquad {}^*K_1 = {}^*\beta_1 = \frac{[\mathrm{UO_2F}^+][\mathrm{H}^+]}{[\mathrm{UO}_2^{2+}][\mathrm{HF(aq)}]}$$

$$3\,\mathrm{UO}_2^{2+} + 5\,\mathrm{H_2O(l)} \rightleftharpoons (\mathrm{UO}_2)_3(\mathrm{OH})_5^+ + 5\,\mathrm{H}^+ \qquad {}^*\beta_{5,3} = \frac{[(\mathrm{UO}_2)_3(\mathrm{OH})_5^+][\mathrm{H}^+]^5}{[\mathrm{UO}_2^{2+}]^3}$$

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

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

Example:

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

II.1.7.3 Solubility constants

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

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

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

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

Example:

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

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

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

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

Example:

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

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

II.1.7.4 Equilibria involving the addition of a gaseous ligand

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

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

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

Example:

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

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

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

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

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

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

II.1.7.5 Redox equilibria

Redox reactions are usually quantified in terms of their electrode (half cell) potential, *E*, which is identical to the potential difference of a galvanic cell in which the electrode on the left is the standard hydrogen electrode, SHE[1], in accordance with the "1953 Stockholm Convention" [1993MIL/CVI]. Therefore, electrode potentials are given as reduction potentials relative to the standard hydrogen electrode, which acts as an electron donor. In the standard hydrogen electrode, H_2(g) is at unit fugacity (an ideal gas at unit pressure, 0.1 MPa), and $\mathrm{H^+}$ is at unit activity. The sign of the electrode potential, *E*, is that of the observed sign of its polarity when coupled with the standard hydrogen electrode. The standard electrode potential, E°, *i.e.*, the potential of a standard galvanic cell relative to the standard hydrogen electrode (all components in their standard state, *cf.* Section II.3.1, and with no liquid junction potential) is related to the standard Gibbs energy change $\Delta_\mathrm{r}G^\circ_\mathrm{m}$ and the standard (or thermodynamic) equilibrium constant K° as outlined in Eq. (II.21):

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

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

and the potential, E, is related to E^{o} by:

$$E = E^{\mathrm{o}} - (RT/nF)\sum \nu_i \ln a_i. \qquad \text{(II.22)}$$

For example, for the hypothetical galvanic cell:

$$\mathrm{Pt} \;\Big|\; \mathrm{H_2(g,}\ p = 1\ \mathrm{bar)} \;\Big|\; \mathrm{HCl(aq,}\ a_{\mathrm{H^+}} = 1,\ f_{\mathrm{H_2}} = 1) \;\vdots\; \begin{array}{l} \mathrm{Fe(ClO_4)_2\ (aq,}\ a_{\mathrm{Fe^{2+}}} = 1) \\ \mathrm{Fe(ClO_4)_3\ (aq,}\ a_{\mathrm{Fe^{3+}}} = 1) \end{array} \;\Big|\; \mathrm{Pt} \qquad \text{(II.23)}$$

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

$$\mathrm{Fe^{3+}} + ½\ \mathrm{H_2(g)} \rightleftharpoons \mathrm{Fe^{2+}} + \mathrm{H^+} \qquad \text{(II.24)}$$

Formally Reaction (II.24) can be represented by two half cell reactions, each involving an equal number of electrons, (designated "$\mathrm{e^-}$"), as shown in the following equations:

$$\mathrm{Fe^{3+}} + \mathrm{e^-} \rightleftharpoons \mathrm{Fe^{2+}} \qquad \text{(II.25)}$$

$$½\ \mathrm{H_2(g)} \rightleftharpoons \mathrm{H^+} + \mathrm{e^-} \qquad \text{(II.26)}$$

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

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

$$E = E^{\mathrm{o}}\,(\text{II.26}) + \frac{RT}{F}\ln\left(\sqrt{f_{\mathrm{H_2}}}\,/\,(a_{\mathrm{H^+}}\,a_{e^-})\right) \qquad \text{(II.27)}$$

According to the SHE convention E^{o} (II.26) = 0, $f_{\mathrm{H_2}} = 1$, $a_{\mathrm{H^+}} = 1$, hence

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

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

$$K^{\mathrm{o}}\,(\text{II.25}) = \frac{a_{\mathrm{Fe^{2+}}}}{a_{\mathrm{Fe^{3+}}} \cdot a_{\mathrm{e^-}}} \qquad \text{(II.29)}$$

$$K^{\mathrm{o}}\,(\text{II.26}) = \frac{a_{\mathrm{H^+}} \cdot a_{\mathrm{e^-}}}{\sqrt{f_{\mathrm{H_2}}}} = 1 \quad \text{(by definition)} \qquad \text{(II.30)}$$

In addition, $\Delta_r G_m^\circ$ (II.26) = 0, $\Delta_r H_m^\circ$ (II.26) = 0, $\Delta_r S_m^\circ$ (II.26) = 0 by definition, at all temperatures, and therefore $\Delta_r G_m^\circ$ (II.25) = $\Delta_r G_m^\circ$ (II.24). From $\Delta_r G_m^\circ$ (II.26) and the values given at 298.15 K in selected auxiliary data for H_2(g) and H^+, the corresponding values for e^- can be calculated to be used in thermodynamic cycles involving half cell reactions. The following equations describe the change in the redox potential of Reaction (II.24), if p_{H_2} and a_{H^+} are equal to unity (*cf.* Eq. (II.22)):

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

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):

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

and

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

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 H^+ can be chosen as components and they can be treated numerically in a similar way: equilibrium constants, mass balance, *etc.* may be defined for both. However, while H^+ represents the hydrated proton in aqueous solution, the above equations use only the activity of "e^-", and never the concentration of "e^-". Concentration to activity conversions (or activity coefficients) are never needed for the electron (*cf.* Appendix B, Example B.3).

In the literature on geochemical modelling of natural waters, it is customary to represent the "electron activity" of an aqueous solution with the symbol "pe" or "pε" ($= -\log_{10} a_{e^-}$) by analogy with pH ($= -\log_{10} a_{H^+}$), and the redox potential of an aqueous solution relative to the standard hydrogen electrode is usually denoted by either "Eh" or "E_H" (see for example [1981STU/MOR], [1982DRE], [1984HOS], [1986NOR/MUN]).

In this review, the symbol $E^{\circ\prime}$ is used to denote the so-called "formal potential" [1974PAR]. The formal (or "conditional") potential can be regarded as a standard potential for a particular medium in which the activity coefficients are independent (or approximately so) of the reactant concentrations [1985BAR/PAR] (the definition of $E^{o\prime}$ parallels that of "concentration quotients" for equilibria). Therefore, from

$$E = E^{o\prime} - \frac{RT}{nF}\sum \nu_i \ln c_i \tag{II.34}$$

$E^{o\prime}$ 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

$$E_c^{o\prime} = E_c^{o} - \frac{RT}{nF}\sum \nu_i \ln \gamma_{c,i} \tag{II.35a}$$

$$E_c^{o\prime} = E_c^{o} - \frac{RT}{nF}\sum \nu_i \ln(\xi\cdot\gamma_{m,i}\cdot\rho^{*}_{\mathrm{H_2O}}) \tag{II.35b}$$

$$\gamma_{c,i} = \left(\frac{m_i/m^{o}}{c_i/c^{o}}\right)(\rho^{*}_{\mathrm{H_2O}}/\rho^{o})\gamma_{m,i} \tag{II.35c}$$ [1]

where the $\gamma_{c,i}$ and $\gamma_{m,i}$ are the activity coefficients on amount concentration and molality basis, respectively [2008GAM/LOR], related by Eq. (II.35c), $\rho^{*}_{\mathrm{H_2O}}$ is the density of pure water, and ξ is $\left({}^{m_i}\!/_{c_i}\right)$, the ratio of molality to molarity (*cf.* Section II.2). The medium must be specified. Equation (II.35c) has been derived most elegantly by [1959ROB/STO].

II.1.8 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. For a comprehensive account, see [2002BUC/RON].

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

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

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

The determination of pH is often performed by potential-difference measurements of galvanic cells involving liquid junctions [1969ROS], [1973BAT]. A common

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[1] $\rho^{*}_{\mathrm{H_2O}}$ is a variable depending on T, $m^{o} = 1\ \mathrm{mol\cdot kg^{-1}}$, $c^{o} = 1\ \mathrm{mol\cdot dm^{-3}}$.

setup is a cell made up of a reference half cell (*e.g.*, Ag(s)|AgCl(s) in a solution of constant chloride concentration), a salt bridge, the test solution, and a glass electrode (which encloses a solution of constant acidity and an internal reference half cell):

$$\mathrm{Pt(s)} \;\Big|\; \mathrm{Ag(s)} \;\Big|\; \mathrm{AgCl(s)} \;\Big|\; \mathrm{KCl(sln)} \;\underset{a}{\vdots}\; \begin{matrix}\text{salt}\\ \text{bridge}\end{matrix} \;\underset{b}{\vdots}\; \begin{matrix}\text{test}\\ \text{solution}\end{matrix} \;\wr\; \mathrm{KCl(sln)} \;\Big|\; \mathrm{AgCl(s)} \;\Big|\; \mathrm{Ag(s)} \;\Big|\; \mathrm{Pt(s)} \qquad \text{(II.36)}$$

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

The potential difference of such a cell is given by:

$$E = E^{*} - \frac{RT}{nF}\ln a_{\mathrm{H}^+} + E_{\mathrm{j}}$$

where E^{*} is a constant, and E_{j} is the liquid junction potential. The purpose of the salt bridge is to minimise the junction potential in junction "*b*", while keeping constant the junction potential for junction "*a*". Two methods are most often used to reduce and control the value of E_{j}. An electrolyte solution of *high* concentration (the "salt bridge") is a requirement of both methods. In the first method, the salt bridge is a saturated (or nearly saturated) solution of potassium chloride. A problem with a bridge of high potassium concentration is that potassium perchlorate might precipitate[1] inside the liquid junction when the test solution contains a high concentration of perchlorate ions.

In the other method the salt bridge contains the same *high* concentration of the same inert electrolyte as the test solution (for example, 3 M $NaClO_4$). However, if the concentration of the background electrolyte in the salt bridge and test solutions is reduced, the values of E_{j} are dramatically increased. For example, if both the bridge and the test solution have $[\mathrm{ClO}_4^-] = 0.1$ M as background electrolyte, the dependence of the liquid junction at "*b*" on acidity is $E_{\mathrm{j}} \approx -440\,[\mathrm{H}^+]$ $\mathrm{mV{\cdot}dm^3{\cdot}mol^{-1}}$ at 25 °C [1969ROS] (p.110), which corresponds to an error of ≥ 0.07 in pH at a pH value of 2.

Because of the problems in eliminating the liquid junction potentials and in defining individual ionic activity coefficients, an "operational" definition of pH is given by IUPAC [1993MIL/CVI]. This definition involves the measurement of pH differences between the test solution and standard solutions of known pH and similar ionic strength (in this way similar values of γ_{H^+} and E_{j} cancel each other when potential-difference values are subtracted).

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

$$\log_{10} a_{\mathrm{HCl}} = ½\,(\log_{10} m_{\mathrm{H}^+} + \log_{10} m_{\mathrm{Cl}^-} + \log_{10} \gamma_{\mathrm{H}^+} + \log_{10} \gamma_{\mathrm{Cl}^-}) \qquad \text{(II.37)}$$

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

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

The measurement and use of pH in equilibrium analytical investigations creates many problems that have not always been taken into account by the investigators, as discussed in many reviews in Appendix A. In order to deduce the stoichiometry and equilibrium constants of complex formation reactions and other equilibria, it is necessary to vary the concentrations of reactants and products over fairly large concentration ranges under conditions where the activity coefficients of the species are either known, or constant. Only in this manner is it possible to use the mass balance equations for the various components together with the measurement of one or more free concentrations to obtain the information desired [1961ROS/ROS], [1990BEC/NAG], [1997ALL/BAN], pp. 326–327. For equilibria involving hydrogen ions, it is necessary to use concentration units, rather than hydrogen ion activity. For experiments in an ionic medium, where the concentration of an "inert" electrolyte is much larger than the concentration of reactants and products we can ensure that, as a first approximation, their trace activity coefficients remain constant even for moderate variations of the corresponding total concentrations. Under these conditions of fixed ionic strength the free proton concentration may be measured directly, thereby defining it in terms of $-\log_{10}[\mathrm{H}^+]$ (also often referred to as pH_c, and correspondingly pH_m for $\log_{10} m_{\mathrm{H}^+}$) rather than on the activity scale as pH, and the value of $-\log_{10}[\mathrm{H}^+]$ and pH will differ by a constant term, *i.e.*, $\log_{10} \gamma_{\mathrm{H}^+}$. Equilibrium constants deduced from measurements in such ionic media are therefore *conditional* constants, because they refer to the given medium, not to the standard state. In order to compare the magnitude of equilibrium constants obtained in different ionic media it is necessary to have a method for estimating activity coefficients of ionic species in mixed electrolyte systems to a *common* standard state. Such procedures are discussed in Appendix B.

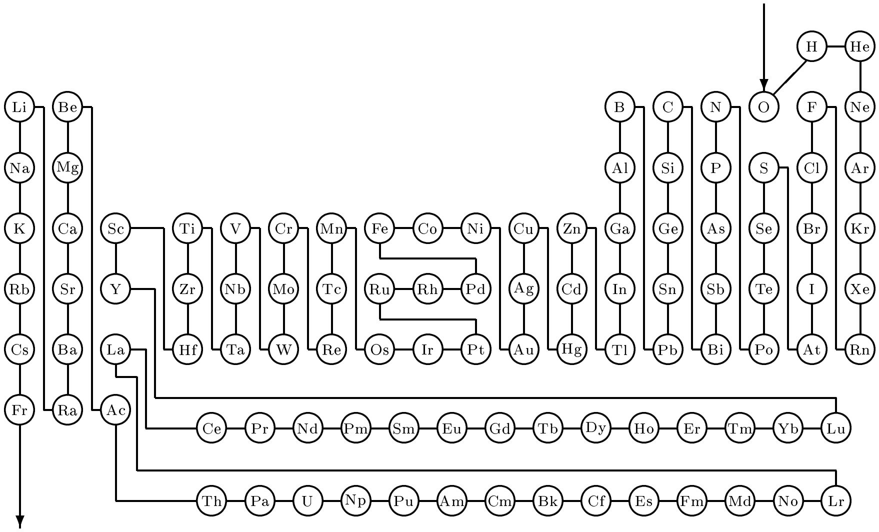
Note that the precision of the measurement of $-\log_{10}[\mathrm{H}^+]$ and pH is virtually the same, in very good experiments, ± 0.001. However, the accuracy is generally considerably poorer, depending in the case of glass electrodes largely on the response of the electrode (linearity, age, pH range,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

II.1.9 Order of formulae

To be consistent with CODATA, the data tables are given in "*Standard Order of Arrangement*" [1982WAG/EVA]. This scheme is presented in Figure II-1 below, and shows the sequence of the ranks of the elements in this convention. The order follows the ranks of the elements.

For example, for uranium, this means that, after elemental uranium and its monoatomic ions (*e.g.*, U^{4+}), the uranium compounds and complexes with oxygen would be listed, then those with hydrogen, then those with oxygen and hydrogen, and so on, with decreasing rank of the element and combinations of the elements. Within a class, increasing coefficients of the higher rank elements go before increasing coefficients of the lower rank elements. For example, in the U–O–F class of compounds and complexes, a typical sequence would be $UOF_2(cr)$, $UOF_4(cr)$, $UOF_4(g)$, $UO_2F(aq)$, UO_2F^+, $UO_2F_2(aq)$, $UO_2F_2(cr)$, $UO_2F_2(g)$, $UO_2F_3^-$, $UO_2F_4^{2-}$, $U_2O_3F_6(cr)$, *etc.* [1992GRE/FUG]. Formulae with identical stoichiometry are in alphabetical order of their designators.

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



II.1.10 Reference codes

The references cited in the review are ordered chronologically and alphabetically by the first two authors within each year, as described by CODATA [1987GAR/PAR]. A reference code is made up of the four digits of the year of appearance, followed by the first three letters of the surnames of the first two authors, separated by a slash.

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

II.2 Units and conversion factors

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

Table II-4: Unit conversion factors.

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

Since a large part of the NEA TDB Project deals with the thermodynamics of aqueous solutions, the units describing the amount of dissolved substance are used very frequently. For convenience, this review uses “M” as an abbreviation of “ $\text{mol}\cdot\text{dm}^{-3}$ ” for molarity, c, and, in Appendices B and C, “m” as an abbreviation of “ $\text{mol}\cdot\text{kg}^{-1}$ ” for molality, m. It is often necessary to convert 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 treatment, which works on molality basis (*cf*. Appendix B). This conversion is made in the following way.

Molality[1], m_B, is defined as the amount of substance, n_B dissolved in the mass of pure solvent, m_A, which in most cases is pure water

$$m_\text{B} = n_\text{B} / m_\text{A}.$$

Molarity (concentration), c_B, is defined as the amount of substance, n_B, dissolved in the volume, V, of solution

$$c_\text{B} = n_\text{B} / V.$$

Density of solution, ρ , is given by mass of solution devided by its volume,

$$\rho = (n_\text{B} M_\text{B} + m_\text{A})/V$$

where M is the molar mass of the solute.

---

[1] In this derivation the symbol m is used with two different meanings: m_B denotes the *molality* of solute B and m_A denotes the *mass* of solvent A.

From this it follows that:

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

When the ionic strength is kept high and constant by an inert electrolyte, I, the ratio $m_\mathrm{B}/c_\mathrm{B}$ can be approximated by

$$\frac{m_\mathrm{B}}{c_\mathrm{B}} = \frac{1}{\rho - c_\mathrm{I} M_\mathrm{I}}$$

where c_I is the concentration of the inert electrolyte and M_I its molar mass.

Baes and Mesmer [1976BAE/MES], (*p*.439) give a table with conversion factors (from molarity to molality) for nine electrolytes at various ionic strengths. Conversion factors at 298.15 K for twenty one electrolytes, calculated using the density equations reported by Söhnel and Novotný [1985SOH/NOV], are reported in Table II-5.

Example:

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

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

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

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

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

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

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

With $(m_\mathrm{B}/c_\mathrm{B}) = \xi$, or $(\log_{10} m_\mathrm{B} - \log_{10} c_\mathrm{B}) = \log_{10} \xi$, the relationship between K_c and K_m becomes very simple, as shown in Eq. (II.38).

$$\log_{10} K_m = \log_{10} K_c + \sum_\mathrm{B} \nu_\mathrm{B} \log_{10} \xi \qquad \text{(II.38)}$$

$\sum_\mathrm{B} \nu_\mathrm{B}$ is the sum of the stoichiometric coefficients of the solutes, *cf*. Eq. (II.55) and the values of ξ are the factors for the conversion of molarity to molality as tabulated in Table II-5 for several electrolyte media at 298.15 K. The differences between the values in Table II-5 and the values listed in the uranium NEA TDB review [1992GRE/FUG] (*p*.23) are found at the highest concentrations, and are no larger than ± 0.003 $\mathrm{dm^3{\cdot}kg^{-1}}$, reflecting the accuracy expected in this type of conversion. The uncertainty introduced by the use of Eq. (II.38) in the values of $\log_{10} K_m$ will be no larger than $\pm 0.001 \sum_\mathrm{B} \nu_\mathrm{B}$.

Table II-5: Factors ξ for the conversion of molarity, c_B, to molality, m_B, of a substance B, in various media at 298.15 K (calculated from densities in [1985SOH/NOV]).

	$\xi = m_B / c_B$ (dm^3 of solution per kg of H_2O)							
c (M)	$HClO_4$	$NaClO_4$	$LiClO_4$	NH_4ClO_4	$Ba(ClO_4)_2$	HCl	NaCl	LiCl
0.10	1.0077	1.0075	1.0074	1.0091	1.0108	1.0048	1.0046	1.0049
0.25	1.0147	1.0145	1.0141	1.0186	1.0231	1.0076	1.0072	1.0078
0.50	1.0266	1.0265	1.0256	1.0351	1.0450	1.0123	1.0118	1.0127
0.75	1.0386	1.0388	1.0374	1.0523	1.0685	1.0172	1.0165	1.0177
1.00	1.0508	1.0515	1.0496	1.0703	1.0936	1.0222	1.0215	1.0228
1.50	1.0759	1.0780	1.0750	1.1086	1.1491	1.0324	1.0319	1.0333
2.00	1.1019	1.1062	1.1019		1.2125	1.0430	1.0429	1.0441
3.00	1.1571	1.1678	1.1605		1.3689	1.0654	1.0668	1.0666
4.00	1.2171	1.2374	1.2264			1.0893	1.0930	1.0904
5.00	1.2826	1.3167				1.1147	1.1218	1.1156
6.00	1.3547	1.4077				1.1418		1.1423
c (M)	KCl	NH_4Cl	$MgCl_2$	$CaCl_2$	NaBr	HNO_3	$NaNO_3$	$LiNO_3$
0.10	1.0057	1.0066	1.0049	1.0044	1.0054	1.0056	1.0058	1.0059
0.25	1.0099	1.0123	1.0080	1.0069	1.0090	1.0097	1.0102	1.0103
0.50	1.0172	1.0219	1.0135	1.0119	1.0154	1.0169	1.0177	1.0178
0.75	1.0248	1.0318	1.0195	1.0176	1.0220	1.0242	1.0256	1.0256
1.00	1.0326	1.0420	1.0258	1.0239	1.0287	1.0319	1.0338	1.0335
1.50	1.0489	1.0632	1.0393	1.0382	1.0428	1.0478	1.0510	1.0497
2.00	1.0662	1.0855	1.0540	1.0546	1.0576	1.0647	1.0692	1.0667
3.00	1.1037	1.1339	1.0867	1.0934	1.0893	1.1012	1.1090	1.1028
4.00	1.1453	1.1877	1.1241	1.1406	1.1240	1.1417	1.1534	1.1420
5.00		1.2477		1.1974	1.1619	1.1865	1.2030	1.1846
6.00					1.2033	1.2361	1.2585	1.2309
c (M)	NH_4NO_3	H_2SO_4	Na_2SO_4	$(NH_4)_2SO_4$	H_3PO_4	Na_2CO_3	K_2CO_3	NaSCN
0.10	1.0077	1.0064	1.0044	1.0082	1.0074	1.0027	1.0042	1.0069
0.25	1.0151	1.0116	1.0071	1.0166	1.0143	1.0030	1.0068	1.0130
0.50	1.0276	1.0209	1.0127	1.0319	1.0261	1.0043	1.0121	1.0234
0.75	1.0405	1.0305	1.0194	1.0486	1.0383	1.0065	1.0185	1.0342
1.00	1.0539	1.0406	1.0268	1.0665	1.0509	1.0094	1.0259	1.0453
1.50	1.0818	1.0619	1.0441	1.1062	1.0773	1.0170	1.0430	1.0686
2.00	1.1116	1.0848		1.1514	1.1055	1.0268	1.0632	1.0934
3.00	1.1769	1.1355		1.2610	1.1675		1.1130	1.1474
4.00	1.2512	1.1935		1.4037	1.2383		1.1764	1.2083
5.00	1.3365	1.2600			1.3194		1.2560	1.2773
6.00	1.4351	1.3365			1.4131			1.3557

II.3 Standard and reference conditions

II.3.1 Standard state

A precise definition of the term “standard state” has been given by IUPAC [1982LAF]. The fact that only changes in thermodynamic parameters, but not their absolute values, can be determined experimentally, makes it important to have a well–defined standard state that forms a base line to which the effect of variations can be referred. The IUPAC [1982LAF] definition of the standard state has been adopted in the NEA TDB Project. The standard state pressure, $p^{\circ} = 0.1$ MPa (1 bar), has therefore also been adopted, *cf.* Section II.3.2. The application of the standard state principle to pure substances and mixtures is summarised below. It should be noted that the standard state is always linked to a reference temperature, *cf.* Section II.3.3.

- The standard state for a gaseous substance, whether pure or in a gaseous mixture, is the pure substance at the standard state pressure and in a (hypothetical) state in which it exhibits ideal gas behaviour.
- The standard state for a pure liquid substance is (ordinarily) the pure liquid at the standard state pressure.
- The standard state for a pure solid substance is (ordinarily) the pure solid at the standard state pressure.
- The standard state for a solute B in a solution is the (hypothetical) state of solute at the standard molality m°, standard pressure p° or standard concentration c° and exhibiting infinitely dilute solution behaviour.

It should be emphasised that the use of superscript, $^{\circ}$, *e.g.*, in $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$, implies that the compound in question is in the standard state and that the elements are in their reference states. The reference states of the elements at the reference temperature (*cf.* Section II.3.3) are listed in Table II-6.

Table II-6: Reference states for some elements at the reference temperature of 298.15 K and standard pressure of 0.1 MPa [1982WAG/EVA], [1989COX/WAG], [1991DIN], [2005GAM/BUG], [2005OLI/NOL].

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

II.3.2 Standard state pressure

The standard state pressure chosen for all selected data is 0.1 MPa (1 bar) as recommended by IUPAC [1982LAF].

However, the majority of the thermodynamic data published in the scientific literature, and used for the evaluations in this review, refers to the old standard state pressure of 1 “standard atmosphere” (= 0.101325 MPa). The difference between the thermodynamic data for the two standard state pressures is not large and lies in most cases within the uncertainty limits. It is nevertheless essential to make the corrections for the change in the standard state pressure in order to avoid inconsistencies and propagation of errors. In practice the parameters affected by the change between these two standard state pressures are the Gibbs energy and entropy changes of all processes that involve gaseous species. Consequently, changes occur also in the Gibbs energies of formation of species that consist of elements whose reference state is gaseous (H, O, F, Cl, N, and the noble gases). No other thermodynamic quantities are affected significantly. A large part of the following discussion has been taken from the NBS tables of chemical thermodynamic properties [1982WAG/EVA], see also Freeman [1984FRE].

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

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p = V(1-\alpha T) \tag{II.39}$$

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p \tag{II.40}$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -V\alpha = -\left(\frac{\partial V}{\partial T}\right)_p \tag{II.41}$$

$$\left(\frac{\partial G}{\partial p}\right)_T = V \tag{II.42}$$

$$\text{where } \alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \tag{II.43}$$

For ideal gases, $V = RT/p$ and $\alpha = R/pV = 1/T$. The conversion equations listed below (Eqs. (II.44) to (II.51)) apply to the small pressure change from 1 atm to 1 bar (0.1 MPa). The quantities that refer to the old standard state pressure of 1 atm are assigned the superscript $^{(\mathrm{atm})}$, and those that refer to the new standard state pressure of 1 bar are assigned the superscript $^{(\mathrm{bar})}$.

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

$$\Delta_\mathrm{f} H^{(\mathrm{bar})}(T) - \Delta_\mathrm{f} H^{(\mathrm{atm})}(T) = 0 \tag{II.44}$$

$$C_p^{(\mathrm{bar})}(T) - C_p^{(\mathrm{atm})}(T) = 0 \tag{II.45}$$

For gaseous substances, the entropy difference is:

$$\begin{aligned} S^{(\mathrm{bar})}(T) - S^{(\mathrm{atm})}(T) &= R \ln\left(\frac{p^{(\mathrm{atm})}}{p^{(\mathrm{bar})}}\right) = R\ \ln 1.01325 \\ &= 0.1094\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}} \end{aligned} \tag{II.46}$$

This is exactly true for ideal gases, as follows from Eq. (II.41) with $\alpha = R/pV$. The entropy change of a reaction or process is thus dependent on the number of moles of gases involved:

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

where δ is the net increase in moles of gas in the process.

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

$$\Delta_r G^{(\text{bar})} - \Delta_r G^{(\text{atm})} = -\delta RT \ln\left(\frac{p^{(\text{atm})}}{p^{(\text{bar})}}\right)$$
$$= -\,0.03263\ \delta\ \text{kJ·mol}^{-1} \text{ at } 298.15\ \text{K}. \qquad \text{(II.48)}$$

Eq. (II.48) 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:

$$\Delta_f G^{(\text{bar})} - \Delta_f G^{(\text{atm})} = -\,0.03263\ \delta\ \text{kJ·mol}^{-1} \text{ at } 298.15\ \text{K}. \qquad \text{(II.49).}$$

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.48),

$$\log_{10} K^{(\text{bar})} - \log_{10} K^{(\text{atm})} = -\frac{\Delta_r G^{(\text{bar})} - \Delta_r G^{(\text{atm})}}{RT \ln 10}$$
$$= \delta \frac{\ln\left(\frac{p^{(\text{atm})}}{p^{(\text{bar})}}\right)}{\ln 10} = \delta \log_{10}\left(\frac{p^{(\text{atm})}}{p^{(\text{bar})}}\right)$$
$$= 0.005717\ \delta \qquad \text{(II.50)}$$

$$E^{(\text{bar})} - E^{(\text{atm})} = -\frac{\Delta_r G^{(\text{bar})} - \Delta_r G^{(\text{atm})}}{nF}$$
$$= \delta \frac{RT \ln\left(\frac{p^{(\text{atm})}}{p^{(\text{bar})}}\right)}{nF}$$
$$= \delta \frac{0.0003382}{n}\ \text{V} \quad \text{at } 298.15\ \text{K} \qquad \text{(II.51)}$$

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

$$\text{H}^+ + \text{e}^- \rightleftharpoons \tfrac{1}{2}\text{H}_2\text{(g)} \qquad E^{\circ} \overset{\text{def}}{=} 0.00\text{V} \qquad \text{(II.52).}$$

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

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

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

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

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

Example:

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

II.3.3 Reference temperature

The definitions of standard states given in Section II.3 make no reference to fixed temperature. Hence, it is theoretically possible to have an infinite number of standard states of a substance as the temperature varies. It is, however, convenient to complete the definition of the standard state in a particular context by choosing a reference temperature. As recommended by IUPAC [1982LAF], the reference temperature chosen in the NEA TDB Project is T = 298.15 K or t = 25.00 °C. Where necessary for the discussion, values of experimentally measured temperatures are reported after conversion to the IPTS–68 [1969COM]. The relation between the absolute temperature T (K, kelvin) and the Celsius temperature t (°C) is defined by t / °C = T /K – 273.15.

II.4 Fundamental physical constants

To ensure the consistency with other NEA TDB Reviews, the fundamental physical constants are taken from a publication by CODATA [1986COD]. Those relevant to this review are listed in Table II-7. Updated values of the fundamental constants can be obtained from CODATA, notably through its Internet site. In most cases, recalculation of the NEA TDB database entries with the updated values of the fundamental constants will not introduce significant (with respect to their quoted uncertainties) excursions from the current NEA TDB selections.

Table II-7: Fundamental physical constants. These values have been taken from CODATA [1986COD]. The digits in parentheses are the one-standard-deviation uncertainty in the last digits of the given value.

Quantity	Symbol	Value	Units
speed of light in vacuum	c_0	299 792 458	$\mathrm{m \cdot s^{-1}}$
permeability of vacuum	μ_0	$4\pi \times 10^{-7}$ = 12.566 370 614…	$10^{-7}\ \mathrm{N \cdot A^{-2}}$
permittivity of vacuum	ϵ_0	$1/\mu_0\ c^2$ = 8.854 187 817…	$10^{-12}\ \mathrm{C^2 \cdot J^{-1} \cdot m^{-1}}$
Planck constant	h	6.626 0755(40)	$10^{-34}\ \mathrm{J \cdot s}$
elementary charge	e	1.602 177 33(49)	$10^{-19}\ \mathrm{C}$
Avogadro constant	N_A	6.022 1367(36)	$10^{23}\ \mathrm{mol^{-1}}$
Faraday constant	F	96 485.309(29)	$\mathrm{C \cdot mol^{-1}}$
molar gas constant	R	8.314 510(70)	$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$
Boltzmann constant, R/N_A	k_B	1.380 658(12)	$10^{-23}\ \mathrm{J \cdot K^{-1}}$
Non–SI units used with SI:			
electronvolt, (e/C) J	eV	1.602 177 33(49)	10^{-19} J
atomic mass unit,	u	1.660 5402(10)	10^{-27} kg
$1\,\mathrm{u} = m_u = \frac{1}{12} m\,(^{12}\mathrm{C})$			

II.5 Uncertainty estimates

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

II.6 The NEA TDB system

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

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

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

For aqueous neutral species and ions, the values of $\Delta_\mathrm{f} G^\circ_\mathrm{m}$, $\Delta_\mathrm{f} H^\circ_\mathrm{m}$, S°_m and $C^\circ_{p,\mathrm{m}}$ correspond to the standard partial molar quantities, and for individual aqueous ions they are relative quantities, defined with respect to the aqueous hydrogen ion, according to the convention [1989COX/WAG] that $\Delta_\mathrm{f} H^\circ_\mathrm{m}(\mathrm{H^+}, T) = 0$ and that $S^\circ_\mathrm{m}(\mathrm{H^+}, T) = 0$. Furthermore, for an *ionised solute* B containing any number of different cations and anions:

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

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

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

$$\begin{aligned} X(T) \;=\; & a_X + b_X T + c_X T^2 + d_X T^{-1} + e_X T^{-2} + f_X \ln T + g_X T \ln T \\ & + h_X \sqrt{T} + \frac{i_X}{\sqrt{T}} + j_X T^3 + k_X T^{-3}. \end{aligned} \qquad \text{(II.53)}$$

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

$$C^\circ_{p,\mathrm{m}}(T) = a + bT + cT^2 + dT^{-1} + eT^{-2} + fT^3 \qquad \text{(II.54)}$$

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

The pressure dependence of thermodynamic data has not been the subject of critical analysis in the present compilation. The reader interested in higher temperatures and pressures, or the pressure dependency of thermodynamic functions for geochemical applications, is referred to the specialised literature in this area, *e.g.*, [1982HAM], [1984MAR/MES], [1988SHO/HEL], [1988TAN/HEL], [1989SHO/HEL], [1989SHO/HEL2], [1990MON], [1991AND/CAS].

Selected standard thermodynamic data referring to chemical reactions are also compiled in the database. A chemical reaction “r”, involving reactants and products “B”, can be abbreviated as:

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

where the stoichiometric coefficients ν_{B} are positive for products, and negative for reactants. The reaction parameters considered in the NEA TDB system include:

$\log_{10} K_{\mathrm{r}}^{\mathrm{o}}$	the equilibrium constant of the reaction, logarithmic
$\Delta_{\mathrm{r}}G_{\mathrm{m}}^{\mathrm{o}}$	the molar Gibbs energy of reaction ($\mathrm{kJ\cdot mol^{-1}}$)
$\Delta_{\mathrm{r}}H_{\mathrm{m}}^{\mathrm{o}}$	the molar enthalpy of reaction ($\mathrm{kJ\cdot mol^{-1}}$)
$\Delta_{\mathrm{r}}S_{\mathrm{m}}^{\mathrm{o}}$	the molar entropy of reaction ($\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$)
$\Delta_{\mathrm{r}}C_{p,\mathrm{m}}^{\mathrm{o}}$	the molar heat capacity of reaction ($\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$) at constant pressure.

The temperature functions of these data, if available, are stored according to Eq. (II.53).

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

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

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

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

II.7 Presentation of the selected data

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

Chapter III contains a table of selected thermodynamic data for individual compounds and complexes of iron (Table III-1), a table of selected reaction data (Table III-2) for reactions concerning iron species and a table containing the heat capacities of individual species of iron (Table III-3) that have been used in the evaluations. The selection of all these data is discussed in Chapters V to XI.

Chapter IV contains tables of thermodynamic data for individual species (Table IV-1) and reaction data (Table IV-2), for auxiliary compounds and complexes that do not contain iron. Most of these values are the CODATA Key Values [1989COX/WAG]. The selection of the remaining auxiliary data is discussed in [1992GRE/FUG], [1999RAR/RAN], [2001LEM/FUG], [2005GAM/BUG], [2005OLI/NOL] and [2008RAN/FUG].

All the selected data presented in Table III-1, Table III-2, Table III-3, Table IV-1 and Table IV-2 are internally consistent. This consistency is maintained by the internal consistency verification and recalculation software developed at the NEA Data Bank in conjunction with the NEA TDB database system, *cf.* Section II.6. Therefore, when using the selected data, the auxiliary data of Chapter IV must be used together with the data in Chapter III to ensure internal consistency of the data set.

It is important to note that Table III-2 and Table IV-2 include only those species for which the primary selected data are reaction data. The formation data derived therefrom and listed in Table III-1 are obtained using auxiliary data, and their uncertainties are propagated accordingly. In order to maintain the uncertainties originally assigned to the selected data in this review, the user is advised to make direct use of the reaction data presented in Table III-2 and Table IV-2, rather than taking the derived values in Table III-1 and Table IV-1 to calculate the reaction data with Eq. (II.56). The latter approach would imply a twofold propagation of the uncertainties and result in reaction data whose uncertainties would be considerably larger than those originally assigned.

The thermodynamic data in the selected set refer to a temperature of 298.15 K (25.00 °C), but they can be recalculated to other temperatures if the corresponding data (enthalpies, entropies, heat capacities) are available [1997PUI/RAR]. For example, the temperature dependence of the standard reaction Gibbs energy as a function of the standard reaction entropy at the reference temperature ($T_0 =$ 298.15 K), and of the heat capacity function is:

$$\Delta_{\mathrm{r}}G^{\mathrm{o}}_{\mathrm{m}}(T) \;=\; \Delta_{\mathrm{r}}H^{\mathrm{o}}_{\mathrm{m}}(T_0) + \int_{T_0}^{T} \Delta_{\mathrm{r}}C^{\mathrm{o}}_{p,\mathrm{m}}(T)\,\mathrm{d}T - T\left(\Delta_{\mathrm{r}}S^{\mathrm{o}}_{\mathrm{m}}(T_0) + \int_{T_0}^{T} \frac{\Delta_{\mathrm{r}}C^{\mathrm{o}}_{p,\mathrm{m}}(T)}{T}\mathrm{d}T\right),$$

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

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

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

In the case of aqueous species, for which enthalpies of reaction are selected or can be calculated from the selected enthalpies of formation, but for which there are no selected heat capacities, it is in most cases possible to recalculate equilibrium constants to temperatures up to 100 to 150 °C, with an additional uncertainty of perhaps about ± 1 to ± 2 in $\log_{10} K$, due to neglect of the heat-capacity contributions to the temperature correction. For isocoulombic/isoelectric reactions the uncertainty may be smaller; for a detailed discussion see [1997PUI/RAR]. However, it is important to observe that "new" aqueous species, *i.e.*, species not present in significant amounts at 298.15 K and therefore not detected, may be significant at higher temperatures, see for example the work by Ciavatta *et al.* [1987CIA/IUL]. Additional high–temperature experiments may therefore be needed in order to ascertain that proper chemical models are used in the modelling of hydrothermal systems. For many species, experimental thermodynamic data are not available to allow a selection of parameters describing the temperature dependence of equilibrium constants and Gibbs energies of formation. The user may find information on various procedures to estimate the temperature dependence of these thermodynamic parameters in [1997PUI/RAR]. The thermodynamic data in the selected set refer to infinite dilution for soluble species. Extrapolation of an equilibrium constant K, usually measured at high ionic strength, to K° at $I = 0$ using activity coefficients γ, is explained in Appendix B. The corresponding Gibbs energy of dilution is:

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

$$= -\,RT\ \Delta_{\text{r}} \ln \gamma_{\pm} \tag{II.58}$$

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

$$\Delta_{\text{dil}}H_{\text{m}} = RT^{2}\frac{\partial}{\partial T}(\Delta_{\text{r}} \ln \gamma_{\pm})_{p} \tag{II.59}$$

depends only on the variation of γ with T, which is neglected in this review, when no data on the temperature dependence of γs are available. In this case the Gibbs energy of dilution $\Delta_{\text{dil}}G_{\text{m}}$ is entirely assigned to the entropy difference. This entropy of reaction is calculated using $\Delta_{\text{r}}G^{\circ}_{\text{m}} = \Delta_{\text{r}}H^{\circ}_{\text{m}} - T\Delta_{\text{r}}S^{\circ}_{\text{m}}$, the value of $\Delta_{\text{dil}}G_{\text{m}}$ and with the approximation that $\Delta_{\text{dil}}H_{\text{m}} = 0$.

Part 2

Tables of selected data

Chapter III

Selected iron data

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

The species and reactions in the tables appear in standard order of arrangement. Table III-2 contains information only on those reactions for which primary data selections are made in Chapters V to XI of this review. These selected reaction data are used, together with data for key iron species and auxiliary data selected in this review, to derive the corresponding formation data in Table III-1. The uncertainties associated with values for key iron species and the auxiliary data are in some cases substantial, leading to comparatively large uncertainties in the formation quantities derived in this manner.

The values of $\Delta_{\mathrm{r}}G_{\mathrm{m}}^{\circ}$ for many reactions are known more accurately than would be calculated directly from the uncertainties of the $\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ}$ values in Table III-1 and auxiliary data. The inclusion of a table for reaction data (Table III-2) in this report allows the use of equilibrium constants with total uncertainties that are based directly on the experimental accuracies. This is the main reason for including both Table III-1 and Table III-2.

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

$$C_{p,\mathrm{m}}^{\circ}(T) = a + bT + cT^{2} + dT^{-1} + eT^{-2} + fT^{3}$$

A detailed discussion of the selection procedure is presented in Chapters V to XI. 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 database 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 iron compounds and complexes. All ionic species listed in this table are aqueous species. Unless noted otherwise, all data refer to the reference temperature of 298.15 K and to the standard state, *i.e.*, a pressure of 0.1 MPa and, for aqueous species, infinite dilution ($I = 0$). The uncertainties listed below each value represent total uncertainties and correspond in principle to the statistically defined 95% confidence interval. Values obtained from internal calculation, *cf.* footnotes (a) and (b), are rounded at the third digit after the decimal point and may therefore not be exactly identical to those given in Chapters V to XI. 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	$\Delta_f G_m^o$ (kJ·mol^{-1})	$\Delta_f H_m^o$ (kJ·mol^{-1})	S_m^o (J·K^{-1}·mol^{-1})	$C_{p,m}^o$ (J·K^{-1}·mol^{-1})
α-Fe	0.000	0.000	27.085 ± 0.160	25.084 ± 0.500
Fe^{2+}	– 90.719 (b) ± 0.641	– 90.295 ± 0.522	– 102.171 (a) ± 2.778	– 23.000 ± 10.000
Fe^{3+}	– 16.226 (b) ± 0.650	– 50.056 (b) ± 0.973	– 282.404 (b) ± 3.927	– 108.000 ± 20.000
$Fe_{0.932}O$(cr)	– 244.593 (a) ± 1.906	– 265.800 ± 1.900	56.690 ± 0.490(c)	48.970 ± 0.290
α-Fe_2O_3(cr)	– 744.448 (a) ± 2.632	– 826.290 ± 2.630	87.400 ± 0.160	103.930 ± 0.170
γ-Fe_2O_3(cr)	– 727.830 (a) ± 3.027	– 807.990 (b) ± 3.023	93.040 ± 0.400	104.690 ± 0.350
α-Fe_3O_4(cr)	– 1012.719 (a) ± 1.609	– 1115.780 ± 1.600	145.890 ± 0.300	150.780 ± 1.250
α-FeOOH(cr)	– 489.537 (a) ± 1.996	– 560.460 ± 1.990	59.700 ± 0.500	74.360 ± 0.420
γ-FeOOH(cr)	– 479.881 (a) ± 2.005	– 549.200 ± 2.000	65.080 ± 0.460	69.140 ± 0.560
$FeOH^{+}$	– 275.916 (b) ± 2.372			
$FeOH^{2+}$	– 241.094 (b) ± 0.764	– 299.886 (b) ± 3.154	-132.871 (b) ± 10.886	
$Fe(OH)_2^{+}$	– 463.107 (b) ± 2.375			
$Fe_2(OH)_2^{4+}$	– 490.635 (b) ± 1.446	– 627.773 (b) ± 3.576	-331.321 (b) ± 12.942	

(Continued on next page)

Table III-1 (continued)

Compound	$\Delta_f G_m^o$ (kJ·mol^{-1})	$\Delta_f H_m^o$ (kJ·mol^{-1})	S_m^o (J·K^{-1}·mol^{-1})	$C_{p,m}^o$ (J·K^{-1}·mol^{-1})
FeF^+	– 381.946 [(b)] ± 1.481			
FeF_2(cr)	– 669.499 [(a)] ± 8.500	– 712.100 ± 8.500	86.990 ± 0.200	68.090 ± 0.500
FeF_3(cr)		– 991.700 ± 10.000		91.300 ± 2.000
$FeCl^+$		– 235.824 [(b)] ± 1.853		
$FeCl^{2+}$	– 156.119 [(b)] ± 0.873	– 194.656 [(b)] ± 4.703	-121.309 [(b)] ± 16.043	
$FeCl_2^+$	– 291.332 [(b)] ± 1.442			
$FeCl_2$(cr)	– 302.190 [(a)] ± 0.527	– 341.534 ± 0.502	118.206 ± 0.517	76.760 ± 1.000
$FeCl_2\cdot H_2O$(cr)	– 505.772 [(b)] ± 2.069			
$FeCl_2\cdot 2H_2O$(cr)	– 803.802 [(b)] ± 1.661			
$FeCl_2\cdot 4H_2O$(cr)	– 1284.545 [(b)] ± 0.709	– 1547.654 [(b)] ± 3.243	300.718 [(b)] ± 11.135	
$FeCl_3$(aq)	– 415.700 [(b)] ± 1.843			
$FeCl_3$(cr)	– 331.505 [(a)] ± 0.260	– 395.976 ± 0.091	145.470 ± 0.800	96.590 ± 1.000
$FeCl_3\cdot 2H_2O$(cr)		– 1011.446 ± 1.503		
$FeCl_3\cdot 2.5H_2O$(cr)		– 1162.386 ± 1.503		
$FeCl_3\cdot 3.5H_2O$(cr)		– 1473.416 ± 1.503		
$FeCl_3\cdot 6H_2O$(cr)		– 2221.926 ± 1.503		342.000 ± 4.000
$FeCl_4^-$	– 535.501 [(b)] ± 4.402			
FeOCl(cr)	– 358.618 [(a)] ± 3.002	– 405.875 [(b)] ± 3.001	82.700 ± 0.200	70.490 ± 0.200

(Continued on next page)

Table III-1 (continued)

Compound	$\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}$ (kJ·mol^{-1})	$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ (kJ·mol^{-1})	S°_{m} (J·K^{-1}·mol^{-1})	$C^{\circ}_{p,\mathrm{m}}$ (J·K^{-1}·mol^{-1})
$FeBr_2$(cr)	– 235.779 (a) ± 1.337	– 247.495 ± 0.989	140.000 ± 3.000	80.230 ± 1.200
$FeBr_3$(cr)	– 240.767 (a) ± 2.471	– 262.592 ± 0.628	182.200 ± 8.000	
FeI_2(cr)	– 127.076 (a) ± 7.783	– 117.900 ± 5.000	174.000 ± 20.000	83.690 ± 5.000
FeS(cr)	– 96.677 (b) ± 3.178			
$FeSO_4^+$	– 784.488 (b) ± 0.960			
$FeSO_4$(aq)	– 848.651 (b) ± 0.784	– 991.235 (b) ± 6.235	– 8.785 (b) ± 21.077	
$FeSO_4$(cr)				100.780 ± 2.000
$FeSO_4\cdot H_2O$(cr)	– 1077.518 (b) ± 5.048	– 1244.000 ± 1.500	144.316 (a) ± 17.664	
$FeSO_4\cdot 4H_2O$(cr)	– 1792.724 (b) ± 0.671	– 2128.504 (b) ± 1.621	276.254 (b) ± 5.885	
$FeSO_4\cdot 7H_2O$(cr)	– 2507.710 (b) ± 0.652	– 3012.512 (b) ± 0.602	409.118 (b) ± 0.825	
$Fe_2(SO_4)_3$(cr)	– 2263.397 (a) ± 3.906	– 2584.100 ± 3.900	305.600 ± 0.600	272.930 ± 1.000
$Fe_2(SO_4)_3\cdot 5H_2O$(cr)		– 4106.500 ± 5.900		
$Fe(SO_4)_2^-$	– 1539.738 (b) ± 1.284			
$Fe_{4.78}(SO_4)_6(OH)_{2.34}(H_2O)_{20.71}$(cr)		– 12046.200 ± 12.600		
$(H_3O)_{0.91}Fe_{2.91}(SO_4)_2(OH)_{5.64}(H_2O)_{0.18}$(cr)	– 3163.853 (a) ± 6.925	– 3693.900 ± 6.500	446.500 ± 8.000	
$(H_3O)_{1.34}Fe(SO_4)_{2.17}(H_2O)_{3.06}$(cr)		– 3201.220 ± 3.560		
$(H_3O)Fe_3(SO_4)_2(OH)_6$(cr)			448.200 ± 0.700	437.500 ± 2.000
$FeO(SO_4)_{0.157}(OH)_{0.686}(H_2O)_{0.972}$(cr)		– 884.100 ± 2.000		

(Continued on next page)

Table III-1 (continued)

Compound	$\Delta_f G_m^o$ (kJ·mol^{-1})	$\Delta_f H_m^o$ (kJ·mol^{-1})	S_m^o (J·K^{-1}·mol^{-1})	$C_{p,m}^o$ (J·K^{-1}·mol^{-1})
$FeO(SO_4)_{0.168}(OH)_{0.664}(H_2O)_{1.226}(cr)$		– 960.600 ± 2.000		
$FeCO_3(aq)$	– 648.677 (b) ± 1.285			
$FeCO_3(cr)$	– 679.557 (a) ± 0.917	– 752.609 ± 0.895	95.537 ± 0.646	82.450 ± 2.000
$Fe(CO_3)_2^{2-}$	– 1186.670 (b) ± 1.293			
$Fe(CO_3)_3^{3-}$	– 1736.918 (b) ± 11.494			
$Fe(OH)CO_3(aq)$	– 842.342 (b) ± 11.441			
$FeSiO_3$(clino)				90.600 ± 5.000
$FeSiO_3$(ortho)			94.600 ± 3.000	
α-Fe_2SiO_4	– 1377.720 (a) ± 1.076	– 1476.790 ± 1.070	151.000 ± 0.200	132.030 ± 0.300
γ-Fe_2SiO_4				128.000 ± 3.000
$((Fe^{2+})_{4.87}(Fe^{3+})_{2.76}Mn_{1.07}Mg_{0.15}Ti_{0.15}O_3)$ $(Si_{5.94}Al_{0.03}Ti_{0.03}O_{17})(cr)$				786.100 ± 0.800
$((Fe^{2+})_{5.38}(Fe^{3+})_{0.66}Mn_{0.08}Mg_{0.8}Ca_{0.05})(Si_8O_{22})$ $\{(OH)_{1.37}Cl_{0.03}O_{0.6}\}(cr)$				684.900 ± 2.600
$((Fe^{2+})_{5.2766}(Fe^{3+})_{0.12}Mn_{0.0825}Mg_{1.5209})$ $(Si_{7.9163}Al_{0.0837}O_{22.0363})(OH)_{1.9637}(cr)$				684.900 ± 3.000

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

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

(c) This value excludes a possible small zero-point entropy contribution (see Section VII.2.8.2).

Table III-2: Selected thermodynamic data for reactions involving iron compounds and complexes. All ionic species listed in this table are aqueous species. Unless noted otherwise, all data refer to the reference temperature of 298.15 K and to the standard state, *i.e.*, a pressure of 0.1 MPa and, for aqueous species, infinite dilution (I = 0). The uncertainties listed below each value represent total uncertainties and correspond in principal to the statistically defined 95% confidence interval. Values obtained from internal calculation, *cf.* footnote (a), are rounded at the third digit after the decimal point and may therefore not be exactly identical to those given in Chapters V to XI. Systematically, all the values are presented with three digits after the decimal point, regardless of the significance of these digits. The data presented in this table are available on computer media from the OECD Nuclear Energy Agency.

Species	Reaction			
	$\log_{10} K^\circ$	$\Delta_r G^\circ_m$ (kJ·mol^{-1})	$\Delta_r H^\circ_m$ (kJ·mol^{-1})	$\Delta_r S^\circ_m$ (J·K^{-1}·mol^{-1})
Fe^{2+}	$Fe(cr) + 2H^+ \rightleftharpoons Fe^{2+} + H_2(g)$			
	15.893 ± 0.112	-90.719 ± 0.641		
Fe^{3+}	$Fe^{2+} + H^+ \rightleftharpoons Fe^{3+} + 0.5H_2(g)$			
	-13.051 (b) ± 0.160	74.494 ± 0.913	40.238 (a) ± 1.699	-114.894 ± 4.805
γ-Fe_2O_3	α-$Fe_2O_3 \rightarrow \gamma$-$Fe_2O_3$			
			18.300 ± 1.490	
$FeOH^+$	$Fe^{2+} + H_2O(l) \rightleftharpoons FeOH^+ + H^+$			
	-9.100 ± 0.400	51.943 ± 2.283		
$FeOH^{2+}$	$Fe^{3+} + H_2O(l) \rightleftharpoons FeOH^{2+} + H^+$			
	-2.150 ± 0.070	12.272 ± 0.400	36.000 ± 3.000	79.583 (a) ± 10.151
$Fe(OH)_2^+$	$Fe^{3+} + 2H_2O(l) \rightleftharpoons Fe(OH)_2^+ + 2H^+$			
	-4.800 ± 0.400	27.399 ± 2.283		
$Fe_2(OH)_2^{4+}$	$2Fe^{3+} + 2H_2O(l) \rightleftharpoons Fe_2(OH)_2^{4+} + 2H^+$			
	-2.820 ± 0.110	16.097 ± 0.628	44.000 ± 3.000	93.588 (a) ± 10.280
FeF^+	$F^- + Fe^{2+} \rightleftharpoons FeF^+$			
	1.700 ± 0.200	-9.704 ± 1.142		

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Table III-2 (continued)

Species	Reaction			
	$\log_{10} K^{\circ}$	$\Delta_r G^{\circ}_m$ (kJ·mol^{-1})	$\Delta_r H^{\circ}_m$ (kJ·mol^{-1})	$\Delta_r S^{\circ}_m$ (J·K^{-1}·mol^{-1})
$FeCl^{+}$	$Cl^{-} + Fe^{2+} \rightleftharpoons FeCl^{+}$			
			21.551	
			± 1.775	
$FeCl^{2+}$	$Cl^{-} + Fe^{3+} \rightleftharpoons FeCl^{2+}$			
	1.520	-8.676	22.480	104.498 (a)
	± 0.100	± 0.571	± 4.600	± 15.547
$FeCl_2^{+}$	$Cl^{-} + FeCl^{2+} \rightleftharpoons FeCl_2^{+}$			
	0.700	-3.996		
	± 0.200	± 1.142		
$FeCl_2{\cdot}H_2O(cr)$	$FeCl_2(cr) + H_2O(g) \rightleftharpoons FeCl_2{\cdot}H_2O(cr)$			
	-4.380	25.000		
	± 0.350	± 2.000		
$FeCl_2{\cdot}2H_2O(cr)$	$FeCl_2\ 4H_2O(cr) \rightleftharpoons FeCl_2{\cdot}2H_2O(cr) + 2H_2O(g)$			
	-4.131	23.580		
	± 0.263	± 1.500		
$FeCl_2{\cdot}4H_2O(cr)$	$FeCl_2(cr) + 4H_2O(l) \rightleftharpoons FeCl_2{\cdot}4H_2O(cr)$			
	5.921 (c)	-33.795	-62.800	-97.283 (a)
	± 0.176	± 1.007	± 3.200	± 11.252
$FeCl_3(aq)$	$Cl^{-} + FeCl_2^{+} \rightleftharpoons FeCl_3(aq)$			
	-1.200	6.850		
	± 0.200	± 1.142		
$FeCl_4^{-}$	$Cl^{-} + FeCl_3(aq) \rightleftharpoons FeCl_4^{-}$			
	-2.000	11.416		
	± 0.700	± 3.996		
$FeOCl(cr)$	$FeCl_3(cr) + 0.5O_2(g) \rightleftharpoons Cl_2(g) + FeOCl(cr)$			
			-9.900	
			± 3.000	
$FeS(cr)$	$Fe^{2+} + H_2S(aq) \rightleftharpoons FeS(cr) + 2H^{+}$			
	-3.800	21.691		
	± 0.400	± 2.283		
$FeSO_4^{+}$	$Fe^{3+} + SO_4^{2-} \rightleftharpoons FeSO_4^{+}$			
	4.250	-24.259		
	± 0.100	± 0.571		

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Table III-2 (continued)

Species	Reaction			
	$\log_{10} K^{\circ}$	$\Delta_r G_m^{\circ}$ (kJ·mol^{-1})	$\Delta_r H_m^{\circ}$ (kJ·mol^{-1})	$\Delta_r S_m^{\circ}$ (J·K^{-1}·mol^{-1})
$FeSO_4(aq)$	$Fe^{2+} + SO_4^{2-} \rightleftharpoons FeSO_4(aq)$			
	2.440	-13.928	8.400	74.887 [(a)]
	± 0.030	± 0.171	± 6.200	± 20.803
$FeSO_4 \cdot H_2O(cr)$	$FeSO_4 \cdot 7H_2O(cr) \rightleftharpoons FeSO_4 \cdot H_2O(cr) + 6H_2O(g)$			
	-10.284	58.700		
	± 0.876	± 5.000		
$FeSO_4 \cdot 4H_2O(cr)$	$FeSO_4 \cdot 7H_2O(cr) \rightleftharpoons FeSO_4 \cdot 4H_2O(cr) + 3H_2O(g)$			
	-5.123 [(c)]	29.240	158.530	433.641 [(a)]
	± 0.018	± 0.100	± 1.500	± 5.042
$FeSO_4 \cdot 7H_2O(cr)$	$Fe^{2+} + 7H_2O(l) + SO_4^{2-} \rightleftharpoons FeSO_4 \cdot 7H_2O(cr)$			
	2.279 [(c)]	-13.006	-12.068	3.146 [(a)]
	± 0.230	± 1.310	± 0.845	± 5.229
$Fe(SO_4)_2^-$	$FeSO_4^+ + SO_4^{2-} \rightleftharpoons Fe(SO_4)_2^-$			
	1.970	-11.245		
	± 0.130	± 0.742		
$FeCO_3(aq)$	$FeCO_3(cr) \rightleftharpoons FeCO_3(aq)$			
	-5.410	30.880		
	± 0.158	± 0.900		
$Fe(CO_3)_2^{2-}$	$CO_2(g) + FeCO_3(cr) + H_2O(l) \rightleftharpoons Fe(CO_3)_2^{2-} + 2H^+$			
	-21.794	124.400		
	± 0.158	± 0.900		
$Fe(CO_3)_3^{3-}$	$3CO_3^{2-} + Fe^{3+} \rightleftharpoons Fe(CO_3)_3^{3-}$			
	24.000	-136.993		
	± 2.000	± 11.416		
$Fe(OH)CO_3(aq)$	$CO_3^{2-} + Fe^{3+} + H_2O(l) \rightleftharpoons Fe(OH)CO_3(aq) + H^+$			
	10.700	-61.076		
	± 2.000	± 11.416		

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

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

Table III-3: Selected temperature coefficients for heat capacities in the form $C^{\circ}_{p,\mathrm{m}}(T) = a + bT + cT^2 + dT^{-1} + eT^{-2} + fT^3$ for solids containing iron. The functions are valid between the temperatures $T_{\min}$ and $T_{\max}$ (in K). Units for $C^{\circ}_{p,\mathrm{m}}$ are J·K^{-1}·mol^{-1}.

compound	a	b	c/f^{*}	d	e	$T_{\min}$	$T_{\max}$
α-Fe	2.72410×10^{1}	-5.09090×10^{-3}	2.35100×10^{-5}	0	-2.42610×10^{5}	298.15	800
$Fe_{0.932}O$	5.09417×10^{1}	4.52846×10^{-3}	$1.91856\times10^{-10\,(f)}$	0	-2.93969×10^{5}	298.15	1000
α-Fe_2O_3	5.19344×10^{2}	-5.07197×10^{-1}	2.83429×10^{-4}	-1.26376×10^{5}	1.19544×10^{7}	298.15	775
γ-Fe_2O_3	2.54629×10^{2}	-2.14079×10^{-1}	2.26847×10^{-4}	-3.81757×10^{4}	1.94111×10^{6}	273	400
α-Fe_3O_4 **	1.24795×10^{3}	-1.66142	1.05758×10^{-3}	-2.99131×10^{5}	2.73311×10^{7}	298.15	516.66
α-Fe_3O_4	1.75512×10^{4}	-1.97310×10^{1}	8.50170×10^{-3}	-6.78706×10^{6}	9.89090×10^{8}	516.66	713.66
α-FeOOH ***	8.03613×10^{1}	-8.75604×10^{-2}	3.76891×10^{-4}	-2.01424×10^{3}	-5.940812×10^{5}	200	372.6
α-FeOOH	7.79757×10^{5}	-1.45505×10^{3}	1.01228	-1.84429×10^{8}	1.62331×10^{10}	372.6	396
γ-FeOOH	9.09807×10^{1}	4.38991×10^{-2}	-2.98183×10^{-5}	-1.09226×10^{4}	3.86790×10^{5}	200	387
FeF_2	6.87299×10^{1}	2.69560×10^{-2}	0	0	-7.70919×10^{5}	250	675
$FeCl_2$	7.87960×10^{1}	9.21200×10^{-3}	0	0	-4.24935×10^{5}	240	950
$FeCl_3$ ****	6.91730×10^{1}	9.36200×10^{-2}	0	0	-4.36190×10^{4}	200	550
FeOCl	6.70320×10^{1}	2.90370×10^{-2}	0	0	-4.61900×10^{5}	298.15	662.1
$FeBr_2$	7.35970×10^{1}	2.22600×10^{-2}	0	0	0	323	633
FeI_2	8.29690×10^{1}	2.42700×10^{-3}	0	0	0	298	633
$Fe_2(SO_4)_3$	2.02960×10^{2}	3.31520×10^{-1}	0	0	-2.56680×10^{6}	250	395
$Fe_2(SO_4)_3$	2.63770×10^{2}	2.17630×10^{-1}	0	0	-5.10870×10^{6}	350	800
$(H_3O)_{0.91}Fe_{2.91}(SO_4)_2(OH)_{5.64}(H_2O)_{0.18}$	2.80600×10^{2}	6.14900×10^{-1}	0	0	-3.19970×10^{6}	274.74	394.94
$(H_3O)Fe_3(SO_4)_2(OH)_6$	2.87200×10^{2}	6.28100×10^{-1}	0	0	-3.28600×10^{6}	273	400
$FeCO_3$	5.23900×10^{1}	1.25798×10^{-1}	-3.30800×10^{-5}	0	-4.00400×10^{5}	230	500
α-Fe_2SiO_4 ****	3.15410×10^{2}	-1.43430×10^{-1}	6.95410×10^{-5}	-5.69590×10^{4}	3.93230×10^{6}	230	1450
γ-Fe_2SiO_4	1.13400×10^{1}	1.38210×10^{-1}	0	6.165000×10^{4}	-1.16740×10^{7}	298.15	1000
$FeSiO_3$	1.24260×10^{2}	1.45400×10^{-2}	0	0	-3.37770×10^{6}	350	610
$\{Fe^{2+}_{5.2766}Fe^{3+}_{0.12}Mn_{0.0825}Mg_{1.5209})(Si_{7.9163}Al_{0.0837}O_{22.0363})\{(OH)_{1.9637}\}$	6.14270×10^{2}	5.71720×10^{-1}	0	0	-8.88035×10^{6}	240	850

* Term is cT^2 if unmarked, or fT^3 if marked "f".

** The heat-capacity values generated from this expression are approximate.

*** The values of the coefficients for this temperature range are highly correlated. See Section VII.2.9.2 for a consistent heat-capacity equation for this temperature range.

**** The 298.15 K values for $FeCl_3$(cr) and α-Fe_2SiO_4 from these equations show very minor mismatches when compared with those in the selected values tables. This is because of rounding of the coefficients. There are slightly larger mismatches, still well within the specified uncertainties, in the 298.15 K values for γ-Fe_2O_3, $Fe_{0.932}O$ and α-FeOOH, and these differences are discussed in the appropriate sections of the text.

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 iron data in Tables III-1, III-2 and III-3. It is therefore essential to always use these auxiliary data in conjunction with the selected data for iron. The use of other auxiliary data can lead to inconsistencies and erroneous results.

The values in the tables of this chapter for auxiliary compounds and complexes are either CODATA Key Values, taken from [1989COX/WAG], or were evaluated within the NEA TDB Project, as described in the corresponding chapters of the uranium review [1992GRE/FUG], the technetium review [1999RAR/RAN], the neptunium and plutonium review [2001LEM/FUG], the Update review [2003GUI/FAN], the nickel review [2005GAM/BUG], the selenium review [2005OLI/NOL], the thorium review [2008RAN/FUG] and the tin review [2012GAM/GAJ].

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

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

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

- for CODATA values from [1989COX/WAG], the ± terms have the meaning: “it is probable, but not at all certain, that the true values of the thermodynamic quantities differ from the recommended values given in this report by no more than twice the ± terms attached to the recommended values".

- for values from [1992GRE/FUG], [1999RAR/RAN], [2003GUI/FAN], [2005GAM/BUG], [2005OLI/NOL], [2008RAN/FUG] and [2012GAM/GAJ], the ± terms are derived from total uncertainties in the corresponding equilibrium constant of reaction (*cf.* Table IV-2), and from the ± terms listed for the necessary CODATA key values.

CODATA [1989COX/WAG] values are available for CO_2(g), HCO_3^-, CO_3^{2-}, $H_2PO_4^-$ and HPO_4^{2-}. From the values given for $\Delta_f H_m^o$ and S_m^o the values of $\Delta_f G_m^o$ and, consequently, all the relevant equilibrium constants and enthalpy changes can be calculated. The propagation of errors during this procedure, however, leads to uncertainties in the resulting equilibrium constants that are significantly higher than those obtained from experimental determination of the constants. Therefore, reaction data for CO_2(g), HCO_3^-, CO_3^{2-}, which were absent form the corresponding Table IV-2 in [1992GRE/FUG], are included in this volume to provide the user of selected data for the organic ligands (*cf.* Chapter III) with the data needed to obtain the lowest possible uncertainties on reaction properties.

Note that the values in Table IV-1 and Table IV-2 may contain more digits than those listed in either [1989COX/WAG] or in the chapters devoted to data selection in [1992GRE/FUG], [1995SIL/BID], [2001LEM/FUG], [2003GUI/FAN], [2005GAM/BUG], [2005OLI/NOL], [2008RAN/FUG] and [2012GAM/GAJ] because the data in the present chapter are retrieved directly from the computerised database and rounded to three digits after the decimal point throughout.

Table IV-1: Selected thermodynamic data for auxiliary compounds and complexes adopted in the NEA TDB Project, including the CODATA Key Values [1989COX/WAG]. All ionic species listed in this table are aqueous species. Unless noted otherwise, all data refer to 298.15 K and a pressure of 0.1 MPa and, for aqueous species, a standard state of infinite dilution (I = 0). The uncertainties listed below each value represent total uncertainties and correspond in principle to the statistically defined 95% confidence interval. Values in bold typeface are CODATA Key Values and are taken directly from [1989COX/WAG] without further evaluation. Values obtained from internal calculation, *cf.* footnotes (a) and (b), are rounded at the third digit after the decimal point and may therefore not be exactly identical to those given in the chapters devoted to data selection in [1992GRE/FUG], [1995SIL/BID], [2001LEM/FUG], [2003GUI/FAN], [2005GAM/BUG], [2005OLI/NOL], [2008RAN/FUG] and [2012GAM/BUG]. Systematically, all the values are presented with three digits after the decimal point, regardless of the significance of these digits. The reference listed for each entry in this table indicates the NEA TDB Review where the corresponding data have been adopted as NEA TDB Auxiliary data. The data presented in this table are available on computer media from the OECD Nuclear Energy Agency.

Compound and review where adopted	$\Delta_f G_m^o$ (kJ·mol^{-1})	$\Delta_f H_m^o$ (kJ·mol^{-1})	S_m^o (J·K^{-1}·mol^{-1})	$C_{p,m}^o$ (J·K^{-1}·mol^{-1})
O(g) [1992GRE/FUG]	**231.743** (a) **±0.100**	**249.180** **±0.100**	**161.059** **±0.003**	**21.912** **±0.001**
O_2(g) [1992GRE/FUG]	**0.000**	**0.000**	**205.152** **±0.005**	**29.378** **±0.003**
H(g) [1992GRE/FUG]	**203.276** (a) **±0.006**	**217.998** **±0.006**	**114.717** **±0.002**	**20.786** **±0.001**
H^+ [1992GRE/FUG]	**0.000**	**0.000**	**0.000**	**0.000**
H_2(g) [1992GRE/FUG]	**0.000**	**0.000**	**130.680** **±0.003**	**28.836** **±0.002**
D_2(g) [2008RAN/FUG]	0.000 ±0.000	0.000 ±0.000	144.958 ±0.005	29.195 ±0.005
T_2(g) [2008RAN/FUG]	0.000 ±0.000	0.000 ±0.000	153.327 ±0.005	29.199 ±0.005
OH^- [1992GRE/FUG]	**– 157.220** (a) **±0.072**	**– 230.015** **±0.040**	**– 10.900** **±0.200**	
H_2O(g) [1992GRE/FUG]	**– 228.582** (a) **±0.040**	**– 241.826** **±0.040**	**188.835** **±0.010**	**33.609** **±0.030**
H_2O(l) [1992GRE/FUG]	**– 237.140** (a) **±0.041**	**– 285.830** **±0.040**	**69.950** **±0.030**	**75.351** **±0.080**

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Table IV-1 (continued)

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

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Table IV-1 (continued)

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

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Table IV-1 (continued)

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

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Table IV-1 (continued)

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

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_f G_m^o$ (kJ·mol^{-1})	$\Delta_f H_m^o$ (kJ·mol^{-1})	S_m^o (J·K^{-1}·mol^{-1})	$C_{p,m}^o$ (J·K^{-1}·mol^{-1})
SeO_3^{2-} [2005OLI/NOL]	–362.392 (b) ±1.756	–507.160 ±1.130	–5.055 (a) ±7.011	
SeO_4^{2-} [2005OLI/NOL]	–439.485 (b) ±1.431	–603.500 (b) ±3.500	32.965 (b) ±12.687	
Se_2O_5(cr) [2005OLI/NOL]		–414.590 (b) ±2.577		
HSe^- [2005OLI/NOL]	43.471 (b) ±2.024			
H_2Se(g) [2005OLI/NOL]	15.217 (a) ±2.003	29.000 ±2.000	219.000 ±0.100	34.700 (c) ±0.100
H_2Se(aq) [2005OLI/NOL]	21.495 (b) ±2.003	14.300 (b) ±2.022	148.637 (b) ±1.029	
$HSeO_3^-$ [2005OLI/NOL]	–410.112 (b) ±1.166	–512.330 ±1.010	137.656 (a) ±5.184	
$HSeO_4^-$ [2005OLI/NOL]	–449.474 (b) ±1.312	–582.700 (d) ±4.700	136.232 (a) ±16.370	
H_2SeO_3(cr) [2005OLI/NOL]		–524.720 (b) ±0.650		
H_2SeO_3(aq) [2005OLI/NOL]	–425.181 (b) ±0.849	–505.320 ±0.650	211.710 (a) ±3.601	
H_2SeO_4(cr) [2005OLI/NOL]		–530.500 ±1.880		
Te(cr) [1992GRE/FUG]	0.000	0.000	49.221 ±0.050	25.550 ±0.100
TeO_2(cr) [2003GUI/FAN]	– 265.996 (a) ±2.500	– 321.000 ±2.500	69.890 ±0.150	60.670 ±0.150
N(g) [1992GRE/FUG]	**455.537 (a)** **±0.400**	**472.680** **±0.400**	**153.301** **±0.003**	**20.786** **±0.001**
N_2(g) [1992GRE/FUG]	**0.000**	**0.000**	**191.609** **±0.004**	**29.124** **±0.001**
N_3^- [1992GRE/FUG]	348.200 ±2.000	275.140 ±1.000	107.710 (a) ±7.500	
NO_3^- [1992GRE/FUG]	**– 110.794 (a)** **±0.417**	**– 206.850** **±0.400**	**146.700** **±0.400**	
HN_3(aq) [1992GRE/FUG]	321.372 ±2.051	260.140 ±10.050	147.381 ±34.403	

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_{\mathrm{f}}G^{\mathrm{o}}_{\mathrm{m}}$ (kJ·mol^{-1})	$\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ (kJ·mol^{-1})	$S^{\mathrm{o}}_{\mathrm{m}}$ (J·K^{-1}·mol^{-1})	$C^{\mathrm{o}}_{p,\mathrm{m}}$ (J·K^{-1}·mol^{-1})
NH_3(aq)	– 26.673	– 81.170	109.040	
[1992GRE/FUG]	±0.305	±0.326	±0.913	
NH_3(g)	**– 16.407** (a)	**– 45.940**	**192.770**	**35.630**
[1992GRE/FUG]	**±0.350**	**±0.350**	**±0.050**	**±0.005**
NH_4^+	**– 79.398** (a)	**– 133.260**	**111.170**	
[1992GRE/FUG]	**±0.278**	**±0.250**	**±0.400**	
P(am)(red)		– 7.500		
[1992GRE/FUG]		±2.000		
P(cr)(white, cubic)	**0.000**	**0.000**	**41.090**	**23.824**
[1992GRE/FUG]			**±0.250**	**±0.200**
P(g)	**280.093** (a)	**316.500**	**163.199**	**20.786**
[1992GRE/FUG]	**±1.003**	**±1.000**	**±0.003**	**±0.001**
P_2(g)	**103.469** (a)	**144.000**	**218.123**	**32.032**
[1992GRE/FUG]	**±2.006**	**±2.000**	**±0.004**	**±0.002**
P_4(g)	**24.419** (a)	**58.900**	**280.010**	**67.081**
[1992GRE/FUG]	**±0.448**	**±0.300**	**±0.500**	**±1.500**
PO_4^{3-}	– 1025.491	– 1284.400	– 220.970	
[1992GRE/FUG]	±1.576	±4.085	±12.846	
$P_2O_7^{4-}$	– 1935.503			
[1992GRE/FUG]	±4.563			
HPO_4^{2-}	**– 1095.985** (a)	**– 1299.000**	**– 33.500**	
[1992GRE/FUG]	**±1.567**	**±1.500**	**±1.500**	
$H_2PO_4^-$	**– 1137.152** (a)	**– 1302.600**	**92.500**	
[1992GRE/FUG]	**±1.567**	**±1.500**	**±1.500**	
H_3PO_4(aq)	– 1149.367	– 1294.120	161.912	
[1992GRE/FUG]	±1.576	±1.616	±2.575	
$HP_2O_7^{3-}$	– 1989.158			
[1992GRE/FUG]	±4.482			
$H_2P_2O_7^{2-}$	– 2027.117			
[1992GRE/FUG]	±4.445			
$H_3P_2O_7^-$	– 2039.960			
[1992GRE/FUG]	±4.362			
$H_4P_2O_7$(aq)	– 2045.668	– 2280.210	274.919	
[1992GRE/FUG]	±3.299	±3.383	±6.954	
As(cr)	0.000	0.000	35.100	24.640
[1992GRE/FUG]			±0.600	±0.500

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_f G_m^o$ (kJ·mol^{-1})	$\Delta_f H_m^o$ (kJ·mol^{-1})	S_m^o (J·K^{-1}·mol^{-1})	$C_{p,m}^o$ (J·K^{-1}·mol^{-1})
AsO_2^- [1992GRE/FUG]	– 350.022 (a) ±4.008	– 429.030 ±4.000	40.600 ±0.600	
AsO_4^{3-} [1992GRE/FUG]	– 648.360 (a) ±4.008	– 888.140 ±4.000	– 162.800 ±0.600	
As_2O_5(cr) [1992GRE/FUG]	– 782.449 (a) ±8.016	– 924.870 ±8.000	105.400 ±1.200	116.520 ±0.800
As_4O_6(cubic) [1992GRE/FUG]	– 1152.445 (a) ±16.032	– 1313.940 ±16.000	214.200 ±2.400	191.290 ±0.800
As_4O_6(monoclinic) [1992GRE/FUG]	– 1154.009 (a) ±16.041	– 1309.600 ±16.000	234.000 ±3.000	
As_4O_6(g) [2005GAM/BUG]	– 1092.716 (a) ±16.116	– 1196.250 ±16.000	408.600 ±6.000	
$HAsO_2$(aq) [1992GRE/FUG]	– 402.925 (a) ±4.008	– 456.500 ±4.000	125.900 ±0.600	
$H_2AsO_3^-$ [1992GRE/FUG]	– 587.078 (a) ±4.008	– 714.790 ±4.000	110.500 ±0.600	
H_3AsO_3(aq) [1992GRE/FUG]	– 639.681 (a) ±4.015	– 742.200 ±4.000	195.000 ±1.000	
$HAsO_4^{2-}$ [1992GRE/FUG]	– 714.592 (a) ±4.008	– 906.340 ±4.000	– 1.700 ±0.600	
$H_2AsO_4^-$ [1992GRE/FUG]	– 753.203 (a) ±4.015	– 909.560 ±4.000	117.000 ±1.000	
H_3AsO_4(aq) [1992GRE/FUG]	– 766.119 (a) ±4.015	– 902.500 ±4.000	184.000 ±1.000	
$(As_2O_5)_3 \cdot 5\,H_2O$(cr) [1992GRE/FUG]		– 4248.400 ±24.000		
Sb(cr) [1992GRE/FUG]	0.000	0.000	45.520 ±0.210	25.260 ±0.200
Bi(cr) [2001LEM/FUG]	0.000	0.000	56.740 ±0.420	25.410 ±0.200
C(cr) [1992GRE/FUG]	**0.000**	**0.000**	**5.740** **±0.100**	**8.517** **±0.080**
C(g) [1992GRE/FUG]	**671.254 (a)** **±0.451**	**716.680** **±0.450**	**158.100** **±0.003**	**20.839** **±0.001**
CO(g) [1992GRE/FUG]	**– 137.168 (a)** **±0.173**	**– 110.530** **±0.170**	**197.660** **±0.004**	**29.141** **±0.002**

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Table IV-1 (continued)

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

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_f G_m^o$ (kJ·mol^{-1})	$\Delta_f H_m^o$ (kJ·mol^{-1})	S_m^o (J·K^{-1}·mol^{-1})	$C_{p,m}^o$ (J·K^{-1}·mol^{-1})
$Si_4O_8(OH)_4^{4-}$	– 4075.179			
[1992GRE/FUG]	±5.437			
$Si_4O_7(OH)_5^{3-}$	– 4136.826			
[1992GRE/FUG]	±4.934			
SiF_4(g)	**– 1572.773** (a)	**– 1615.000**	**282.760**	**73.622**
[1992GRE/FUG]	**±0.814**	**±0.800**	**±0.500**	**±0.500**
Ge(cr)	**0.000**	**0.000**	**31.090**	**23.222**
[1992GRE/FUG]			**±0.150**	**±0.100**
Ge(g)	**331.209** (a)	**372.000**	**167.904**	**30.733**
[1992GRE/FUG]	**±3.000**	**±3.000**	**±0.005**	**±0.001**
GeO_2(tetragonal)	**– 521.404** (a)	**– 580.000**	**39.710**	**50.166**
[1992GRE/FUG]	**±1.002**	**±1.000**	**±0.150**	**±0.300**
GeF_4(g)	**– 1150.018** (a)	**– 1190.200**	**301.900**	**81.602**
[1992GRE/FUG]	**±0.584**	**±0.500**	**±1.000**	**±1.000**
Sn(cr)	**0.000**	**0.000**	**51.180**	**27.110**
[2012GAM/GAJ]			**±0.080**	**±0.080**
Sn(g)	**266.223** (a)	**301.200**	**168.492**	**21.259**
[1992GRE/FUG]	**±1.500**	**±1.500**	**±0.004**	**±0.001**
Sn^{2+}	**– 27.390** (a)	**– 9.617**	**– 19.889**	
[2012GAM/GAJ]	**±0.300**	**±1.236**	**±4.266**	
Sn^{4+}	**– 46.711** (b)			
[2012GAM/GAJ]	**±3.871**			
SnO(tetragonal)	**– 255.446** (a)	**– 284.240**	**57.180**	**47.760**
[2012GAM/GAJ]	**±0.763**	**±0.760**	**±0.220**	**±0.080**
SnO_2(cassiterite, tetragonal)	**– 516.640** (a)	**– 577.630**	**51.770**	**55.260**
[2012GAM/GAJ]	**±0.206**	**±0.200**	**±0.140**	**±0.090**
Pb(cr)	**0.000**	**0.000**	**64.800**	**26.650**
[1992GRE/FUG]			**±0.300**	**±0.100**
Pb(g)	**162.232** (a)	**195.200**	**175.375**	**20.786**
[1992GRE/FUG]	**±0.805**	**±0.800**	**±0.005**	**±0.001**
Pb^{2+}	**– 24.238** (a)	**0.920**	**18.500**	
[1992GRE/FUG]	**±0.399**	**±0.250**	**±1.000**	
$PbSO_4$(cr)	**– 813.036** (a)	**– 919.970**	**148.500**	
[1992GRE/FUG]	**±0.447**	**±0.400**	**±0.600**	
B(cr)	**0.000**	**0.000**	**5.900**	**11.087**
[1992GRE/FUG]			**±0.080**	**±0.100**

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_f G_m^o$ (kJ·mol^{-1})	$\Delta_f H_m^o$ (kJ·mol^{-1})	S_m^o (J·K^{-1}·mol^{-1})	$C_{p,m}^o$ (J·K^{-1}·mol^{-1})
B(g) [1992GRE/FUG]	**521.012** [(a)] **±5.000**	**565.000** **±5.000**	**153.436** **±0.015**	**20.796** **±0.005**
B_2O_3(cr) [1992GRE/FUG]	**– 1194.324** [(a)] **±1.404**	**– 1273.500** **±1.400**	**53.970** **±0.300**	**62.761** **±0.300**
$B(OH)_3$(aq) [1992GRE/FUG]	**– 969.268** [(a)] **±0.820**	**– 1072.800** **±0.800**	**162.400** **±0.600**	
$B(OH)_3$(cr) [1992GRE/FUG]	**– 969.667** [(a)] **±0.820**	**– 1094.800** **±0.800**	**89.950** **±0.600**	**86.060** **±0.400**
BF_3(g) [1992GRE/FUG]	**– 1119.403** [(a)] **±0.803**	**– 1136.000** **±0.800**	**254.420** **±0.200**	**50.463** **±0.100**
Al(cr) [1992GRE/FUG]	**0.000**	**0.000**	**28.300** **±0.100**	**24.200** **±0.070**
Al(g) [1992GRE/FUG]	**289.376** [(a)] **±4.000**	**330.000** **±4.000**	**164.554** **±0.004**	**21.391** **±0.001**
Al^{3+} [1992GRE/FUG]	**– 491.507** [(a)] **±3.338**	**– 538.400** **±1.500**	**– 325.000** **±10.000**	
Al_2O_3(corundum) [1992GRE/FUG]	**– 1582.257** [(a)] **±1.302**	**– 1675.700** **±1.300**	**50.920** **±0.100**	**79.033** **±0.200**
AlF_3(cr) [1992GRE/FUG]	**– 1431.096** [(a)] **±1.309**	**– 1510.400** **±1.300**	**66.500** **±0.500**	**75.122** **±0.400**
Tl^+ [1999RAR/RAN]	– 32.400 ±0.300			
Zn(cr) [1992GRE/FUG]	**0.000**	**0.000**	**41.630** **±0.150**	**25.390** **±0.040**
Zn(g) [1992GRE/FUG]	**94.813** [(a)] **±0.402**	**130.400** **±0.400**	**160.990** **±0.004**	**20.786** **±0.001**
Zn^{2+} [1992GRE/FUG]	**– 147.203** [(a)] **±0.254**	**– 153.390** **±0.200**	**– 109.800** **±0.500**	
ZnO(cr) [1992GRE/FUG]	**– 320.479** [(a)] **±0.299**	**– 350.460** **±0.270**	**43.650** **±0.400**	
Cd(cr) [1992GRE/FUG]	**0.000**	**0.000**	**51.800** **±0.150**	**26.020** **±0.040**
Cd(g) [1992GRE/FUG]	**77.230** [(a)] **±0.205**	**111.800** **±0.200**	**167.749** **±0.004**	**20.786** **±0.001**
Cd^{2+} [1992GRE/FUG]	**– 77.733** [(a)] **±0.750**	**– 75.920** **±0.600**	**– 72.800** **±1.500**	

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_f G_m^o$ (kJ·mol^{-1})	$\Delta_f H_m^o$ (kJ·mol^{-1})	S_m^o (J·K^{-1}·mol^{-1})	$C_{p,m}^o$ (J·K^{-1}·mol^{-1})
CdO(cr)	**– 228.661** (a)	**– 258.350**	**54.800**	
[1992GRE/FUG]	**±0.602**	**±0.400**	**±1.500**	
$CdSO_4 \cdot \frac{8}{3} H_2O$(cr)	**– 1464.959** (a)	**– 1729.300**	**229.650**	
[1992GRE/FUG]	**±0.810**	**±0.800**	**±0.400**	
Hg(g)	**31.842** (a)	**61.380**	**174.971**	**20.786**
[1992GRE/FUG]	**±0.054**	**±0.040**	**±0.005**	**±0.001**
Hg(l)	**0.000**	**0.000**	**75.900**	
[1992GRE/FUG]			**±0.120**	
Hg^{2+}	**164.667** (a)	**170.210**	**– 36.190**	
[1992GRE/FUG]	**±0.313**	**±0.200**	**±0.800**	
Hg_2^{2+}	**153.567** (a)	**166.870**	**65.740**	
[1992GRE/FUG]	**±0.559**	**±0.500**	**±0.800**	
HgO(montroydite, red)	**– 58.523** (a)	**– 90.790**	**70.250**	
[1992GRE/FUG]	**±0.154**	**±0.120**	**±0.300**	
Hg_2Cl_2(cr)	**– 210.725** (a)	**– 265.370**	**191.600**	
[1992GRE/FUG]	**±0.471**	**±0.400**	**±0.800**	
Hg_2SO_4(cr)	**– 625.780** (a)	**– 743.090**	**200.700**	
[1992GRE/FUG]	**±0.411**	**±0.400**	**±0.200**	
Cu(cr)	**0.000**	**0.000**	**33.150**	**24.440**
[1992GRE/FUG]			**±0.080**	**±0.050**
Cu(g)	**297.672** (a)	**337.400**	**166.398**	**20.786**
[1992GRE/FUG]	**±1.200**	**±1.200**	**±0.004**	**±0.001**
Cu^{2+}	**65.040** (a)	**64.900**	**– 98.000**	
[1992GRE/FUG]	**±1.557**	**±1.000**	**±4.000**	
CuCl(g)		76.800		
[2003GUI/FAN]		±10.000		
$CuSO_4$(cr)	**– 662.185** (a)	**– 771.400**	**109.200**	
[1992GRE/FUG]	**±1.206**	**±1.200**	**±0.400**	
Ag(cr)	**0.000**	**0.000**	**42.550**	**25.350**
[1992GRE/FUG]			**±0.200**	**±0.100**
Ag(g)	**246.007** (a)	**284.900**	**172.997**	**20.786**
[1992GRE/FUG]	**±0.802**	**±0.800**	**±0.004**	**±0.001**
Ag^+	**77.096** (a)	**105.790**	**73.450**	
[1992GRE/FUG]	**±0.156**	**±0.080**	**±0.400**	
AgCl(cr)	**– 109.765** (a)	**– 127.010**	**96.250**	
[1992GRE/FUG]	**±0.098**	**±0.050**	**±0.200**	
Ni(cr)	0.000	0.000	29.870	26.070
[2005GAM/BUG]	±0.000	±0.000	±0.200	±0.100

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_f G_m^o$ (kJ·mol^{-1})	$\Delta_f H_m^o$ (kJ·mol^{-1})	S_m^o (J·K^{-1}·mol^{-1})	$C_{p,m}^o$ (J·K^{-1}·mol^{-1})
Ni^{2+}	– 45.773	– 55.012 (a)	– 131.800	– 46.100
[2005GAM/BUG]	±0.771	±0.878	±1.400	±7.500
NiF_2(cr)	–609.852 (a)	–657.300	73.520	63.210
[2005GAM/BUG]	±8.001	±8.000	±0.400	±2.000
Ti(cr)	**0.000**	**0.000**	**30.720**	**25.060**
[1992GRE/FUG]			**±0.100**	**±0.080**
Ti(g)	**428.403 (a)**	**473.000**	**180.298**	**24.430**
[1992GRE/FUG]	**±3.000**	**±3.000**	**±0.010**	**±0.030**
TiO_2(rutile)	**– 888.767 (a)**	**– 944.000**	**50.620**	**55.080**
[1992GRE/FUG]	**±0.806**	**±0.800**	**±0.300**	**±0.300**
$TiCl_4$(g)	**– 726.324 (a)**	**– 763.200**	**353.200**	**95.408**
[1992GRE/FUG]	**±3.229**	**±3.000**	**±4.000**	**±1.000**
Am^{3+}	–598.698 (a)	–616.700	–201.000	
[1995SIL/BID]	±4.755	±1.500	±15.000	
Pu^{3+}	–578.984	–591.790	–184.510 (b)	
[2001LEM/FUG]	±2.688	±1.964	±6.154	
Np^{4+}	–491.774 (a)	–556.022	–426.390 (b)	
[2001LEM/FUG]	±5.586	±4.185	±12.386	
NpO_2^+	–907.765 (a)	–978.181	–45.904	–4.000
[2001LEM/FUG]	±5.628	±4.629	±10.706	±25.000
U(cr)	0.000	0.000	50.200	27.660
[1992GRE/FUG]			±0.200	±0.050
U^{4+}	–529.860 (b)	–591.200	–416.895 (a)	–220.000
[2003GUI/FAN]	±1.765	±3.300	±12.553	±50.000
UO_2^{2+}	**–952.551 (a)**	**–1019.000**	**–98.200**	**42.400**
[1992GRE/FUG]	**±1.747**	**±1.500**	**±3.000**	**±3.000**
Be(cr)	**0.000**	**0.000**	**9.500**	**16.443**
[1992GRE/FUG]			**±0.080**	**±0.060**
Be(g)	**286.202 (a)**	**324.000**	**136.275**	**20.786**
[1992GRE/FUG]	**±5.000**	**±5.000**	**±0.003**	**±0.001**
BeO(bromellite)	**– 580.090 (a)**	**– 609.400**	**13.770**	**25.565**
[1992GRE/FUG]	**±2.500**	**±2.500**	**±0.040**	**±0.100**
Mg(cr)	**0.000**	**0.000**	**32.670**	**24.869**
[1992GRE/FUG]			**±0.100**	**±0.020**
Mg(g)	**112.521 (a)**	**147.100**	**148.648**	**20.786**
[1992GRE/FUG]	**±0.801**	**±0.800**	**±0.003**	**±0.001**

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_f G_m^o$ (kJ·mol^{-1})	$\Delta_f H_m^o$ (kJ·mol^{-1})	S_m^o (J·K^{-1}·mol^{-1})	$C_{p,m}^o$ (J·K^{-1}·mol^{-1})
Mg^{2+} [1992GRE/FUG]	**– 455.375** (a) **±1.335**	**– 467.000** **±0.600**	**– 137.000** **±4.000**	
MgO(cr) [1992GRE/FUG]	**– 569.312** (a) **±0.305**	**– 601.600** **±0.300**	**26.950** **±0.150**	**37.237** **±0.200**
MgF$_2$(cr) [1992GRE/FUG]	**– 1071.051** (a) **±1.210**	**– 1124.200** **±1.200**	**57.200** **±0.500**	**61.512** **±0.300**
Ca(cr) [1992GRE/FUG]	**0.000**	**0.000**	**41.590** **±0.400**	**25.929** **±0.300**
Ca(g) [1992GRE/FUG]	**144.021** (a) **±0.809**	**177.800** **±0.800**	**154.887** **±0.004**	**20.786** **±0.001**
Ca^{2+} [1992GRE/FUG]	**– 552.806** (a) **±1.050**	**– 543.000** **±1.000**	**– 56.200** **±1.000**	
CaO(cr) [1992GRE/FUG]	**– 603.296** (a) **±0.916**	**– 634.920** **±0.900**	**38.100** **±0.400**	**42.049** **±0.400**
CaF(g) [2003GUI/FAN]	– 302.118 ±5.104	– 276.404 ±5.100	229.244 ±0.500	33.671 ±0.500
CaCl(g) [2003GUI/FAN]	– 129.787 ±5.001	– 103.400 ±5.000	241.634 ±0.300	35.687 ±0.010
Sr(cr) [1992GRE/FUG]	0.000	0.000	55.700 ±0.210	
Sr^{2+} [1992GRE/FUG]	– 563.864 (a) ±0.781	– 550.900 ±0.500	– 31.500 ±2.000	
SrO(cr) [1992GRE/FUG]	– 559.939 (a) ±0.914	– 590.600 ±0.900	55.440 ±0.500	
SrCl$_2$(cr) [1992GRE/FUG]	– 784.974 (a) ±0.714	– 833.850 ±0.700	114.850 ±0.420	
Sr(NO$_3$)$_2$(cr) [1992GRE/FUG]	– 783.146 (a) ±1.018	– 982.360 ±0.800	194.600 ±2.100	
Ba(cr) [1992GRE/FUG]	0.000	0.000	62.420 ±0.840	
Ba(g) [2003GUI/FAN]	152.852 ±5.006	185.000 ±5.000	170.245 ±0.010	20.786 ±0.001
Ba^{2+} [1992GRE/FUG]	– 557.656 (a) ±2.582	– 534.800 ±2.500	8.400 ±2.000	
BaO(cr) [1992GRE/FUG]	– 520.394 (a) ±2.515	– 548.100 ±2.500	72.070 ±0.380	

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\mathrm{o}}$ (kJ·mol^{-1})	$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}$ (kJ·mol^{-1})	$S_{\mathrm{m}}^{\mathrm{o}}$ (J·K^{-1}·mol^{-1})	$C_{p,\mathrm{m}}^{\mathrm{o}}$ (J·K^{-1}·mol^{-1})
BaF(g)	– 349.569	– 324.992	246.219	34.747
[2003GUI/FAN]	±6.705	±6.700	±0.210	±0.300
$BaCl_2$(cr)	– 806.953 (a)	– 855.200	123.680	
[1992GRE/FUG]	±2.514	±2.500	±0.250	
Li(cr)	**0.000**	**0.000**	**29.120**	**24.860**
[1992GRE/FUG]			**±0.200**	**±0.200**
Li(g)	**126.604 (a)**	**159.300**	**138.782**	**20.786**
[1992GRE/FUG]	**±1.002**	**±1.000**	**±0.010**	**±0.001**
Li^+	**– 292.918 (a)**	**– 278.470**	**12.240**	
[1992GRE/FUG]	**±0.109**	**±0.080**	**±0.150**	
Na(cr)	**0.000**	**0.000**	**51.300**	**28.230**
[1992GRE/FUG]			**±0.200**	**±0.200**
Na(g)	**76.964 (a)**	**107.500**	**153.718**	**20.786**
[1992GRE/FUG]	**±0.703**	**±0.700**	**±0.003**	**±0.001**
Na^+	**– 261.953 (a)**	**– 240.340**	**58.450**	
[1992GRE/FUG]	**±0.096**	**±0.060**	**±0.150**	
NaF(cr)	– 546.327 (a)	– 576.600	51.160	
[2001LEM/FUG]	±0.704	±0.700	±0.150	
NaCl(cr)	– 384.221	– 411.260	72.150	50.500
[2001LEM/FUG]	±0.147	±0.120	±0.200	
$NaNO_3$(cr)		– 467.580		
[2003GUI/FAN]		±0.410		
K(cr)	**0.000**	**0.000**	**64.680**	**29.600**
[1992GRE/FUG]			**±0.200**	**±0.100**
K(g)	**60.479 (a)**	**89.000**	**160.341**	**20.786**
[1992GRE/FUG]	**±0.802**	**±0.800**	**±0.003**	**±0.001**
K^+	**– 282.510 (a)**	**– 252.140**	**101.200**	
[1992GRE/FUG]	**±0.116**	**±0.080**	**±0.200**	
KCl(cr)		– 436.461		
[2005GAM/BUG]		±0.129		
KBr(cr)		– 393.330		
[2005GAM/BUG]		±0.188		
KI(cr)		– 329.150		
[2005GAM/BUG]		±0.137		
Rb(cr)	**0.000**	**0.000**	**76.780**	**31.060**
[1992GRE/FUG]			**±0.300**	**±0.100**

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ}$ (kJ·mol^{-1})	$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}$ (kJ·mol^{-1})	S_{m}° (J·K^{-1}·mol^{-1})	$C_{p,\mathrm{m}}^{\circ}$ (J·K^{-1}·mol^{-1})
Rb(g)	**53.078 (a)**	**80.900**	**170.094**	**20.786**
[1992GRE/FUG]	**±0.805**	**±0.800**	**±0.003**	**±0.001**
Rb^+	**– 284.009 (a)**	**– 251.120**	**121.750**	
[1992GRE/FUG]	**±0.153**	**±0.100**	**±0.250**	
Cs(cr)	**0.000**	**0.000**	**85.230**	**32.210**
[1992GRE/FUG]			**±0.400**	**±0.200**
Cs(g)	**49.556 (a)**	**76.500**	**175.601**	**20.786**
[1992GRE/FUG]	**±1.007**	**±1.000**	**±0.003**	**±0.001**
Cs^+	**– 291.456 (a)**	**– 258.000**	**132.100**	
[1992GRE/FUG]	**±0.535**	**±0.500**	**±0.500**	
CsCl(cr)	– 413.807 (a)	– 442.310	101.170	52.470
[2001LEM/FUG]	±0.208	±0.160	±0.200	
CsBr(cr)	– 391.171	– 405.600	112.940	52.930
[2001LEM/FUG]	±0.305	±0.250	±0.400	

(a) Value calculated internally using $\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ} = \Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ} - T\sum_i S_{\mathrm{m},i}^{\circ}$.

(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 [1992GRE/FUG] and [2005OLI/NOL]. Unless noted otherwise, all data refer to 298.15 K and a pressure of 0.1 MPa and, for aqueous species, a standard state of infinite dilution (I = 0). The uncertainties listed below each value represent total uncertainties and correspond in principle to the statistically defined 95% confidence interval. Systematically, all the values are presented with three digits after the decimal point, regardless of the significance of these digits. The reference listed for each entry in this table indicates the NEA TDB Review where the corresponding data have been adopted as NEA TDB Auxiliary data. The data presented in this table are available on computer media from the OECD Nuclear Energy Agency.

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

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Table IV-2 (continued)

Species and review where adopted	Reaction			
	$\log_{10} K^{\circ}$	$\Delta_{r}G^{\circ}_{m}$ (kJ·mol^{-1})	$\Delta_{r}H^{\circ}_{m}$ (kJ·mol^{-1})	$\Delta_{r}S^{\circ}_{m}$ (J·K^{-1}·mol^{-1})
$HIO_3(aq)$	$H^+ + IO_3^- \rightleftharpoons HIO_3(aq)$			
[1992GRE/FUG]	0.788 ±0.029	– 4.498 ±0.166		
S^{2-}	$HS^- \rightleftharpoons H^+ + S^{2-}$			
[1992GRE/FUG]	– 19.000 ±2.000	108.450 ±11.416		
SO_3^{2-}	$H_2O(l) + SO_4^{2-} + 2\ e^- \rightleftharpoons 2OH^- + SO_3^{2-}$			
[1992GRE/FUG]	– 31.400 (b) ±0.700	179.230 ±3.996		
$S_2O_3^{2-}$	$3H_2O(l) + 2SO_3^{2-} + 4\ e^- \rightleftharpoons 6OH^- + S_2O_3^{2-}$			
[1992GRE/FUG]	– 39.200 (b) ±1.400	223.760 ±7.991		
$H_2S(aq)$	$H_2S(aq) \rightleftharpoons H^+ + HS^-$			
[1992GRE/FUG]	– 6.990 ±0.170	39.899 ±0.970		
HSO_3^-	$H^+ + SO_3^{2-} \rightleftharpoons HSO_3^-$			
[1992GRE/FUG]	7.220 ±0.080	– 41.212 ±0.457	66.000 ±30.000	359.590 (a) ±100.630
$HS_2O_3^-$	$H^+ + S_2O_3^{2-} \rightleftharpoons HS_2O_3^-$			
[1992GRE/FUG]	1.590 ±0.150	– 9.076 ±0.856		
$H_2SO_3(aq)$	$H^+ + HSO_3^- \rightleftharpoons H_2SO_3(aq)$			
[1992GRE/FUG]	1.840 ±0.080	– 10.503 ±0.457	16.000 ±5.000	88.891 (a) ±16.840
HSO_4^-	$H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$			
[1992GRE/FUG]	1.980 ±0.050	– 11.302 ±0.285		
$Se(g)$	$\frac{1}{2}\ Se_2(g) \rightleftharpoons Se(g)$			
[2005OLI/NOL]			–165.520 ±0.250	
Se^{2-}	$Se(cr) + 2\ e^- \rightleftharpoons Se^{2-}$			
[2005OLI/NOL]	–22.530 ±0.526	128.600 ±3.000		

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Table IV-2 (continued)

Species and review where adopted	Reaction			
	$\log_{10} K^{\circ}$	$\Delta_r G^{\circ}_m$ ($kJ \cdot mol^{-1}$)	$\Delta_r H^{\circ}_m$ ($kJ \cdot mol^{-1}$)	$\Delta_r S^{\circ}_m$ ($J \cdot K^{-1} \cdot mol^{-1}$)
Se_2^{2-}	$2Se^{2-} \rightleftharpoons Se_2^{2-} + 2\,e^-$			
[2005OLI/NOL]	25.320 ±0.333	–144.530 ±1.900		
Se_3^{2-}	$3Se^{2-} \rightleftharpoons Se_3^{2-} + 4\,e^-$			
[2005OLI/NOL]	49.966 ±0.333	–285.210 ±1.900		
Se_4^{2-}	$4Se^{2-} \rightleftharpoons Se_4^{2-} + 6\,e^-$			
[2005OLI/NOL]	73.023 ±0.333	–416.820 ±1.900		
$SeO_2(g)$	$SeO_2(cr) \rightleftharpoons SeO_2(g)$			
[2005OLI/NOL]			114.800 ±2.500	
SeO_3^{2-}	$HSeO_3^- \rightleftharpoons H^+ + SeO_3^{2-}$			
[2005OLI/NOL]	–8.360 ±0.230	47.719 ±1.313		
SeO_4^{2-}	$HSeO_4^- \rightleftharpoons H^+ + SeO_4^{2-}$			
[2005OLI/NOL]	–1.750 ±0.100	–9.989 ±0.571	–20.800 ±3.200	–103.267 (a) ±10.902
$Se_2O_5(cr)$	$SeO_2(cr) + SeO_3(cr) \rightleftharpoons Se_2O_5(cr)$			
[2005OLI/NOL]			–26.100 ±1.200	
HSe^-	$H_2Se(aq) \rightleftharpoons H^+ + HSe^-$			
[2005OLI/NOL]	–3.850 ±0.050	21.976 ±0.285		
$H_2Se(aq)$	$H_2Se(g) \rightleftharpoons H_2Se(aq)$			
[2005OLI/NOL]	–1.100 ±0.010	6.279 ±0.057	–14.700 ±0.300	–70.363 (a) ±1.024
$HSeO_3^-$	$H_2SeO_3(aq) \rightleftharpoons H^+ + HSeO_3^-$			
[2005OLI/NOL]	–2.640 ±0.140	15.069 ±0.799		
$HSeO_4^-$	$H_2O(l) + H_2SeO_3(aq) \rightleftharpoons 3H^+ + HSeO_4^- + 2\,e^-$			
[2005OLI/NOL]	–37.289 (c) ±0.175	212.847 ±1.000		

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Table IV-2 (continued)

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

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Table IV-2 (continued)

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

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Table IV-2 (continued)

Species and review where adopted	Reaction			
	$\log_{10} K^{\circ}$	$\Delta_r G_m^{\circ}$ (kJ·mol^{-1})	$\Delta_r H_m^{\circ}$ (kJ·mol^{-1})	$\Delta_r S_m^{\circ}$ (J·K^{-1}·mol^{-1})
$Si_3O_5(OH)_5^{3-}$	$3Si(OH)_4(aq) \rightleftharpoons 3H^+ + 2H_2O(l) + Si_3O_5(OH)_5^{3-}$			
[1992GRE/FUG]	– 27.500 ±0.300	156.970 ±1.712		
$Si_4O_8(OH)_4^{4-}$	$4Si(OH)_4(aq) \rightleftharpoons 4H^+ + 4H_2O(l) + Si_4O_8(OH)_4^{4-}$			
[1992GRE/FUG]	– 36.300 ±0.500	207.200 ±2.854		
$Si_4O_7(OH)_5^{3-}$	$4Si(OH)_4(aq) \rightleftharpoons 3H^+ + 4H_2O(l) + Si_4O_7(OH)_5^{3-}$			
[1992GRE/FUG]	– 25.500 ±0.300	145.560 ±1.712		

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

(b) Value calculated from a selected standard potential.

Part 3

Discussion of data selection

Chapter V

Elemental iron

V.1 Introduction

Over the last 30 years there have been several reviews on the thermophysical properties of iron metal. These have been done for several different purposes. Some reviews (*e.g.*, [1991DIN], [1985FER/GUS], [2001CHE/SUN]) have focused on establishing sets of coherent thermodynamic properties near the transitions between the α- (bcc), γ- (fcc), δ- (bcc), amorphous and liquid phases. Several of these assessments have been done incorporating a sound theoretical basis for the magnetic properties, and complex expressions have been derived to describe the thermodynamic quantities. In such reviews there is generally less emphasis on the properties below 500 K, and on minor inconsistencies in selected values for S°_{m} (Fe, α, 298.15 K) and $C^{\circ}_{p,\mathrm{m}}$ (Fe, T). Other reviews (*e.g.*, [1986DES], [1998CHA]) have analyzed available data from low temperatures to temperatures above the melting point. Another full re-evaluation of the thermodynamic data for iron metal would be a substantial (and probably unproductive) undertaking, and is outside the scope of the present review.

V.2 Heat-capacity values to 800 K and the entropy of α-Fe at 298.15 K

For the present review, a set of values must be selected that is consistent with thermodynamic properties of iron compounds primarily for temperatures to 800 K. It is also helpful if the equations for the temperature dependence of the thermodynamic quantities have a fairly simple functional form. These selected values and functions allow proper evaluation of thermodynamic properties of other iron compounds from low-temperature entropy and heat-capacity measurements, and allow equilibrium data for moderately higher temperatures to be properly evaluated using third-law methods. The JANAF review [1998CHA] of the properties of Fe(cr) was last updated in 1978, and for temperatures ≥ 400 K was based largely on the earlier review by Hultgren *et al.* [1973HUL/DES]. Thus, the JANAF review actually preceded the 1986 review by Desai [1986DES].

For 5 to 298 K, the heat-capacity and entropy values listed in the JANAF tables [1998CHA] relied primarily on measurements by Keesom and Kurrelmeyer [1939KEE/KUR], [1939KEE/KUR2], Duyckaerts [1939DUY], [1939DUY2], Eucken and Werth [1930EUC/WER], Stepakoff and Kaufman [1968STE/KAU], Kelley [1943KEL], and Simon and Swain [1935SIM/SWA]. In the JANAF review an assessment problem was identified for data from 20 to 55 K, as the calculated contributions to S°_{m} based on measurements by Eucken and Werth [1930EUC/WER] and Simon and Swain [1935SIM/SWA] disagree with those based on measurements by Keesom and Kurrelmeyer [1939KEE/KUR] and Duyckaerts [1939DUY] by ~ 0.06 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$. Also, the JANAF review noted a difference of 0.04 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ that could result from inconsistencies between the work of Kelley [1943KEL] and Stepakoff and Kaufman [1968STE/KAU] between 50 and 298 K.

For the temperature range from 5 to 20 K, Desai [1986DES] relied primarily on the work of Keesom and Kurrelmeyer [1939KEE/KUR], [1939KEE/KUR2], Duyckaerts [1939DUY2] and Eucken and Werth [1930EUC/WER]. For the low-temperature extrapolation (0 to 5 K), $\gamma = (4.942 \pm 0.11)\ \mathrm{mJ{\cdot}K^{-2}{\cdot}mol^{-1}}$ and $\theta_{\mathrm{D}} = (465 \pm 3)$ K were used[1]. For 20 to 298 K, highest weight was given to values from Eucken and Werth [1930EUC/WER], Stepakoff and Kaufman [1968STE/KAU], Kelley [1943KEL], Simon and Swain [1935SIM/SWA] and Reddy and Reddy [1974RED/RED], though values from Griffiths and Griffiths [1914GRI/GRI], Gunther [1916GUN], Rodebush and Michalek [1925ROD/MIC], Schroder and MacInnes [1969SCH/MAC] and Bendick and Pepperoff [1982BEN/PEP] were also considered.

For temperatures below 300 K, the selected heat-capacity values in [1986DES] are systematically lower than those selected in [1998CHA]. The value of S°_{m} (Fe, α, 298.15 K) from [1986DES] is also less than that assessed in [1998CHA]. The values are marginally inconsistent, *i.e.*, $(27.08_5 \pm 0.08)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ as opposed to $(27.32 \pm 0.13)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ if the reported uncertainties are assumed to be 2σ, rather than 1σ. The value of S°_{m} (Fe, α, 298.15 K) in the JANAF tables is essentially the same as the value compiled by Hultgren *et al.* [1973HUL/DES], and the equations in Chen and Sundman [2001CHE/SUN] are consistent with a value of 27.21 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$. The lower value in [1986DES] seems to have arisen from the lower assessed values [1986DES] of $C^{\circ}_{p,\mathrm{m}}$ (Fe, α) for temperatures between 30 and 100 K. In both the Desai and JANAF reviews, the values near 298.15 K were obtained by also considering some of the measurements slightly above 300 K.

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[1] In this section, γ is the symbol used for the electronic specific heat coefficient and θ_{D} is the symbol used for the Debye temperature. The earlier review of Hultgren *et al.* [1973HUL/DES] used $\gamma = (1.2 \pm 0.1)\ \mathrm{mcal{\cdot}K^{-2}{\cdot}mol^{-1}}$ (*i.e.*, $(5.02 \pm 0.42)\ \mathrm{mJ{\cdot}K^{-2}{\cdot}mol^{-1}}$). Castanet *et al.* [1985CAS/COL], a CODATA review (also, see [1994WHI/MIN]) primarily based on [1973HUL/DES], recommended $\gamma = 4.8\ \mathrm{mJ{\cdot}K^{-2}{\cdot}mol^{-1}}$, $\theta_{\mathrm{D}} = 470$ K. Phillips [1971PHI] gave 4.78 $\mathrm{mJ{\cdot}K^{-2}{\cdot}mol^{-1}}$, $\theta_{\mathrm{D}} = 477$ K and a somewhat different analysis than [1986DES] for γ and θ_{D} from many of the same data). These differences have effects on S°_{m} (Fe, α) that are well within the uncertainties. Chen and Sundman [2001CHE/SUN] recently reported $\gamma = 6.48\ \mathrm{mJ{\cdot}K^{-2}{\cdot}mol^{-1}}$.

In the present review

$$S^{\circ}_{m}\ (\text{Fe}, \alpha, 298.15\ \text{K}) = (27.085 \pm 0.160)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

and

$$C^{\circ}_{p,m}\ (\text{Fe}, \alpha, 298.15\ \text{K}) = (25.084 \pm 0.500)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

have been selected based on the analysis by Desai [1986DES]. The uncertainty in S°_{m} has been assigned by assuming that the reported uncertainty in [1986DES] was a 1σ uncertainty. The uncertainty in $C^{\circ}_{p,m}$ (Fe, α, 298.15 K) is estimated in the present review based on Figure 1 in [1986DES].

For temperatures between 300 and 800 K, the values of $C^{\circ}_{p,m}$ as tabulated by JANAF [1998CHA] and Desai [1986DES] from consideration of the available experimental data, are very similar (differences are < 0.05 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$). The equally-weighted $C^{\circ}_{p,m}$ values tabulated by Desai [1986DES] and JANAF [1998CHA] have been fit separately by functions of temperature between 273.15 and 800 K:

(a) from the table in [1986DES]

$$[C^{\circ}_{p,m}]^{800\,\text{K}}_{273.15\,\text{K}}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 27.304 - 5.273 \times 10^{-3}\,(T/\text{K}) - 2.439 \times 10^{5}\,(T/\text{K})^{-2} + 2.365 \times 10^{-5}\,(T/\text{K})^{2} \qquad (\text{V.1})$$

(b) from the table in [1998CHA]

$$[C^{\circ}_{p,m}]^{800\,\text{K}}_{298.15\,\text{K}}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 26.869 - 4.183 \times 10^{-3}\,(T/\text{K}) - 2.305 \times 10^{5}\,(T/\text{K})^{-2} + 2.301 \times 10^{-5}\,(T/\text{K})^{2} \qquad (\text{V.2})$$

Over this temperature range, the equations of Fernández Guillermet and Gustafson [1985FER/GUS] (and in Dinsdale's compilation [1991DIN]) generate somewhat lower values for $C^{\circ}_{p,m}(T)$, though still well within the 1.5 to 3% uncertainties based on the analysis of Desai [1986DES].

The differences between the smoothed reported values and those from the corresponding Eqs. (V.1) and (V.2) are < 0.10 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ (average 0.05 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) and < 0.15 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ (average 0.04 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), and the values from Eq.(V.2) tend to be slightly less than those from Eq. (V.1) for temperatures below 500 K, and greater than those from Eq. (V.1) for temperatures above 500 K.

For use in the present review, a fitted equation based on the values tabulated by Desai [1986DES], but further constrained to generate the selected value for $C^{\circ}_{p,m}$ (Fe, α, 298.15 K), is selected:

$$[C^{\circ}_{p,m}]^{800\,\text{K}}_{298.15\,\text{K}}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 27.241 - 5.0909 \times 10^{-3}\,(T/\text{K}) - 2.4261 \times 10^{5}\,(T/\text{K})^{-2} + 2.3510 \times 10^{-5}\,(T/\text{K})^{2} \qquad (\text{V.3})$$

V.3 Heat-capacity values for temperatures between 800 and 1800 K

Equation (V.3) should not be used for temperatures above 800 K. Above 900 K there is a λ-transition in the heat capacity-temperature curve for Fe(α), with a maximum at 1043 K. Between 1185 and 1667 K, Fe(γ) is stable with respect to Fe(α), but by less than 0.1 kJ·mol^{-1}. The Fe(γ) phase then is the stable form between 1667 and 1811 K [1986DES].

For temperatures above 800 K, all Gibbs-energy and heat-capacity values for Fe(α) and Fe(γ) required in the present review were calculated using the equations from the assessment of Chen and Sundman [2001CHE/SUN]. These equations (see the entry for [2001CHE/SUN] in Appendix A) were generated not just from experimental data, but also with consideration of the theory for magnetic properties of Fe(γ) and Fe(α), and the heat capacity of Fe(l). The treatment is less empirical than those done earlier by Fernández Guillermet and Gustafson [1985FER/GUS] and Dinsdale [1991DIN]. It matches the experimental data in the region of the λ-transition at 1043 K better than the equations from these two earlier papers, though all underestimate the maximum $C^{\circ}_{p,\mathrm{m}}$ value [1986DES]. The value of the heat capacity of Fe(α) at 800 K calculated using the equations of Chen and Sundman is 0.8 J·K^{-1}·mol^{-1} more positive than the assessed value by Desai [1986DES], and 0.9 J·K^{-1}·mol^{-1} more positive than the value calculated using Eq. (V.3). Nevertheless, the slight mismatch at 800 K is unlikely to introduce significant additional errors or uncertainties in any third-law analysis involving values for Fe(cr). For higher temperatures, the equations for $G(T)$ from Chen and Sundman [2001CHE/SUN] give a good representation of the current understanding of the system.

In preparing other parts of the present review there has been no need for selected values of thermodynamic quantities for amorphous iron solid at any temperature, nor for liquid iron. A recent thorough review and theoretical discussion of data for high-temperature amorphous and liquid iron has been provided by Chen and Sundman [2001CHE/SUN].

Chapter VI

Simple iron aquo ions

VI.1 Iron oxidation potentials

Knowledge of precise standard oxidation potentials values, E°, for electrochemical couples between a metallic element and its ions is essential in obtaining many of the chemical thermodynamic constants needed for the database tables.

E° is directly related to the $\Delta_r G_m^\circ$ of the redox Reaction (VI.1) for which n electrons are exchanged between the M^{m+} (oxidized) and $M^{(m-n)+}$ (reduced) ions:

$$M^{m+} + \tfrac{1}{2}n\, H_2(g) \rightleftharpoons M^{(m-n)+} + n\, H^+ \qquad \text{(VI.1)}$$

$$\text{by } \Delta_r G_m^\circ = -\, n\, F\, E^\circ \qquad \text{(VI.2)}$$

Assuming that the ΔH value for the reaction does not vary within the temperature range investigated, the variation of the $\Delta_r G_m^\circ$ value with temperature is then related to the $\Delta_r S_m^\circ$ value for the reaction by:

$$\Delta_r S_m^\circ = n\, F\, (\partial E/\partial T) \qquad \text{(VI.3)}$$

The value of $\Delta_r H_m^\circ$ then can be obtained by applying:

$$\Delta_r H_m^\circ = \Delta_r G_m^\circ + T\Delta_r S_m^\circ \qquad \text{(VI.4)}$$

Thus, when reliable standard potential measurements can be carried out as a function of temperature, all of the thermodynamic parameters for an oxidation or reduction reaction can be easily determined.

Iron has rather simple redox chemistry within the conditions prevailing in nuclear waste repositories. Only the oxidation states + III, + II and 0 are important, as the ions of the + IV, + V, and + VI oxidation states are too strongly oxidizing to be encountered in the waste or in the natural environment of the repositories. The lower oxidation states of iron such as − II (d^{10} electronic configuration), − I (d^9 configuration) and + I (d^7) have been observed in complexes with strong π-acceptor ligands that are able to stabilize these unusual oxidation states. As there is little chance that such ligands will be encountered in nuclear waste, discussion in the present review is limited to the values for the couples $Fe^{2+}/Fe(0)$ and Fe^{3+}/Fe^{2+}.

VI.1.1 The standard oxidation potential of the couple Fe^{2+}/Fe(0)

VI.1.1.1 Electrochemical methods, electrochemical-cell potential-difference measurements

Many authors have attempted to determine the value of the standard potential of the Fe^{2+}/Fe(0) couple by measuring the potential difference of cells constructed with one reference half cell and one half cell having a metallic iron electrode immersed in a solution containing a dissolved Fe(II) salt as the electrolyte.

As discussed by Heusler [1982HEU], the older results (primarily those prior to ~ 1905) lead to values for the standard Fe^{2+}/Fe(0) potential that are too positive. This is mainly because the measurements were done using such highly acidic solutions that there was extensive interference from the couple H^+/H_2 ($E^\circ = 0.0$ V). The procedure used in the preparation of metallic iron electrodes also had an important effect on the measured values of E_{cell}, and thus on the published standard potential values [1907RIC/BEH], [1909KRA].

From 1926 [1926HAM] onwards, E° values close to − 0.44 V were obtained and, as they were more compatible with the thermodynamic constants obtained by other methods, − 0.44 V was reported in the established thermodynamic tables [1952LAT], [1952ROS/WAG], [1969WAG/EVA].

However, other cell measurements, such as those of Patrick and Thompson [1953PAT/THO], done with great care, and incorporating many precautions, led to less negative $E^\circ(Fe^{2+}/Fe(0))$ potentials. Patrick and Thompson recommended − 0.409 V, a value that is significantly different from the former − 0.44 V. The authors pointed out that traces of hydrogen in the metallic iron can shift the potentials to more negative values.

Later Johnson and Baumann [1978JOH/BAU] reported a slightly more negative value, − 0.415 V, but close to the value of Patrick and Thompson. Johnson and Baumann pointed out the effect of pH on the potential-difference values, and concluded that the pH of the iron(II) solution, which was not mentioned in many of the previous papers, was one of the essential parameters required to determine a final result. At low pH, the measured potentials are much less negative because of the strong influence of the H^+/H_2 couple. Above pH 5.8 the E° values deduced from the measured values of E_{cell} were constant, and this was attributed to the effect of the H^+/H_2 couple above pH 6 being negligible. Clearly at high acidities the potential-difference values for all the cells measured were affected by the mixed potentials imposed on the iron electrode by the two irreversible couples, H^+/H_2 and Fe^{2+}/Fe(0) [1952KOL/LIN].

The main results concerning the $E^\circ(Fe^{2+}/Fe(0))$ values from potential-difference measurements are shown in Table VI-1. In spite of the experimental care used by most of the authors, important discrepancies in the standard Fe^{2+}/Fe(0) potential have been found. The Gibbs energy of formation values for Fe^{2+} calculated from these potentials are uncertain, and cannot be used to get other thermodynamic constant values with any degree of accuracy. In more recent reviews, especially the one by Parker and Khodakovskii [1995PAR/KHO], the authors prefer to rely on other thermodynamic data for evaluation of the value of $\Delta_f G_m^o$ (Fe^{2+}).

Table VI-1: Electrochemical studies for the determination of the value of E^o (Fe^{2+}/Fe(0)), at 298.15 K unless otherwise noted.

Reference	E^o (Fe^{2+}/Fe(0))/V *vs.* SHE	$\Delta_f G_m^o$ (Fe^{2+})/kJ·mol^{-1}
[1926HAM]	− 0.4413	− 84.65
	− 0.4387 (a)	
[1953PAT/THO]	− 0.409 (d)	− 78.92
	− 0.44 (b)	− 84.90
	− 0.473 (c)	− 91.27
[1978JOH/BAU]	− 0.417 to − 0.415 V (above pH 5.8)	− 80.08
[1960HUR]	− 0.467 at 293.15 K	− 90.11 at 293.15 K

(a) − 0.4387 V with the corrections proposed by [1932RAN/FRA2].

(b) If impure $H_2(g)$ is present.

(c) With completely deoxygenated $H_2(g)$.

(d) Recommended by the authors.

VI.1.1.2 Electrochemical methods, electrochemical kinetics measurements

Potential-difference measurements that are carried out at very low current densities, close to 0 A·cm^{-2}, are generally not adopted for determination of the formal potentials of irreversible couples. Often the electron exchange, which takes place at the working electrode and indicates its potential, includes contributions from various redox couples present in solution. Thus, a reversible couple involving impurities, even those present at low concentration, can strongly influence the potential-difference measurements because of the importance of the impurity couple to the exchange of electrons.

An aqueous solution of Fe^{2+} in the presence of metallic iron has the redox couples H^+/H_2 and Fe^{2+}/Fe(0), both irreversible, with $E^o(H^+/H_2) > E^o(Fe^{2+}/Fe(0))$. The presence of impurities can be important, but as most of the authors carefully purified their solids and their reagents, this effect was not seen unambiguously. Therefore, an iron electrode immersed in an aqueous solution generates a potential between the couples H^+/H_2 (0 V) and Fe^{2+}/Fe (close to − 0.47 V, according to independent thermochemical data).

The E_{cell} measurements indicated clearly that mixed potentials H^+/H_2 (0 V) and $Fe^{2+}/Fe(0)$ were involved.

a) The measurements in the most acidic solutions yielded E° values that are too high, closer to the H^+/H_2 potential values (H^+ is the oxidant in the H^+/H_2 couple).

b) The presence of hydrogen in iron metal produced a shift towards more negative potentials (H_2 is the reducing species in the H^+/H_2 couple).

Electrochemical kinetic methods, which are carried out using non-negligible current densities, can lead to better estimates of the formal potentials [1983BAR/FAU] for the irreversible couples. The influence of trace impurities, which can be important for low current densities close to 0, diminishes at higher current densities with the electrochemical reaction corresponding to the irreversible couple becoming more rapid. The diffusion-limiting current is generally attained in the presence of low concentrations of impurities (with respect to concentrations of species involved in the main electrochemical reaction) when the current density deviates from 0.

In the case where the potential-difference measurements are influenced by two irreversible couples, as here, H^+/H_2 and $Fe^{2+}/Fe(0)$, it may be possible to take advantage of changes in the kinetics of electron exchange with the conditions. It could be advantageous to investigate the conditions for which the reaction for the couple of interest, $Fe^{2+}/Fe(0)$, is the fastest and the contribution of the interfering couple is lowest. The electrochemical kinetic investigations will be used to define these conditions. The exchange current of the different couples at the equilibrium potential can be evaluated, and a better understanding of the significance of mixed potentials can be achieved.

Electrochemical kinetic investigations for the couples H^+/H_2 and $Fe^{2+}/Fe(0)$ at the Fe electrode have been undertaken by Hurlen [1960HUR], and the main results are discussed in Appendix A.

As electrochemical kinetic methods are not as familiar as those for potential-difference measurements, and as the work of Hurlen seems important, because it could bring reasonable agreement between the $\Delta_f G_m^{\circ}(Fe^{2+})$ obtained by electrochemistry and the other indirect methods, we will describe it in more detail. In addition, many controversial points, which have been reported by the researchers who measured potentials, can be understood, and the discrepancies in the standard potentials can be partially eliminated.

VI.1.1.2.1 H^+/H_2 couple

Hurlen [1960HUR] investigated the H^+/H_2 couple at the metallic iron electrode, without $FeCl_2$ added in the solutions. He obtained the Tafel lines for the discharge of H^+ which correspond to Tafel's law (Eq. (VI.5)):

$$\eta = a + b \log_{10} i \qquad \text{(VI.5)}$$

where η is the potential of the iron electrode and i the current density expressed as intensity per unit area ($A \cdot cm^{-2}$). In the Hurlen paper, a and b are two coefficients that are characteristic of the irreversible couple. For the H^+/H_2 couple at the iron electrode, Hurlen found $b = -0.116$ V and $(\partial V/\partial \log_{10} i)_{pH} = -(2RT\ln(10))/F$. This value is in agreement with values found for the H^+ discharge on other solid electrodes.

For the variation of the Tafel lines with pH, Hurlen found two zones. At lower pH, $(\partial \log_{10} i/\partial pH)_V = -1$ and $(\partial V/\partial pH)_i = -(2RT\ln(10))/F$. At higher pH values (greater than 6.8), the Tafel lines become independent of pH. This corresponds to two H^+ discharge modes: the irreversible reduction of H^+, for which the concentration varies with the pH at lower pH; and the irreversible reduction of the solvent water, above pH 6.8.

For the pH dependent part, the exchange current i_0 obtained by extrapolation of the Tafel lines into the equilibrium potential region of the H^+/H_2 electrode at solid iron is given [1960HUR] by the relation:

$$\log_{10} i_0 \,(293.15\ \text{K}) = -5.36 - 0.5\ \text{pH}. \qquad \text{(VI.6)}$$

VI.1.1.2.2 $Fe^{2+}/Fe(0)$ couple[1]

The anodic dissolution of iron obeys Tafel's law in the pH region where there is no passivation of the iron electrode. It has been found: $b = (RT\ln(10))/2F = 0.029$ V; $(\partial \log_{10} i/\partial pOH)_V = -1$ and $(\partial V/\partial pOH)_i = -(RT\ln(10))/2F$.

Iron deposition obeys a law symmetrical with the dissolution law; it has been found that: $b = -(RT\ln(10))/2F$; $(\partial \log_{10} i/\partial pFe)_{V,\ pOH} = -2$ and $(\partial V/\partial pFe)_{i,\ pOH} = (RT\ln(10))/F$.

Then, for the exchange current one has:

$$\log_{10} i_0 \,(293.15\ \text{K}) = 3.58 - \text{pFe} - \text{pOH}. \qquad \text{(VI.7)}$$

Values of $E^{\circ\prime}$ (the formal potential of the couple $Fe^{2+}/Fe(0)$ as defined on pg. 22) and i_0 are obtained from the intersection point of the extrapolation of the linear portions of the Tafel curves for the dissolution and deposition of Fe(0) from solutions of $FeCl_2$. An example is shown in Figure VI-1, and further details of the calculations for the determination of the $E^{\circ\prime}$ are given in the Appendix A.

After application of activity coefficient corrections, Hurlen proposed a value of E° ($Fe^{2+}/Fe(0)$, 293.15 K) = – 0.467 V. As no value for the uncertainty was given in the original paper, it has been estimated as ± 0.003 V (95% confidence limit) in the present review. This is slightly greater than the 0.002 V 95% confidence-limit uncertainties

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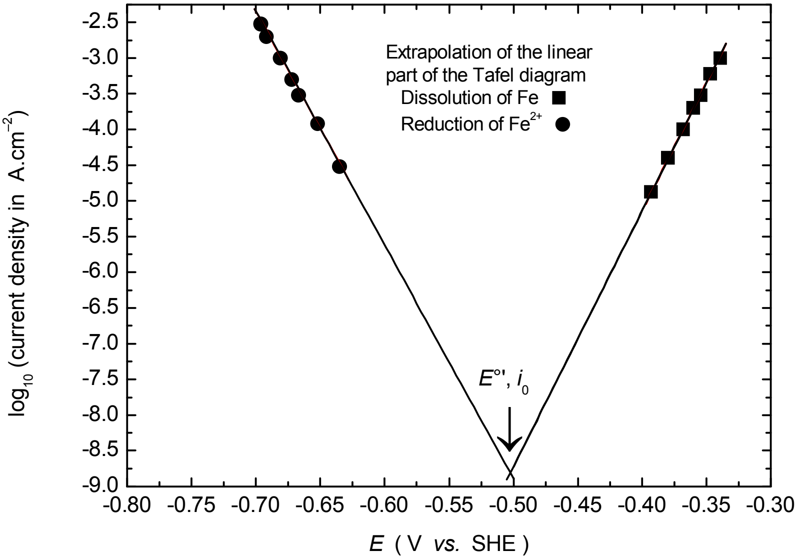
[1] In this Section, pOH is $-\log_{10} a_{OH^-}$ and pFe is $-\log_{10} a_{Fe^{2+}}$ (using the activity coefficients as estimated by Hurlen [1960HUR]).

given in the modern literature for standard potentials as it takes into account the use of different experimental techniques. Then, using Eq. (VI.2), the value of $\Delta_f G^{\circ}_{m}$ (Fe^{2+}, 293.15 K) is − (90.11 ± 0.58) $kJ \cdot mol^{-1}$.

Figure VI-1: Tafel diagrams for the dissolution of Fe and the deposition of iron(0) from a solution: 0.001 m HCl, 0.6 m KCl; 0.2 m $FeCl_2$; (I_m =1.1 (solution VI of [1960HUR])).



VI.1.1.2.3 Electrochemical methods. The view based on electrochemical kinetic investigations of the potential-difference data, and the actual E° (Fe^{2+}/Fe(0)) value.

The Fe^{2+}/Fe(0) couple is irreversible at all known electrodes [1952KOL/LIN] and in particular at the Fe electrode. The H^{+}/H_2 couple is also irreversible at the Fe electrode. Its standard potential, 0 V, is much higher than the Fe^{2+}/Fe(0) potential. This means that the discharge of H^{+} must be much slower than the Fe^{2+} reduction for iron deposition to be observed. The evaluation of the current exchange for the couples Fe^{2+}/Fe(0) and H^{+}/H_2 at the iron electrode, as a function of pH, is given in Table VI-2. It is based on the results of Hurlen [1960HUR], Eqs. (VI.6) and (VI.7).

It can be seen that at low pH values, the H^{+}/H_2 couple exchanges electrons sufficiently fast to impose its potential, which is more positive than the Fe^{2+}/Fe(0) potential. Therefore, those investigators who measured potential differences at low pH did not deal with the Fe^{2+}/Fe(0) electrode, but rather with the H^{+}/H_2 electrode.

It is only at higher pH, ~ 6, that the exchange of electrons from the $Fe^{2+}/Fe(0)$ couple at the Fe electrode becomes faster than the exchange from the H^+/H_2 reaction. At pH values greater than 6.5, the exchange of electrons by the couple $Fe^{2+}/Fe(0)$ is much faster than by the H^+/H_2 couple, but other phenomena such as the hydrolysis of Fe^{2+} and the passivation of the iron metal preclude reliable cell-potential measurements for the determination of $E^{\circ}(Fe^{2+}/Fe(0))$.

Table VI-2: Exchange currents i_0 for the couples H^+/H_2 and $Fe^{2+}/Fe(0)$ at the iron electrode, as a function of pH [1960HUR]*.

pH	i_0 H^+/H_2 / $A\cdot cm^{-2}$	i_0 $Fe^{2+}/Fe(0)$ / $A\cdot cm^{-2}$ $m_{Fe^{2+}} = 1\ mol\cdot kg^{-1}$	i_0 $Fe^{2+}/Fe(0)$ / $A\cdot cm^{-2}$ $m_{Fe^{2+}} = 10^{-2}\ mol\cdot kg^{-1}$
0	4.36×10^{-6}	3.8×10^{-11}	3.8×10^{-13}
1	1.38×10^{-6}	3.8×10^{-10}	3.8×10^{-12}
2	4.36×10^{-7}	3.8×10^{-9}	3.8×10^{-11}
3	1.38×10^{-7}	3.8×10^{-8}	3.8×10^{-10}
4	4.36×10^{-8}	3.8×10^{-7}	3.8×10^{-9}
5	1.38×10^{-8}	3.8×10^{-6}	3.8×10^{-8}
6	4.36×10^{-9}	3.8×10^{-5}	3.8×10^{-7}
7	1.38×10^{-9}	3.8×10^{-4}	3.8×10^{-6}
8	4.36×10^{-10}	3.8×10^{-3}	3.8×10^{-5}

* Calculated by applying formulae (10) and (16b) of the original paper established at 293.15 K and given here in Eqs. (VI.6) and (VI.7).

As pointed out by Hurlen [1960HUR], at pH values around 7 and above, the reduction of the solvent is pH independent. This is qualitatively consistent with the observation of Johnson and Bauman [1978JOH/BAU], who showed that the potential-difference value of the cell $Fe(s)|FeCl_2$ (0.02 m)||sat. KCl|AgCl,Ag(s) becomes pH independent at pH values above 5.8. This is probably due to the same effect, stabilisation of the contribution of the reaction of the solvent component (H^+ or H_2O) to the electron exchange. However, the value of $E^{\circ}(Fe^{2+}/Fe(0))$ found by Johnson and Bauman [1978JOH/BAU] is not sufficiently negative to be in agreement with the values deduced from electrochemical kinetics and the other thermodynamic investigations.

Therefore, there may have been some contribution to the electron exchange from redox couples involving the H^+/H_2 couple or impurities at low concentrations. Because of the low concentrations, such contributions would have become negligible for the higher current densities used in Hurlen's electrochemical kinetic investigations. For the kinetic investigations, the iron(II) concentrations were at least one order of magnitude greater than those used in the potential-difference measurements. That also favoured electron exchange from the $Fe^{2+}/Fe(0)$ couple (Eq. (VI.7)) rather than from other sources of exchange (Eq. (VI.7))). Concentrated solutions were not used by those workers who measured potential-difference values, probably because of the difficulties in evaluation of junction potentials and activity coefficients for concentrated solutions.

VI.1.1.2.4 Application of the SIT formalism to the work of Hurlen [1960HUR]

The arguments given above showed that the discrepancies between the results of many authors who attempted to determine the value of E° (Fe^{2+}/Fe(0)) by potential-difference measurements were not due to the improper evaluation of the activity coefficients, but to the inadequacy of potential-difference measurements for the precise determination of the standard potential of the irreversible couples, without insight into the kinetics of electron exchange at the electrode.

Heusler [1982HEU], and Heusler and Lorenz [1985HEU/LOR] reviewed the value of the Fe^{2+}/Fe(0) standard potential in chapters of two books, and the work of Hurlen was discussed specifically in the second review. They considered that the values of the standard potentials derived from the investigations in both chloride and sulfate solutions contain systematic errors due to junction potentials and improper estimation of the activity coefficients. For the chloride solutions we do not consider that such errors are responsible for the large difference between the standard potential recommended in established tables (– 0.440 V) [1952LAT], [1985BAR/PAR] and the value found by Hurlen ($\approx$ – 0.470 V)). The overall junction potential is presumably very small because of the cell design with two calomel electrodes immersed in the same solution. The evaluation of the activity coefficient has been done using two models, and our application of the SIT method did not yield very different Fe^{2+} activity values. Thus, the work of Hurlen seems convincing, and in reviewing it we have applied the SIT formalism to his experimental results.

We first determined the $E^{\circ\prime}$ potentials from the most reliable diagrams $i = \mathrm{f}(E)$ for the anodic dissolution of Fe(0) and for the cathodic deposition of Fe(II) shown in Figures 8 and 9 of Hurlen's paper. For that, we took the reported values of i as a function of E and determined the values of a and b for the function $E = a + b(\log_{10} i)$ from the linear part of the anodic Tafel diagram, and a' and b' of $E' = a' + b'(\log_{10} i')$ from the cathodic part of the Tafel diagram (for example, see Figure VI-1). The coordinates of the intersection point of the two straight lines are the values of E'° and $\log_{10} i_0$. The results are shown in Table VI-3. To determine the value of E° from the values of $E^{\circ\prime}$ the activity of Fe^{2+} was calculated. The activity coefficients for Fe^{2+} were obtained as discussed in Appendix B by applying Eq. (B.5).

Revised Fe^{2+} and Cl^{-} concentrations and ionic strengths were determined by taking into account the specific interaction between Fe^{2+} and chloride as discussed in this review (Section VIII.2.2.1), $\log_{10} \beta_1^{\circ} = -\ (1.0 \pm 0.8)$. As recommended in this review, the interaction-coefficient values $(0.17 \pm 0.01)\ \mathrm{kg \cdot mol^{-1}}$ for $\varepsilon(Fe^{2+},Cl^{-})$ and $(0.00 \pm 0.01)\ \mathrm{kg \cdot mol^{-1}}$ for $\varepsilon(K^{+},Cl^{-})$ were used.

Table VI-3: Recalculation of the E° values for the Tafel diagrams contained in [1960HUR].

Composition / mol·kg^{-1}				Cl^-/Fe^{2+} association influence		Fe^{2+} activities		Results V *vs*. SHE	
HCl	KCl	Fe	I_m	Fe^{2+} corrected	I_m corrected	$a_{Fe^{2+}}$ [1960HUR]	$a_{Fe^{2+}}$ SIT	E'° SIT V *vs*. SHE	E° SIT V *vs*. SHE
0.001	0	0.5	1.5	0.493	1.487	0.101	0.0977	-0.507 ± 0.016	-0.4776 ± 0.0160
0.001	0.6	0.2	1.2	0.197	1.194	0.040	0.0424	-0.504 ± 0.018	-0.4641 ± 0.0180
0.001	0.8	0.1	1.1	0.099	1.097	0.020	0.0219	-0.522 ± 0.011	-0.4737 ± 0.0110

Tentative correction of the E° (Fe^{2+}/Fe(0)) value to the 298.15 K standard state temperature can be done by using the value of S°_{m} (Fe^{2+}) = – (101.6 ± 3.7) J·K^{-1}·mol^{-1}, recommended by [1995PAR/KHO][1] and Eq. (VI.3). The variations of ΔH and ΔS as functions of temperature have been neglected because the temperature interval considered is small. The trivial correction for using 100 kPa as the standard pressure instead of 1 atm is 0.00017 V. Hence, for the reduction reaction

$$Fe^{2+} + H_2(g) \rightleftharpoons Fe(\alpha) + 2\,H^{+} \qquad \text{(VI.8)}$$

$$E^{\circ}_{0}\,(Fe^{2+}/Fe(0)) = -\,(0.4745 \pm 0.0088)\ \text{V}$$

$$\Delta_{r}G^{\circ}_{m}\,(\text{VI.8}) = (91.56 \pm 1.70)\ \text{kJ·mol}^{-1}$$

and

$$\Delta_{f}G^{\circ}_{m}\,(Fe^{2+}, 298.15\ \text{K}) = -\,(91.56 \pm 1.70)\ \text{kJ·mol}^{-1}.$$

The Gibbs energy of the reduction reaction (VI.8) (as $\Delta_{red}G$(Fe(II)) was used in the optimization calculations done to ensure consistency with other thermodynamic quantities for iron species (Chapter XI); the consistent value for $\Delta_{f}G^{\circ}_{m}$ (Fe^{2+}, 298.15 K) is calculated to be – (90.72 ± 0.64) kJ·mol^{-1}, in agreement with the original assessed value within its assigned uncertainty of ± 1.7 kJ·mol^{-1}.

VI.1.1.3 Standard Fe^{2+}/Fe(0) potential from chemical redox equilibria

Two papers [1926HAM], [1982GAM/REI] describe attempts to obtain the value of the standard potential of the couple Fe^{2+}/Fe(0) by measuring the equilibrium constant of a redox reaction between Fe(0) and an oxidant ion which belongs to a redox couple having a standard potential value close to E° (Fe^{2+}/Fe(0)).

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[1] Use instead of the entropy value selected in the present review would have a trivial effect on the value of the potential of only 0.03 mV.

The couple $Tl^+/Tl(0)$, with $E^o = -0.336$ V, was chosen by the two groups of investigators[1]. Both followed the progress of the reaction:

$$2\ Tl^+ + Fe(0) \rightarrow Fe^{2+} + 2\ Tl(0). \qquad (VI.9)$$

Hampton [1926HAM] also investigated the reverse reaction. He came to the conclusion that equilibrium was not reached even after several months. By using the direct and reverse reaction rate constants he found a value of $E^o(Fe^{2+}/Fe(0))$ consistent with − 0.441 V, the value he had determined by potential-difference measurements.

Gamsjäger *et al.* [1982GAM/REI] reported that $E^o(Fe^{2+}/Fe(0)) = -(0.435 \pm 0.005)$ V. They worked at 323.15 K and claimed that equilibrium was reached after 7 to 11 days at that temperature.

The equilibrium experiments of Fe^{2+} with Tl(0) led generally to $E^o(Fe^{2+}/Fe(0))$ values that were too positive. This is probably because equilibrium was not reached in the work of Hampton at room temperature. For the work of Gamsjäger *et al.* the extrapolation to standard conditions is problematic. Also, as the equilibrium constant of this reaction is much greater than 1, small differences in the concentrations of the products can lead to significant errors in the $E^o(Fe^{2+}/Fe(0))$ values. Another reason for the discrepancy could be the influence of the surface energy of the solids, here Tl(0) and Fe(0), which depends on their state of division.

Because of the slowness of the reactions in which two solids are involved, and also because of the excessively large difference between $E^o(Fe^{2+}/Fe(0))$ and $E^o(Tl^+/Tl(0))$, we do not recommend the values of the standard potentials derived from these experiments.

Redox equilibrium investigations using another couple more favourable than $Tl^+/Tl((0)$, with an E^o value closer to the $Fe^{2+}/Fe(0)$ potential and faster reaction kinetics, would be welcome to confirm the $E^o(Fe^{2+}/Fe(0))$ value, which unlike $E^o(Fe^{3+}/Fe^{2+})$, cannot be determined easily by potential-difference measurements.

VI.1.2 The standard oxidation potential of the Fe^{3+}/Fe^{2+} couple

VI.1.2.1 Electrochemical methods, electrochemical-cell potential-difference measurements

The Fe^{3+}/Fe^{2+} couple is reversible at inert solid electrodes, and the potential-difference measurements are well suited to the precise determination of $E^o(Fe^{3+}/Fe^{2+})$ and its variation as a function of the temperature, allowing calculation of reliable values of $\Delta_r G^o_m(Fe^{3+} \rightarrow Fe^{2+})$, $\Delta_r S^o_m(Fe^{3+} \rightarrow Fe^{2+})$ and $\Delta_r H^o_m(Fe^{3+} \rightarrow Fe^{2+})$.

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[1] The basis for this value is discussed further by Rard *et al.* [1999RAR/RAN] and Parker and Khodakovskii [1995PAR/KHO].

Some values of $E^\circ(\mathrm{Fe^{3+}/Fe^{2+}})$, several of which were taken from measurements tabulated by Parker and Khodakovskii [1995PAR/KHO] in their review, are listed in Table VI-4. Currently there is good agreement between the values of E° claimed in many papers, and the list in Table VI-4 is mainly limited to those papers that have been reanalysed here with the SIT formalism. Thermodynamic quantities for the reduction reaction are given in Table VI-5.

Table VI-4: Selected studies for the determination of the E° ($\mathrm{Fe^{3+}/Fe^{2+}}$) value.

Reference	E° ($\mathrm{Fe^{3+}/Fe^{2+}}$) / V vs. SHE	Method
[2000TAG/DIA]	0.7704 ± 0.0020	E_cell measurements from 293.95 to 363.15 K. Comparison of E_cell data in $\mathrm{HClO_4}$ and HCl
[1972WHI/LAN]	0.770 ± 0.002	E_cell measurements from 278.15 to 308.15 K.
[1953MAG/HUI]	0.738 ± 0.002	E_cell measurements in 0.985 M $\mathrm{HClO_4}$. The formal potential reported is in line with values from other studies.
[1951CON/MCV]	0.739 ± 0.002	E_cell measurements in 0.5036 M $\mathrm{HClO_4}$. The formal potential reported is in line with values from other studies
[1929POP/KUN]	0.7477 ± 0.0005	E_cell at 298.15 K.
[1937SCH/SHE]	0.7701 ± 0.0002	E_cell at 298.15 K.
[1934BRA/HER]	0.772 ± 0.001	Recalculation of the standard potential after corrections to the E_cell data of [1929POP/KUN].
	0.772 ± 0.001	Recalculation of the constant K for $\mathrm{Fe^{3+} + Ag \rightleftharpoons Fe^{2+} + Ag^{+}}$, from the data of [1912NOY/BRA].
	0.772 ± 0.001	Recalculation of the constant K for: $\mathrm{2\,Fe^{3+} + 2\,Hg \rightleftharpoons 2\,Fe^{2+} + Hg_2^{2+}}$, from the data of [1931POP/FLE] at 298.15 K and [1933FLE] at 308.15 K.

The more recent standard potential values agree well with the older ones, and with the standard potentials $E^\circ(\mathrm{Fe^{3+}/Fe^{2+}})$ quoted in standard reference Tables [1985BAR/PAR], [1952LAT]. This stands in contrast to what is observed for the $E^\circ(\mathrm{Fe^{2+}/Fe(0)})$ potentials.

As can be seen in Table VI-4, there is good agreement between different workers on the value for $E^\circ(\mathrm{Fe^{3+}/Fe^{2+}})$ based on cell measurements from 1934 on. All the authors, from [1934BRA/HER] to [2000TAG/DIA], despite using various experimental cells and various approaches for junction-potential and activity-coefficient corrections, derived values within ± 2 mV of $E^\circ(\mathrm{Fe^{3+}/Fe^{2+}}) \cong 0.770$ V.

Table VI-5: Thermodynamic quantities* for the reduction reaction corresponding to data presented in Table VI-4.

reference	$\Delta_r G^o_m$ / (kJ·mol^{-1})	$\Delta_r H^o_m$ / (kJ·mol^{-1})	$\Delta_r S^o_m$ / (J·K^{-1}·mol^{-1})	Comments
[2000TAG/DIA]	– 74.27 ± 0.17	– 39.33 ± 2.09	117.15 ± 6.28	$\Delta_r C^o_{p,m}$ = 62.08 J·K^{-1}·mol^{-1}
[1972WHI/LAN]	– 74.27 ± 0.17	– 42.68 ± 1.67	106.27 ± 6.28	original values
	– 74.27 ± 0.17	– 42.59 ± 1.88	106.27 ± 6.28	recalculation of $\Delta_r H^o_m$ based on the original $\Delta_r G^o_m$ and $\Delta_r S^o_m$
	– 74.27 ± 0.17	– 38.4 ± 1.5	120.27 ± 5.06	$\Delta_r H^o_m$ revision from $E^{o\prime}$ *vs.* T by [1995PAR/KHO], $\Delta_r C^o_{p,m}$ = 0. linear $E^o(T) = f(T)$
	– 74.27 ± 0.17	– 42.8 ± 1.5	105.72 ± 5.06	$\Delta_r C^o_{p,m}$ revision from $E^{o\prime}$ *vs.* T by [1995PAR/KHO], $\Delta_r C^o_{p,m}$ from [1988HOV]
[1937SCH/SHE]	– 74.31 ± 0.02			
[1934BRA/HER]	– 74.5 ± 0.1			revision of the data of [1929POP/KUN]

* The uncertainties are those listed by the original authors, and it is not clear whether they were 1σ or 2σ uncertainties.

VI.1.2.1.1 Selection of the value of the E^o (Fe^{3+}/Fe^{2+}) standard potential based on use of the SIT for ionic strength corrections

VI.1.2.1.1.1 Perchlorate medium

Five papers [1937SCH/SHE], [1951CON/MCV], [1953MAG/HUI], [1972WHI/LAN], [2000TAG/DIA], which are quite consistent in their reported values for E^o (Fe^{3+}/Fe^{2+}), have been reanalyzed with the SIT formalism (see Appendix A for details). The latter four studies also dealt with the variation of the standard potential as a function of the temperature.

Here, for convenience, we define a potential $E^{\ddagger}$ for the Fe^{2+}/Fe^{3+} couple at total ionic strength I_m and perchlorate molality $m_{\mathrm{ClO_4^-}}$

$$E^{\ddagger} = E + (RT/F)\ln(m_{\mathrm{Fe^{2+}}}/m_{\mathrm{Fe^{3+}}}) + (RT/F)\ln m_{\mathrm{H^+}} + (RT/F)\ln\gamma_{\mathrm{H^+}} - E_{\mathrm{j}}$$

and therefore

$$E^{\ddagger} = E^o - (RT/F)\ln(\gamma_{\mathrm{Fe^{2+}}}/\gamma_{\mathrm{Fe^{3+}}})$$

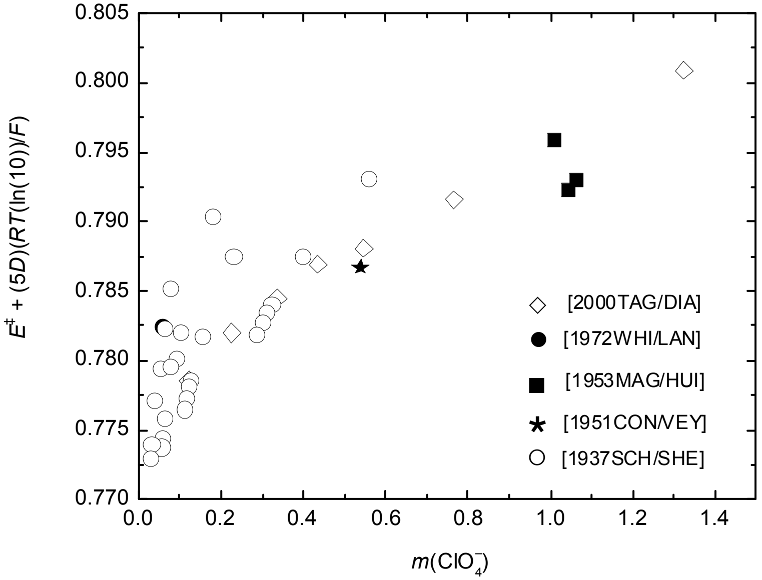
where E_{j} is the junction potential.

When the experimental values from the papers are analyzed in a consistent fashion using the SIT method for calculation of activity effects, and the TDB-selected values for hydrolysis, the values for the standard potential based on these papers do not agree especially well with the original published values.

It was not possible to fit a single curve of the form $E^{\ddagger} + (5D)(RT\ln(10)/F) = \mathrm{f}(m_{\mathrm{ClO}_4^-})$ to all the perchloric-acid-medium data points (for 298.15 K) from all five papers (Figure VI-2).

The value of the standard potential deduced from the data of Whittemore and Langmuir [1972WHI/LAN] using the SIT is 11 mV greater than the value in the original paper (based on experiments carried out at only a single ionic strength). The difference comes mostly from the calculation of the activity coefficient for Fe^{3+}; in the original paper [1972WHI/LAN] an extended Debye-Hückel formulation was applied using an adjusted distance parameter. The two almost identical points for a total perchlorate molality of 0.0571 $\mathrm{mol{\cdot}kg^{-1}}$ [1972WHI/LAN] are well off the line established by the values from the rest of the experimental studies (see Figure VI-2). For these points the concentration of iron (II + III) is not negligible with respect to the ionic strength. However the junction-potential problem is different from that in the study of Schumb *et al.* [1937SCH/SHE] as discussed below because of the use of a silver/silver chloride reference electrode with saturated KCl as the internal solution. The Whittemore and Langmuir results have not been used in our final determination of E°_{0} by the SIT treatment.

Figure VI-2: Plot of all the key data in perchlorate (acid + sodium salt) (298.15 K) in a SIT diagram before the selection of the acceptable points (see criteria in the text).



Part of the data set of Schumb *et al.* [1937SCH/SHE] also does not fall on the common curve $E^{\ddagger} + (5D)(RT\ln(10)/F) = \mathrm{f}(m_{\mathrm{ClO}_4^-})$ (see Figure VI-2). Even the data from that one paper alone cannot be plotted on a single curve (see Appendix A). The difference between the average of the SIT $E^{\ddagger}$ values from the data at different acidities used by the authors (see Appendix A) and those in the original paper is only 0.002V; in good agreement taking into account the uncertainties, but the data must be plotted on four different curves with different slopes. This precludes the exclusive use of the Schumb *et al.* data for the determination of a unique $\varepsilon(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-)$ value. The systematic problem is probably due to substantial junction potentials generated by the more concentrated iron solutions in which iron (II + III) is responsible for a non-negligible part of the ionic strength.

Schumb *et al.* obtained an extrapolated value of 0.770 V for E_0^{o} after a double extrapolation to zero ionic strength—one extrapolation for the iron concentration and one for the perchloric acid. The first extrapolation eliminated the effect of the junction potential due to the presence of Fe^{2+} and Fe^{3+} perchlorate in only one side of the junction between the working cell and the hydrogen reference electrode. The single-extrapolation SIT method does not resolve the problem of the junction potentials. But it is possible to limit the junction-potential deviations by selecting from the Schumb *et al.* data only the measured potential values for solutions having higher $\mathrm{HClO_4}$/Fe ratios. For such solutions the junction potentials are close to 0 mV because they are mostly the result of differences in $\mathrm{HClO_4}$ concentrations between the reference and the measurement compartments of the electrochemical cell. In the experiments of Schumb *et al.*, and also in other work that used hydrogen electrodes as the reference half-cell, the acid concentrations in the reference and the working compartments of the cell were equal. So the results obtained with solutions for which the ratio $\mathrm{HClO_4}$/Fe was lower than 10 have been eliminated from the plot of Figure VI-3, including 12 points (of 25) from the work of Schumb *et al.*

Two points of Magnusson and Huizenga [1953MAG/HUI], obtained in mixed $\mathrm{NaClO_4}$-$\mathrm{HClO_4}$ aqueous media, also were eliminated. This selection was effective in that all the remaining points fall on a common curve (see Figure VI-3).

For the data obtained at several ionic strengths ([2000TAG/DIA], [1937SCH/SHE]) the relation between $E^{\ddagger} + (5D)(RT\ln(10)/F)$ at a value of zero for $m_{\mathrm{ClO}_4^-}$ depends on the type of fitting function. Three types of fitting functions differing in the form of the $\varepsilon(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-)$ interaction coefficient, were tried: linear (Eq. (VI.10)), which is the standard SIT treatment, polynomial (Eq. (VI.11)) and a two-term form with one being logarithmic (Eq. (VI.12)) [1980CIA] (see Appendix B.1.1, Eq. (B.3)).

$$\varepsilon(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-) = \text{constant} \tag{VI.10}$$

$$\varepsilon(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-) = \varepsilon_1 + \varepsilon_2\, m_{\mathrm{ClO}_4^-} + \varepsilon_3\, m_{\mathrm{ClO}_4^-}{}^2 + \ldots + \varepsilon_n\, m_{\mathrm{ClO}_4^-}{}^{n-1} \tag{VI.11}$$

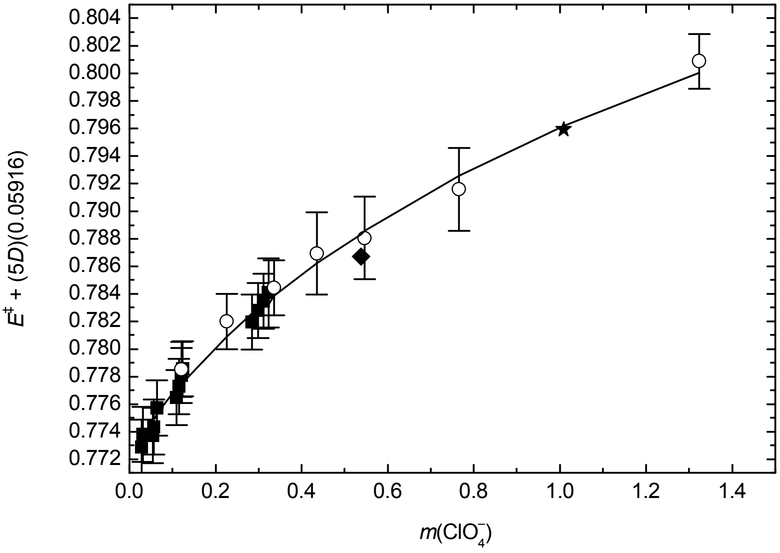
$$\varepsilon(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-) = \varepsilon_1 + \varepsilon_2 \log_{10}(I_m) \tag{VI.12}$$

Therefore, Eq. (VI.13)

$$E^{\ddagger} + (5D)(RT\ln(10)/F) = E_0^{\circ} - (RT\ln(10)/F)\,\Delta\varepsilon(m_{\mathrm{ClO}_4^-}) \qquad \text{(VI.13)}$$

was fitted to all the data shown in Figure VI-3 using four different functions for $\Delta\varepsilon$, $\Delta\varepsilon = (\varepsilon(\mathrm{Fe}^{2+},\mathrm{ClO}_4^-) - \varepsilon(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-))$. The form of $\varepsilon(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-)$ was given by Eqs. (VI.10), (VI.11) (second- and third-degree polynomials) or (VI.12). With the exception of Eq. (VI.10) (see Figure VI-4), all of these functions give a good representation of the selected data plotted in Figure VI-3.

Figure VI-3: Curve $E^{\ddagger} + (5D)(RT(\ln(10)/F)$ *vs.* $m_{\mathrm{ClO}_4^-}$ for 298.15 K after the elimination of some data points contained in Figure VI-2 according to the criteria described in the text (two-term Fe^{3+} interaction coefficient, Eq. (VI.12)). The selected points are from: [2000TAG/DIA] ○, [1953MAG/HUI] ★, [1951CON/MCV] ◆, and [1937SCH/SHE] ■.



The curve corresponding to Eq. (VI.13), with the interaction coefficient $\varepsilon(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-)$ defined according Eq. (VI.12), was fitted to the data by a non-linear analysis: P1 = E_0°; P2 $= 0.05916\{\varepsilon(\mathrm{Fe}^{2+},\mathrm{ClO}_4^-) - \varepsilon_1(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-)\}$; P3 = $0.05916\varepsilon_2(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-)$.

The calculated values are P1 = (0.77197 ± 0.00048) V; P2 = – (0.02428 ± 0.00066) $\mathrm{V\cdot kg\cdot mol^{-1}}$ and P3 = – (0.02421 ± 0.00037) $\mathrm{V\cdot kg.mol^{-1}}$ —1σ uncertainties, and an R^2 value of 0.988.

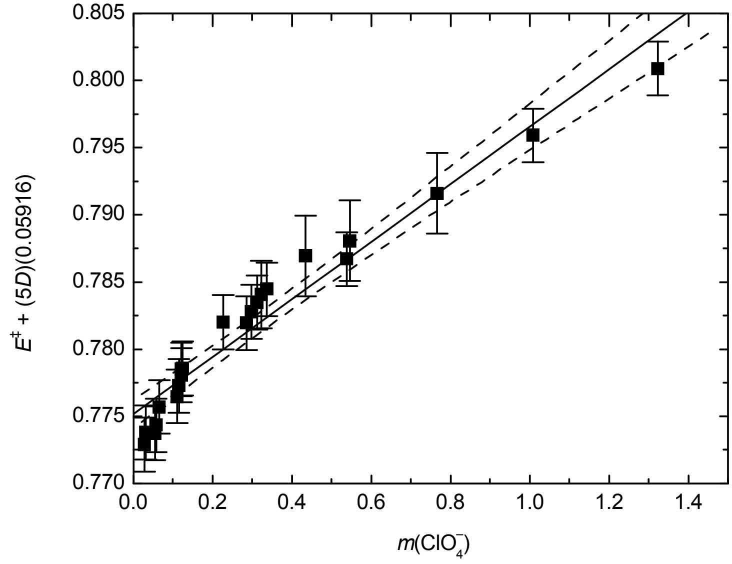
After rounding and increasing the 2σ statistical uncertainties to take into account unidentified systematic errors that surely exist

$$E^{\circ}_{0} = (0.772 \pm 0.002)\ \text{V},\ \Delta\varepsilon = -\ ((0.41 \pm 0.03) - (0.41 \pm 0.05)\ \log_{10} I_m)\ \text{kg·mol}^{-1},$$

and using $\varepsilon(\text{Fe}^{2+}, \text{ClO}_4^-) = (0.37 \pm 0.04)\ \text{kg·mol}^{-1}$,

$$\varepsilon(\text{Fe}^{3+}, \text{ClO}_4^-) = ((0.78 \pm 0.05) - (0.41 \pm 0.05)\ \log_{10} I_m)\ \text{kg·mol}^{-1}.$$

Figure VI-4: Linear fit (Eq. (VI.10)) to the selected 298.15 K data from [1937SCH/SHE], [1951CON/MCV], [1953MAG/HUI], [2000TAG/DIA]: $R^2 = 0.954$; $E^{\circ}_{0} = (0.7753 \pm 0.0004)$ V, $\Delta\varepsilon = -\ (0.36 \pm 0.02)$ kg·mol^{-1}.



The use of a constant value of $\varepsilon(\text{Fe}^{3+}, \text{ClO}_4^-)$ to fit the selected data points as shown in Figure VI-4 is designated here as SIT$_1$. The use of the two-term interaction coefficient ($\varepsilon_1 + \varepsilon_2 \log_{10} I_m$) for $\varepsilon(\text{Fe}^{3+}, \text{ClO}_4^-)$ (Eq. (VI.12)) is designated as SIT$_2$. The linear fit yielded $R^2 = 0.954$ as compared to, for example, $R^2 = 0.988$ for the SIT$_2$ fit using Eq. (VI.12). The discrepancy between the E°_{0} value originally reported by Tagirov *et al.* [2000TAG/DIA] and that determined with the linear SIT$_1$ function (Eq. (VI.10)) is 0.008V. This difference is similar to that found for the work of Whittemore and Langmuir [1972WHI/LAN] (see pg. 95), and there is no overlap within the estimated uncertainties of 0.002 V with the results from the original paper or other literature values.

SIT_1 yields a more positive value for E_0° (0.7753 V as compared to 0.772 V with SIT_2). However the results of the forced linear fit are also reported in this review because in the NEA TDB project this is the standard fitting procedure. Also,

$$\begin{aligned}\Delta\varepsilon &= -\,(\varepsilon(\mathrm{Fe}^{2+},\mathrm{ClO}_4^-) - \varepsilon_1(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-))\\ &= -\,(0.36 \pm 0.02)\ \mathrm{kg{\cdot}mol^{-1}}\ (\mathrm{SIT}_1)\end{aligned}$$

and for SIT_2

$$\begin{aligned}\Delta\varepsilon &= -\,(\varepsilon(\mathrm{Fe}^{2+},\mathrm{ClO}_4^-) - (\varepsilon_1(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-) - \varepsilon_2(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-)\log_{10} I_m))\\ &= -\,(0.41 - 0.41\log_{10} I_m)\ \mathrm{kg{\cdot}mol^{-1}}.\end{aligned}$$

Second- and third-degree polynomial fits to obtain values for $\Delta\varepsilon$ according to Eq. (VI.11) yield fair agreement for values of E_0° (differences of ~ 0.004 V) when compared with the original value from Tagirov *et al.* [2000TAG/DIA]. These fits also give good representations of the experimental data in the range of the ionic strengths investigated, but they diverge from reasonable values of $E^{\ddagger} + (5D)(RT\ln(10)/F)$ outside this range. For example, the data of Tagirov *et al.* are well represented by a third-degree polynomial (R^2 = 0.9999) with a negative second-degree coefficient. However, as shown in the Appendix A entry for [2000TAG/DIA], the variation of the interaction coefficient $\varepsilon(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-)$ as a function of $m_{\mathrm{ClO}_4^-}$ cannot be represented properly by Eq. (VI.11) outside the range of the ionic strengths used by Tagirov *et al.* (0.13 to 1.4 m). Thus the usefulness of the polynomial fits is limited, and they have not been used further for the treatment of the electrochemical data by the SIT formalism.

As seen in Figure VI-3, the $\varepsilon(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-)$ two-term fit Eq. (VI.12) yields E_0° = (0.772 ± 0.002) V, where the estimated uncertainty is increased to 0.002 V, a value adopted in most of the modern determinations of E_0° by potential-difference measurements [1972WHI/LAN],[2000TAG/DIA]. Such uncertainty is also adopted in this review when sufficient data and good fits are available.

The SIT_2 treatment is used in addition to the linear fit, SIT_1, when, as in the case of the work of Tagirov *et al.*, the range of ionic strengths investigated was sufficiently large, especially when low ionic strength data also are available. Contrary to the results from the polynomial fits, the calculated SIT_2 values of $\varepsilon(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-)$ and $E^{\ddagger}$ remain reasonable at ionic strengths beyond the initial fitting range.

Therefore, we recommend the $E_0^{\circ}(\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+})$ values obtained by the SIT_2 treatment as the best value for the TDB review, but with an increased uncertainty of 0.002 V:

$$E_0^{\circ}(\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}) = (0.772 \pm 0.002)\ \mathrm{V}\ \ (\mathrm{SIT}_2).$$

$$\mathrm{Fe^{3+}} + \tfrac{1}{2}\,\mathrm{H_2(g)} \rightleftharpoons \mathrm{Fe^{2+}} + \mathrm{H^+} \qquad \text{(VI.14)}[1]$$

The value found by applying the SIT_1 treatment is (0.7753 ± 0.0005) V. Here the quality of the fit is poorer than for SIT_2 (the deviations are a strong function of $m_{\mathrm{ClO_4^-}}$) and to take that into account it is estimated that the uncertainty must be increased to 0.005 V, yielding:

$$E_0^{\mathrm{o}}(\mathrm{Fe^{3+}/Fe^{2+}}) = (0.775 \pm 0.005)\ \mathrm{V}\ \ (\mathrm{SIT_1}).$$

With the selected value of (0.37 ± 0.04) kg·mol^{-1} for $\varepsilon(\mathrm{Fe^{2+}, ClO_4^-})$, the interaction coefficient $\varepsilon(\mathrm{Fe^{3+}, ClO_4^-})$ is

$$\varepsilon(\mathrm{Fe^{3+}, ClO_4^-}) = (0.73 \pm 0.04)\ \mathrm{kg\cdot mol^{-1}}\ (\mathrm{SIT_1})$$

or

$$\varepsilon(\mathrm{Fe^{3+}, ClO_4^-}) = ((0.78 \pm 0.05) - (0.41 \pm 0.05)\log_{10} I_m)\ \mathrm{kg\cdot mol^{-1}}\ (\mathrm{SIT_2}).$$

VI.1.2.1.1.2 Hydrochloric acid medium

The data of Popoff and Kunz [1929POP/KUN], which have been corrected by Bray and Hershey [1934BRA/HER] for the extrapolation of $E^{\ddagger}$ to zero ionic strength, have been used for the determination of the E_0^{o} for hydrochloric acid medium.

After corrections, the early work of Popoff and Kunz yielded a value for $E_0^{\mathrm{o}}(\mathrm{Fe^{3+}/Fe^{2+}})$ which is quite consistent with the presently accepted value.

For the SIT treatment we took into consideration the hydrolysis of $\mathrm{Fe^{3+}}$ (1:1 species). and the chlorido complexes (1:1 and 2:1 species for $\mathrm{Fe^{3+}}$ and 1:1 species for $\mathrm{Fe^{2+}}$). All the interaction coefficients were those recommended in this review.

For hydrolysis:

$$\log_{10}{}^{*}\beta_1 = -\,2.15 - 4D + (0.22 - 0.21\log_{10} I_m)\ m_{\mathrm{ClO_4^-}} + \log_{10} a_{\mathrm{w}}.$$

For the $\mathrm{Fe^{3+}}$ chlorido complexes the values of $\log_{10}\beta_1^{\mathrm{o}}$ and $\Delta\varepsilon$ for the formation of $\mathrm{FeCl^{2+}}$ are those from the SIT treatment of the data of Tagirov *et al.* [2000TAG/DIA] obtained in aqueous HCl solutions (Section VIII.2.3.1.3). The values of $\log_{10} K_2^{\mathrm{o}}$ and $\Delta\varepsilon$ for the formation of $\mathrm{FeCl_2^+}$ are those based on the SIT treatment of the literature data in various media (Table VIII-8, list 1):

$$\log_{10}\beta_1 = 1.52 - 6D + 0.237\,I_m$$

$$\log_{10} K_2 = 0.70 - 4D + 0.12\,I_m$$

In this review (Section VIII.2.2.1) it is recommended that the weak interaction between $\mathrm{Fe^{2+}}$ and $\mathrm{Cl^-}$ be described by $\log_{10}\beta_1^{\mathrm{o}} = -\,(1.0 \pm 0.8)$ and $\Delta\varepsilon = \varepsilon(\mathrm{FeCl^+, Cl^-})$ –

---

[1] The thermodynamic quantities for Reaction (VI.14) are designated by $\Delta_{\mathrm{red}}G(\mathrm{Fe(III)})$ and $\Delta_{\mathrm{red}}S(\mathrm{Fe(III)})$ in tables in Chapter XI.

$\varepsilon(\mathrm{Fe^{2+}},\mathrm{Cl^-}) - \varepsilon(\mathrm{Cl^-},\mathrm{H^+}) = (0.17 \pm 0.01) - (0.17 \pm 0.01) - (0.12 \pm 0.01) = -(0.12 \pm 0.02)$ kg·mol^{-1}, so, $\log_{10}\beta_1 = -1.0 - 4D + 0.12\,I_m$ for the formation of FeCl$^+$.

Despite the weakness of this interaction, the value of $\log_{10}\beta_1^{\circ}$, which is very difficult to determine, might influence the values of E_0° and $\varepsilon(\mathrm{Fe^{3+}},\mathrm{Cl^-})$, consequently two fits have been carried out: a) one with the recommended values given above; b) one with $\log_{10}\beta_1^{\circ} = -0.11$ and $\Delta\varepsilon = -0.173$ kg·mol^{-1}, which corresponds to a more stable associate.

In addition, some of the experimental E values were obtained with solutions having high concentrations of iron with regard to the HCl concentration, yielding non-negligible junction potentials. As was the case for the work of Schumb *et al.* [1937SCH/SHE] in HClO$_4$, we eliminated the points for which the concentration ratios for HCl/Fe were lower than 10.

It must be stressed that the calculations for Fe^{3+} and Fe^{2+} concentrations are only first approaches because many interaction coefficients in chloride medium are missing and the interaction coefficients used were those available in perchlorate medium.

The plot of $E^{\ddagger} + (5D)(RT\ln(10)/F)$ for $T = 298.15$ K as a function of $m_{\mathrm{Cl^-}}$ for the selected data and its linear fitting is shown in Figure VI-5. The following rounded values were obtained from the extrapolation to zero ionic strength. The uncertainties in these E_0° values are our estimates, and are somewhat greater than the statistical uncertainty values noted in the caption for the figure.

(case a) $E_0^{\circ}(\mathrm{Fe^{3+}/Fe^{2+}}) = (0.777 \pm 0.005)$ V (SIT$_1$) $\log_{10}\beta_1^{\circ}(\mathrm{Fe^{2+}}) = -1.0$

(case b) $E_0^{\circ}(\mathrm{Fe^{3+}/Fe^{2+}}) = (0.776 \pm 0.005)$ V (SIT$_1$) $\log_{10}\beta_1^{\circ}(\mathrm{Fe^{2+}}) = -0.11$.

The fitting of the equations with two Fe^{3+} interaction-coefficient terms (SIT$_2$) to the same data is shown in Figure VI-6. The following rounded values were obtained from the extrapolation to zero ionic strength. The uncertainties in these E_0° values are our estimates, and are somewhat greater than the statistical uncertainty values noted in the figure.

(case a) $E_0^{\circ}(\mathrm{Fe^{3+}/Fe^{2+}}) = (0.772 \pm 0.002)$ V (SIT$_2$) $\log_{10}\beta_1^{\circ}(\mathrm{Fe^{2+}}) = -1.0$

(case b) $E_0^{\circ}(\mathrm{Fe^{3+}/Fe^{2+}}) = (0.772 \pm 0.002)$ V (SIT$_2$) $\log_{10}\beta_1^{\circ}(\mathrm{Fe^{2+}}) = -0.11$.

The SIT$_1$ and SIT$_2$ E_0° values obtained from chloride-medium data, (0.778 ± 0.005) V and (0.772 ± 0.002) V (case a), (0.777 ± 0.005) V and (0.772 ± 0.002) V (case b), are in line with the values given above for perchlorate medium. As was the case for perchlorate medium, the function $E^{\ddagger} + (5D)(0.05916) = \mathrm{f}(m_{\mathrm{Cl^-}})$ is not linear (see Figures VI-5 and VI-6). The determination of the apparent $\varepsilon(\mathrm{Fe^{3+}},\mathrm{Cl^-})$ values was carried out as was done for the $\varepsilon(\mathrm{Fe^{3+}},\mathrm{ClO_4^-})$ values.

Figure VI-5: Linear fit of the selected data [1929POP/KUN] in HCl solutions (298.15 K) treated by the SIT formalism (case a). The molal concentrations of Fe^{3+} and Fe^{2+} have been corrected for hydrolytic ($FeOH^{2+}$) and chloride ($FeCl^{2+}$, $FeCl_2^+$, $FeCl^+$) species. This fit yields: $E^\circ = (0.7770 \pm 0.0014)$ V, $\Delta\varepsilon = -(0.59 \pm 0.02)$ $kg \cdot mol^{-1}$ with $R^2 = 0.984$.

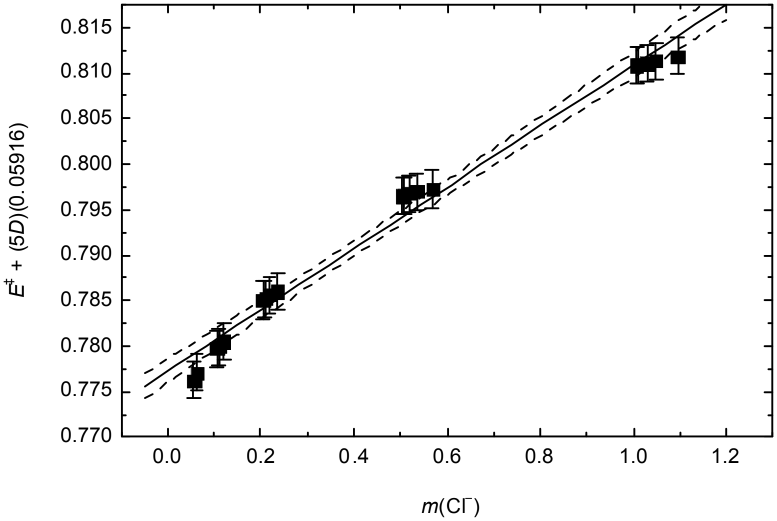
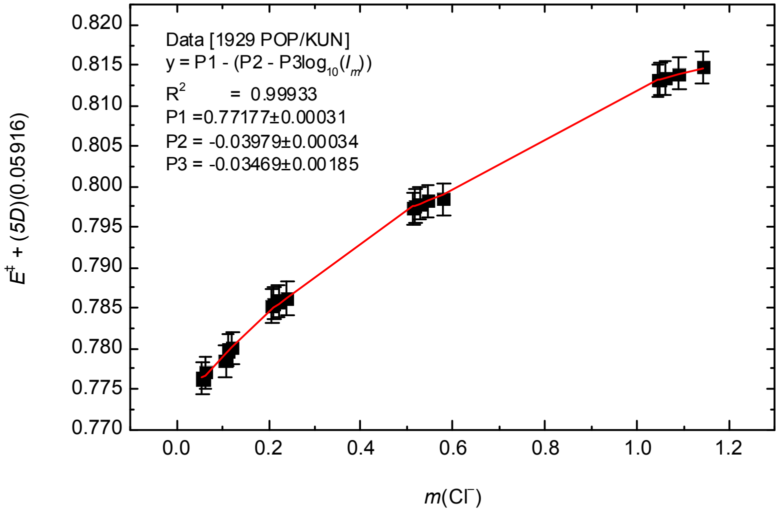


Figure VI-6: Non-linear fit of the selected data (case a) of Popoff and Kunz [1929POP/KUN] (298.15 K). The parameters of the fitting function correspond to those in Eq. (VI.13) as follows: P1 = E_0° (V), P2 = 0.05916 ($\varepsilon(Fe^{2+},Cl^-) - \varepsilon_1(Fe^{3+},Cl^-)$) ($V \cdot kg \cdot mol^{-1}$), P3 = 0.05916 $\varepsilon_2(Fe^{3+},Cl^-)$ ($V \cdot kg \cdot mol^{-1}$).



VI.1.2.2 The variation of E_0° (Fe^{3+}/Fe^{2+}) with temperature

Several studies of the variation of E° (Fe^{3+}/Fe^{2+}) as a function of temperature have been reported in the literature [2000TAG/DIA], [1973NIK/ANT], [1972WHI/LAN], [1951CON/MCV], [1953MAG/HUI]. The values of $\Delta_r H_m^\circ$ (VI.14) and $\Delta_r S_m^\circ$ (VI.14) that can be calculated from [2000TAG/DIA] and [1972WHI/LAN] are in moderately good agreement. The values from the study of Nikolaeva and Antipina [1973NIK/ANT] are not used in this review for the reasons discussed in Appendix A.

The data of [1951CON/MCV], [1953MAG/HUI] and [1972WHI/LAN], which give $E^\ddagger$ values for only one ionic strength, were reanalyzed using the SIT_2-recommended interaction coefficients from this review to obtain activity coefficients necessary for calculation of the $E^\circ(t)$ values (zero ionic strength).

The $E^\circ(t)$ values from the Tagirov *et al.* paper [2000TAG/DIA], in which cell measurements at various ionic strengths at different temperatures are available, have been obtained by extrapolation of $E^\ddagger + (5D)(RT\ln(10)/F) = f(m_{ClO_4^-})$ to zero ionic strength (*cf.* Section B.1.2). The $E^\circ(t)$ values were obtained by linear and non-linear fits according to the SIT_1 and SIT_2 processes described above. However, as there are large discrepancies between the SIT_1 and SIT_2 results and between those results and the results given in the original paper, fits to the data also were done for a single ionic strength as a function of temperature. Such fits yield a value very close to values of $dE^\circ(t)/dt$ obtained using the SIT_1 or SIT_2 formalisms.

All the $E^\circ(t)$ data from each paper were fitted by third-, second- or first-order polynomials for temperatures between 5 and 35 °C (278.15 and 308.15 K). The data are inadequate to support the selection of any functional expression beyond a linear equation, and the result from the linear expression is accepted here (*i.e.,* $\Delta_r C_{p,m}$ (VI.14) is considered to be constant over the temperature range between 278.15 and 308.15 K). The polynomial coefficients other than the first-degree coefficients were poorly defined, with uncertainties larger than the values. So, it was decided to use the linear fits which yielded precise values of $dE^\circ(t)/dt$. Therefore, as discussed in Appendix A, [1972WHI/LAN], [2000TAG/DIA], for this small temperature range the value of $\Delta_r C_{p,m}^\circ$ (VI.14) is too small to impose a noticeable curvature on the $E^\circ(t) = f(t)$ function. For example, the plot of $E^\circ(t)$ as a function of the temperature in °C from [1951CON/MCV] is shown in Figure VI-7.

It was decided to limit the upper temperature to 308.15 K because of the scarcity of experimental values above 308.15 K. Only Tagirov *et al.* [2000TAG/DIA] published electrochemical potential values to 363.15 K, but these values are in poor agreement with values calculated using the Tagirov *et al.* $E^\circ(t)$ values and the SIT_1 or SIT_2 models.

The data from the four papers [1951CON/MCV], [1953MAG/HUI], [1972WHI/LAN], [2000TAG/DIA] have been gathered, and are plotted in Figure VI-8.

Figure VI-7: Linear fit to the data of [1951CON/MCV], R^2 = 0.999, $\mathrm{d}E^{\circ}(t)/\mathrm{d}t$ = $(1.21 \pm 0.01) \times 10^{-3}$ V·K^{-1}.

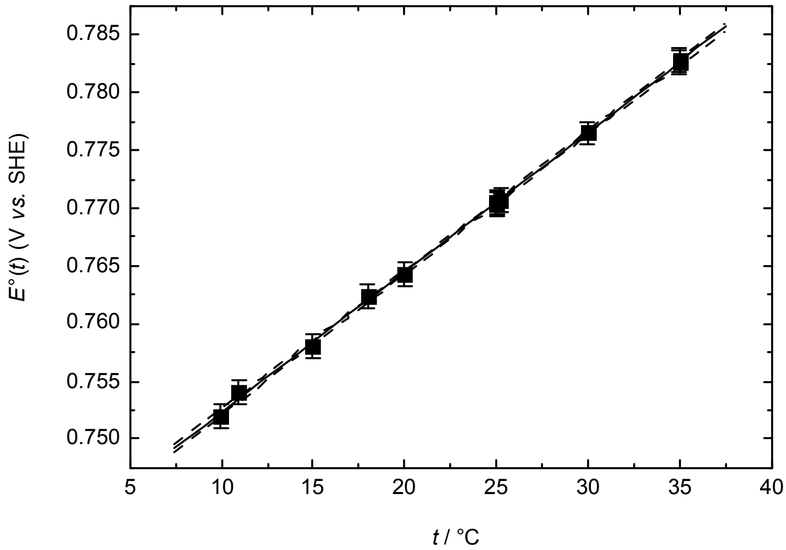
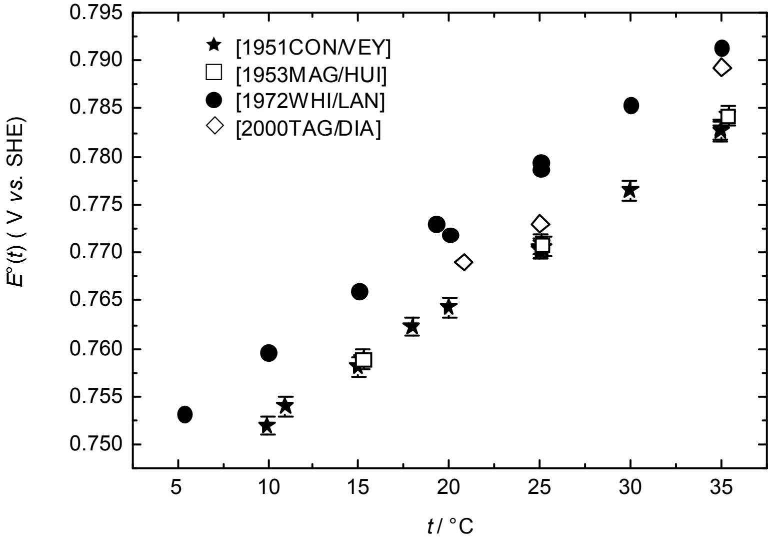


Figure VI-8: Plot of all the selected data for $E^{\circ}(t)$ *vs*. t, $\mathrm{d}E^{\circ}(t)/\mathrm{d}t$ = $(1.21 \pm 0.09) \times 10^{-3}$ V·K^{-1}, R^2 = 0.88.



The constant value of $\mathrm{d}E^{\circ}(t)/\mathrm{d}t$ obtained is (0.00121 ± 0.00009) $\mathrm{V{\cdot}K^{-1}}$. Here the high statistical error on the slope is due to the repartition of the data points among two groups falling on two straight lines, rather far from each other, but having quite similar slopes. This is due to the discrepancy between the Whittemore and Langmuir original $E^{\circ}(t)$ values and the values of $E^{\circ}(t)$ yielded by the SIT_2 treatment of the experimental data.

As discussed in Appendix A entries for Tagirov *et al.* [2000TAG/DIA], and Whittemore and Langmuir [1972WHI/LAN], the value of $\Delta_{\mathrm{r}}C^{\circ}_{p,\mathrm{m}}$ (57.2 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$) is small with respect to $F(\mathrm{d}E^{\circ}(t)/\mathrm{d}t)$. Nevertheless, its influence on the slope of the function $E^{\circ}(t)$ = f(t) has been determined to get the best possible value of $\Delta_{\mathrm{r}}S^{\circ}_{\mathrm{m}}$ ((VI.14), 298.15 K).

The basis of the correction calculations is given in the Appendix A discussions for the papers ([1972WHI/LAN], [2000TAG/DIA]). For the data obtained in the temperature range 278.15 to 308.15 K and with $\Delta_{\mathrm{r}}C^{\circ}_{p,\mathrm{m}}$ (VI.14) = 57.2 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, the correction to 298.15 K is

$$\Delta \mathrm{d}E^{\circ}(t)/\mathrm{d}t = (\Delta C^{\circ}_{p,\mathrm{m}}/F)\ \ln(298.15/T_{½}) \qquad \text{(VI.15)}$$

where $T_{½}$ is the mid temperature, here 293.15 K. Hence, the correction is + 9.6 × 10^{-6} $\mathrm{V{\cdot}K^{-1}}$.

VI.1.2.3 Thermodynamic function values for the reaction $\mathbf{Fe^{3+} + ½\,H_2(g) \rightleftharpoons Fe^{2+} + H^+}$

For $\Delta_{\mathrm{r}}C^{\circ}_{p,\mathrm{m}}$ (VI.14) ≠ 0, the variation of $\Delta_{\mathrm{r}}G^{\circ}_{\mathrm{m}}$ (VI.14) with the temperature is given by Eq. (VI.16):

$$\Delta_{\mathrm{r}}G^{\circ}_{\mathrm{m}}(T) = \Delta_{\mathrm{r}}H^{\circ}_{\mathrm{m}}(T_0) + \int_{T_0}^{T}\Delta_{\mathrm{r}}C^{\circ}_{p,\mathrm{m}}(T)\mathrm{d}T\ - T\,\{\Delta_{\mathrm{r}}S^{\circ}_{\mathrm{m}}(T_0) + \int_{T_0}^{T}(\Delta_{\mathrm{r}}C^{\circ}_{p,\mathrm{m}}(T)/T)\mathrm{d}T\,\} \qquad \text{(VI.16)}$$

where T_0 is 298.15 K. The replacement of $\Delta_{\mathrm{r}}G^{\circ}_{\mathrm{m}}(T)$ by $-FE^{\circ}(T)$ and taking the derivative yields:

$$F\mathrm{d}E^{\circ}(T)/\mathrm{d}T - \int_{T_0}^{T}(\Delta_{\mathrm{r}}C^{\circ}_{p,\mathrm{m}}(T)/T)\mathrm{d}T = \Delta_{\mathrm{r}}S^{\circ}_{\mathrm{m}}(T)\,. \qquad \text{(VI.17)}$$

The experimental values of heat capacities needed to calculate $\Delta_{\mathrm{r}}C^{\circ}_{p,\mathrm{m}}(T)$ of the $\mathrm{Fe^{3+}/Fe^{2+}}$ redox reaction to get the value of $\Delta_{\mathrm{r}}S^{\circ}_{\mathrm{m}}$ (VI.14) have been measured by Hovey [1988HOV] for temperatures between 283.15 and 328.15 K. From those, Tagirov *et al.* [2000TAG/DIA] assumed that the value at 298.15 K, 62.09 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, could be used between 278.15 and 363.15 K.

Here, initially we tried to avoid this simplification and, as discussed above, used the data of [1988HOV] to calculate values of $\Delta_{\mathrm{r}}H^{\circ}_{\mathrm{m}}$ (VI.14) and $\Delta_{\mathrm{r}}S^{\circ}_{\mathrm{m}}$ (VI.14) from the potentiometric data ([2000TAG/DIA], [1972WHI/LAN], [1951CON/MCV], [1953MAG/HUI]). Although third-, second- and first-degree polynomials were fitted to the $E^{\circ}(T)$ data, only the linear fit yielded an unambiguous slope. In addition, the value of the term $\int_{T_0}^{T}(\Delta_r C^o_{p,m}(T)/T)\mathrm{d}T$ is small when compared with the value of $\Delta_r S^o_m(T)$ (~ 2% for a 10 K temperature interval).

The straight lines of Figures VI-7 and VI-8 also indicate that this term plays a minor role in changes in the value of E^o with temperature.

So, assuming that $\Delta_r C^o_{p,m}(T)$ is constant in the range of temperatures 278.15 to 333.15 K does not change the slope of the function $E^o(T)$ = f(T) significantly.

Equations (VI.18) and (VI.19) are derived from Eq. (VI.16) for a constant value of $\Delta_r C^o_{p,m}(T)$

$$E^o(T) = -\Delta_r H^o_m/F + T\Delta_r S^o_m/F + (\Delta_r C^o_{p,m}/F)(T_0 - T) + T(\Delta_r C^o_{p,m}/F)\ln(T/T_0) \quad \text{(VI.18)}$$

$$E^o(T) - ((\Delta_r C^o_{p,m}/F)(T_0 - T) + T(\Delta_r C^o_{p,m}/F)\ln(T/T_0)) = -\Delta_r H^o_m/F + T\Delta_r S^o_m/F \quad \text{(VI.19)}$$

and Eq. (VI.17) gives Eq. (VI.20) for constant $\Delta_r C^o_{p,m}(T)$:

$$F\mathrm{d}E^o(T)/\mathrm{d}T = \Delta_r S^o_m + (\Delta_r C^o_{p,m}/F)\ln(T/T_0)\,. \quad \text{(VI.20)}$$

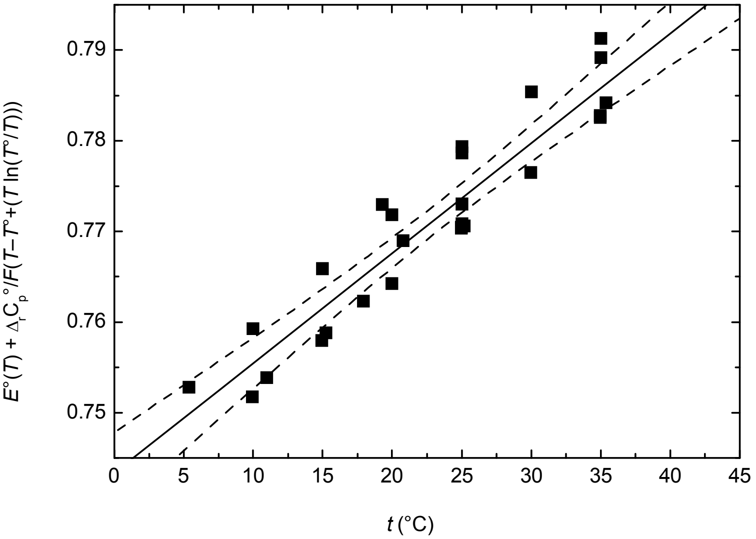
The slope of the function $E^o(T)$ − $(\Delta_r C^o_{p,m}/F)(T_0 - T)$ + $T(\Delta_r C^o_{p,m}/F)\ln(T/T_0)$ = f(t) gives the corrected value of $\mathrm{d}E^o(T)/\mathrm{d}T$ for a constant value of $\Delta_r C^o_{p,m}$ (VI.14). The plot of this function with $\Delta_r C^o_{p,m}(T)$ = 57.2 J·K^{-1}·mol^{-1} is shown in Figure VI-9. As for the plot of Figure VI-8 it is found that the slope is (1.21 ± 0.09) × 10^{-3} V·K^{-1}. The small uncertainty is quite in line with the approximation expressed by Eq. (VI.12) that introduces a limited slope correction of 9.6 × 10^{-6} V·K^{-1}. Even if the slope correction expressed by Eq. (VI.12) is an approximation, it has been preferred to the assumption of a linear relationship, as the large scatter of the $E^o(T)$ values from all the selected literature data does not allow any slope difference to be detected. So the value of 0.00122 V·K^{-1} was used to calculate the value of $\Delta_r S^o_m$ (VI.14) expressed by Eq. (VI.20).

That yields :

$$\Delta_r S^o_m \text{((VI.14), 298.15 K)} = (117.7 \pm 8.6)\ \text{J·K}^{-1}\text{·mol}^{-1}.$$

The $\Delta_r S^o_m$ ((VI.14), 298.15 K) values from the literature determined by $E^o(T)$ measurements are listed in Table VI-6, and are compared with the results of SIT calculations, using the SIT$_2$ formulation as carried out in this review. The $\Delta_r H^o_m$ ((VI.14), 298.15 K) values, which can be deduced from these $\Delta_r S^o_m$ ((VI.14), 298.15 K) values, are also listed with the corresponding values of $\Delta_r G^o_m$ ((VI.14), 298.15 K).

Figure VI-9: Plot of the selected $E^{\circ}(T)$ values corrected according to Eq. (VI.19) for $\Delta_{r}S^{\circ}_{m}$ (VI.14) determination. $\Delta_{r}C^{\circ}_{p,m}$ (VI.14) = 57.2 J·K^{-1}·mol^{-1}.



Whittemore and Langmuir [1972WHI/LAN] established an empirical second-degree equation $E^{\circ\prime}_{T}$ = f(T) from their experimental results, and used the approximation that $\Delta_{r}C^{\circ}_{p,m}$ (VI.14) = 0. Parker and Khodakovskii [1995PAR/KHO] recalculated the thermodynamic values by introducing the $\Delta_{r}C^{\circ}_{p,m}$ (VI.14) values determined from the results of Hovey for 298.15 K [1988HOV]. They also used a linear equation $E^{\circ\prime}_{T} = A + BT$ instead of the equation of Whittemore and Langmuir.

More details of the calculations to obtain values of $\Delta_{r}S^{\circ}_{m}$ (VI.14) and $\Delta_{r}H^{\circ}_{m}$ (VI.14) are given in the Appendix A entries.

Table VI-6: Values of $\Delta_rG^\circ_m$, $\Delta_rH^\circ_m$, and $\Delta_rS^\circ_m$ for Reaction (VI.14) from electrochemical data as a function of the calculation mode.

Original data	Calculation mode	$\Delta_rG^\circ_m$ / kJ·mol^{-1}	$\Delta_rH^\circ_m$ / kJ·mol^{-1}	$\Delta_rS^\circ_m$ / J·K^{-1}·mol^{-1}
[2000TAG/DIA] original paper	Adjustment of the Debye-Hückel parameters. Use of Eq. (VI.16) and constant $\Delta_rC^\circ_{p,m}$ = 62.09 J·K^{-1}·mol^{-1}.	− 74.266 ± 0.167	− 39.34 ± 1.88	117.15 ± 6.27
[2000TAG/DIA]	Original $E^{\circ\prime}$ used with calculation process*	− 74.266 ± 0.167	− 38.51 ± 4.56	119.9 ± 15.3
[2000TAG/DIA]	Tagirov E°_0, SIT$_2$ and dE/dT	− 74.266 ± 0.167	− 39.46 ± 2.57	116.75 ± 8.59
[2000TAG/DIA]	SIT$_2$ E°_0 and dE/dT	− 74.73 ± 0.30	− 39.92 ± 2.57	116.75 ± 8.59
[1972WHI/LAN] original paper	Adjustment of the Debye-Hückel parameters. Use of the second-degree empirical function $E^\circ_T = A + BT + CT^2$, $\Delta_rC^\circ_p = 0$	− 74.266 ± 0.167	− 42.58 ± 1.88	106.27 ± 6.28
[1972WHI/LAN] corrected by [1995PAR/KHO]	Use of $E^\circ_T = A + BT$, $\Delta_rC^\circ_{p,m}$ = 62.09 J·K^{-1}·mol^{-1}	− 74.266 ± 0.167	−42.75 ± 1.52	105.70 ± 5.06
[1972WHI/LAN]	E° (T) from SIT$_2$	− 75.32 ± 0.33	− 40.51 ± 2.58	116.75 ± 8.59
[1951CON/MCV]	E° = f(T) by SIT$_2$ Use of Eq. (VI.16)	− 74.61 ± 0.19	− 39.80 ± 2.57	116.75 ± 8.59
[1953MAG/HUI]	E° = f(T) by SIT$_2$ Use of Eq. (VI.16)	− 74.73 ± 0.19	− 39.92 ± 2.57	116.75 ± 8.59
Present work	Use of all selected literature data and SIT$_2$	− 74.49 ± 0.19	− 39.39 ± 2.57	117.7 ± 8.6

* Taking the $E^{\circ\prime}$ (t) values of Tagirov *et al.* and first fit by a third-degree polynomial; then applying Eq. (VI.16).

VI.1.2.4 Recommended thermodynamic quantity values based on measurements of the Fe^{3+}/Fe^{2+} couple

Two values of E°_0(Fe^{3+}/Fe^{2+}) have been proposed from the SIT treatments of the selected literature data (paragraph VI.1.2.1.1) ((0.775 ± 0.005) V for SIT$_1$ and (0.772 ± 0.002) V for SIT$_2$). With these values one gets

$$\Delta_rG^\circ_m\,(\text{VI.14}) = -\,(74.78 \pm 0.48)\ \text{kJ·mol}^{-1}\ (\text{SIT}_1)$$

$$\Delta_rG^\circ_m\,(\text{VI.14}) = -\,(74.49 \pm 0.19)\ \text{kJ·mol}^{-1}\ (\text{SIT}_2)$$

The value of $\Delta_r S_m^o$ deduced from the slope dE_T^o / dT of the function $E_T^o = f(T)$ treated by SIT_2 is:

$$\Delta_r S_m^o \text{ (VI.14)} = (117.7 \pm 8.6)\ J \cdot K^{-1} \cdot mol^{-1}.$$

It appears that the SIT method leads to values of the thermodynamic constants in the range indicated previously in the literature. The estimated uncertainties are greater than those published in earlier compilations [1995PAR/KHO], but seem reasonable in view of the lack of data for the Fe^{3+} SIT interaction coefficients required for consistent extrapolation to non-zero solute concentrations at temperatures other than 298.15 K.

VI.1.2.5 E^o (Fe^{3+}/Fe^{2+}) from redox equilibria

Values of E^o (Fe^{3+}/Fe^{2+}) also have been derived from redox equilibria between the couples Fe^{3+}/Fe^{2+} and $Ag^+/Ag(0)$ or $Hg_2^{2+}/Hg(0)$. Unlike the same kind of investigations with the $Fe^{2+}/Fe(0)$ couple, which led to rather large discrepancies, these values agree within a few millivolts of those found by potential-difference measurements. One main reason is probably the reversibility of the Fe^{3+}/Fe^{2+} couple, and also the availability of couples that have E^o values close to E^o (Fe^{3+}/Fe^{2+}). Within these conditions the equilibrium constant can be determined precisely, because it does not depart too much from a value of 1, and equilibrium is reached more rapidly. Also, only one solid, Ag(s), is involved in the redox equilibrium, and problems such as the effect of the extent of division of the solid are less crucial than in the equilibrium between Fe(0) and Tl^+ used to assess the value of E^o ($Fe^{2+}/Fe(0)$).

The main data sources in the literature are the papers of Noyes and Brann [1912NOY/BRA], Popoff *et al.* [1931POP/FLE], and Fleharty [1933FLE], which contain experimental data for Reactions (VI.21) and (VI.22) in aqueous solutions of $HClO_4$ for mercury and in aqueous solutions of HNO_3 for silver:

$$2\ Fe^{3+} + 2\ Hg(l) \rightleftharpoons 2\ Fe^{2+} + Hg_2^{2+} \quad \text{(VI.21)}$$

$$Fe^{3+} + Ag(s) \rightleftharpoons Fe^{2+} + Ag^+ \quad \text{(VI.22)}$$

The E^o (Fe^{3+}/Fe^{2+}) values reported by these authors are rather different from the values accepted in more recent assessments. Bray and Hershey [1934BRA/HER] recalculated the standard potentials based on the original experimental data. They took into account the hydrolysis of Fe^{3+} and used a better method for extrapolation of the results to zero ionic strength. With all these considerations, they concluded that the E^o (Fe^{3+}/Fe^{2+}) standard potential has a value of (0.772 ± 0.001) V instead of 0.7473 V.

The SIT formulation and the auxiliary thermodynamic values used in the TDB project were used to redetermine E^o (Fe^{3+}/Fe^{2+}) values based on the experimental results of Noyes and Brann [1912NOY/BRA] and Popoff *et al.* [1931POP/FLE]. Hydrolysis was taken into account as described above. The values of K^o for Reactions

(VI.21) and (VI.22) are required. We followed two procedures:

1) attempted determination of K^{o} by using the values of K_m and equations from Appendix B to calculate the activity coefficients of Fe^{3+}, Fe^{2+}, Hg_2^{2+} and Ag^{+}. That led to several values of K^{o} and their average was calculated.

2) attempted determination of K^{o} by plotting $\log_{10} K_m - \Delta z^2 D$ as a function of I_m and extrapolation to $I = 0$.

For the work of Noyes and Brann we selected the most acidic samples in order to limit the influence of the hydrolysis corrections. The first method led to "K^{o}" values that still appeared to have a residual dependence on I_m. A straight line then was fitted to a plot of these supposed "K^{o}" values against $I_m^{1/2}$, and $K^{\mathrm{o}} = (0.336 \pm 0.064)\ \mathrm{mol\cdot kg^{-1}}$ was found for $I = 0$; thus, E^{o} (Fe^{3+}/Fe^{2+}) = (0.771 ± 0.005) V.

The (procedure 2) standard linear fit to $\log_{10} K_m + 4D$ as a function of I_m yielded E^{o} (Fe^{3+}/Fe^{2+}) = (0.776 ± 0.003) V.

For the work of Popoff and Kunz carried out in perchlorate medium, the two SIT methods of calculation (see Section VI.1.2.1.1.1) were applied for procedure 1. They both led to a cluster of points; the points for each acidity giving distinctive curves. That could be due to partial disproportionation or hydrolysis of the Hg_2^{2+} ions at the higher pH values, so we have based our results only on the more acidic samples.

The results are collected in Table VI-7. It can be seen that there are no significant differences between the values of the standard potentials determined by potential-difference measurements and chemical equilibria. The average of the E^{o} values derived from treatment of the data for the redox reactions carried out in perchlorate medium using the Hg_2^{2+}/Hg(l) redox couple seem to be of comparable quality to the values used above in obtaining the recommended value of the standard potential. The rounded average of the values yielded by the SIT treatments of these redox studies is (0.772 ± 0.004) V (*i.e.*, $\Delta_r G_m^{\mathrm{o}} = -(74.49 \pm 0.38)\ \mathrm{kJ\cdot mol^{-1}}$). This value, which is in excellent agreement with the potential-difference results, (0.775 ± 0.005) V (SIT_1) and (0.772 ± 0.002) V (SIT_2), and with results in earlier tabulations, is used as part of the final data evaluations (Chapter XI).

The SIT treatments of the results of Noyes and Brann [1912NOY/BRA] are less convincing because of the high concentrations of metallic salts in nitrate medium, because the interaction coefficients are less well documented. The results obtained from the experiments in nitrate media were not included in the final data evaluation.

Table VI-7: Results for the E° (Fe^{3+}/Fe^{2+}) standard potential values from chemical redox equilibria based on the experimental measurements of [1912NOY/BRA] and [1931POP/FLE] at 298.15 K.

Reference	E° (Fe^{3+}/Fe^{2+})/V
$Fe^{3+} + Ag(s) \rightleftharpoons Fe^{2+} + Ag^+$ in HNO_3 medium	
[1912NOY/BRA], original paper	E° (Fe^{3+}/Fe^{2+}) = E° ($Ag^+/Ag(s)$)* − 0.053 V = 0.746 V
[1912NOY/BRA], reinterpreted by [1934BRA/HER]	E° (Fe^{3+}/Fe^{2+}) = E° ($Ag^+/Ag(s)$) − (0.026 ± 0.001) V = (0.7725 ± 0.0010) V
[1912NOY/BRA], SIT, $\gamma_{M^{z+}}$ as a function of $[NO_3^-]^-$	E° (Fe^{3+}/Fe^{2+}) = E° ($Ag^+/Ag(s)$) − (0.028 ± 0.005) V = (0.771 ± 0.005) V
[1912NOY/BRA], SIT, $\log_{10}K_m + 4D$ as a function of I_m	E° (Fe^{3+}/Fe^{2+}) = E° ($Ag^+/Ag(s)$) − (0.0231 ± 0.0014) V = (0.776 ± 0.003) V
$2\,Fe^{3+} + 2\,Hg(l) \rightleftharpoons 2\,Fe^{2+} + Hg_2^{2+}$ in $HClO_4$ medium	
[1931POP/FLE], original paper	E° (Fe^{3+}/Fe^{2+}) = E° ($Hg_2^{2+}/Hg(l)$)* − 0.0516 V = 0.7480 V
[1931POP/FLE], reinterpreted by [1934BRA/HER]	E° (Fe^{3+}/Fe^{2+}) = E° ($Hg_2^{2+}/Hg(l)$) − (0.0262 ± 0.001) V = (0.7713 ± 0.0010) V
[1931POP/FLE], SIT_1, $\gamma_{M^{z+}}$ as a function of $[ClO_4^-]$	E° (Fe^{3+}/Fe^{2+}) = E° ($Hg_2^{2+}/Hg(l)$) − (0.0235 ± 0.0010) V = (0.7723 ± 0.0044) V
[1931POP/FLE], SIT_2, $\gamma_{M^{z+}}$ as a function of $[ClO_4^-]$	E° (Fe^{3+}/Fe^{2+}) = E° ($Hg_2^{2+}/Hg(l)$) − (0.0241 ± 0.0010) V = (0.7717 ± 0.0042 V)
[1931POP/FLE], SIT, K_m as a function of I_m acidities: 0.02, 0.01, 0.005, 0.0020, 0.001 M	E° (Fe^{3+}/Fe^{2+}) = E° ($Hg_2^{2+}/Hg(l)$) − (0.0229 ± 0.0030) V = (0.773 ± 0.004 V)

* Standard potentials calculated from the NEA TDB recommended $\Delta_f G_m^{\circ}$ values for the Ag^+ and Hg_2^{2+} aqueous ions: E° ($Ag^+/Ag(s)$) = (0.7990 ± 0.0016) V and $\Delta_f G_m^{\circ}$ (Ag^+) = (77.096 ± 0.156) kJ·mol^{-1}; E° ($Hg_2^{2+}/Hg(l)$) = (0.7958 ± 0.0029) V and $\Delta_f G_m^{\circ}$ (Hg_2^{2+}) = (153.567 ± 0.559) kJ·mol^{-1}.

VI.1.3 Conclusions

After evaluation of the available cycles for iron species and optimization to ensure consistency with other thermodynamic quantities for iron species (Chapter XI), the value $\Delta_{red}G_m^{\circ}$ (Fe(II), 298.15 K) equal to $-\Delta_f G_m^{\circ}$ (Fe^{2+}, 298.15 K) is calculated to be (90.72 ± 0.64) kJ·mol^{-1}, in agreement with the original assessed value. The consistent optimized values of $\Delta_f H_m^{\circ}$ (Fe^{2+}, 298.15 K) and $\Delta_f G_m^{\circ}$ (Fe^{2+}, 298.15 K) are:

$$\Delta_f H_m^{\circ}(\mathrm{Fe^{2+}}, 298.15\ \mathrm{K}) = -(90.29 \pm 0.52)\ \mathrm{kJ\cdot mol^{-1}}$$

and

$$\Delta_f G_m^{\circ}(\mathrm{Fe^{2+}}, 298.15\ \mathrm{K}) = -(90.72 \pm 0.64)\ \mathrm{kJ\cdot mol^{-1}}.$$

After the same evaluation (Chapter XI), the value of $\Delta_{\mathrm{red}}G^{\circ}_{\mathrm{m}}$ (Fe(III), 298.15 K) consistent with the optimized value for $\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}$ ($\mathrm{Fe^{3+}}$, 298.15 K) is calculated to be – (74.49 ± 0.91) $\mathrm{kJ \cdot mol^{-1}}$ and the consistent value of $\Delta_{\mathrm{red}}S^{\circ}_{\mathrm{m}}$ (Fe(III), 298.15 K) is calculated to be (114.9 ± 4.8) $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ which is in moderately good agreement with the original assessed value of (117.7 ± 8.6) $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$.

From these,

$$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}\,(\mathrm{Fe^{3+}},\ 298.15\ \mathrm{K}) = -\,(50.06 \pm 0.97)\ \mathrm{kJ \cdot mol^{-1}}$$

and

$$\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}\,(\mathrm{Fe^{3+}},\ 298.15\ \mathrm{K}) = -\,(16.23 \pm 0.65)\ \mathrm{kJ \cdot mol^{-1}}.$$

VI.2 Partial molar heat capacities

Hovey [1988HOV] reported apparent molar heat capacity measurements for $\mathrm{Fe(ClO_4)_3}$ and $\mathrm{Fe(ClO_4)_2}$ in aqueous $\mathrm{HClO_4}$ solutions for temperatures between 283.15 and 328.15 K. As expected, the apparent molar heat capacity values depend strongly on the salt molalities, and the partial molar heat capacity values are strongly temperature dependent. The extrapolations of the electrolyte apparent molar heat capacities to $I = 0$ by the author are accepted. Thus, the value of $C^{\circ}_{p,\mathrm{m}}$ ($\mathrm{Fe(ClO_4)_3}$, aq, ∞, 298.15 K) is – 77.62 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ and the value of $C^{\circ}_{p,\mathrm{m}}$ ($\mathrm{Fe(ClO_4)_2}$, aq, ∞, 298.15 K) is – 187.0 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$.

As discussed for the case of $\mathrm{Ni^{2+}}$ [2005GAM/BUG], calculations of values for $C^{\circ}_{p,\mathrm{m}}$ ($\mathrm{Fe^{2+}}$, 298.15 K) and $C^{\circ}_{p,\mathrm{m}}$ ($\mathrm{Fe^{3+}}$, 298.15 K) require a value for $C^{\circ}_{p,\mathrm{m}}$ ($\mathrm{HClO_4}$, aq, ∞, 298.15 K).

$C^{\circ}_{p,\mathrm{m}}$ (Fe^{x+}, 298.15 K) = $C^{\circ}_{p,\mathrm{m}}$ ($\mathrm{Fe(ClO_4)}_x$, aq, ∞, 298.15 K) $-\,x$ $C^{\circ}_{p,\mathrm{m}}$ ($\mathrm{HClO_4}$, aq, ∞, 298.15 K),

with the convention that $C^{\circ}_{p,\mathrm{m}}$ ($\mathrm{H^+}$, T) ≡ 0.

The original analysis by Hovey [1988HOV] used a value of – 25.2 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ for the partial molar heat capacity of $\mathrm{HClO_4}$(aq, ∞). Reanalysis and comparison of the apparent molar heat capacity data for $\mathrm{HClO_4}$ are not within the scope of the present review, and $C^{\circ}_{p,\mathrm{m}}$ ($\mathrm{HClO_4}$, aq, ∞, 298.15 K) = – 26.3 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ from Oakes and Rai [2001OAK/RAI] (based on the experimental work of Hovey and Hepler [1989HOV/HEP], and Lemire and Campbell [1996LEM/CAM2]) has been used.

From these, – (25.0 ± 10.0) $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ is calculated for $C^{\circ}_{p,\mathrm{m}}$ ($\mathrm{Fe^{2+}}$, 298.15 K) and – (108.1 ± 20.0) $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ for $C^{\circ}_{p,\mathrm{m}}$ ($\mathrm{Fe^{3+}}$, 298.15 K), where the uncertainties have been estimated in the present review. Bernarducci *et al.* [1979BER/MOR] measured heats of dilution of 4.43 m $\mathrm{FeCl_2}$(sln) at 288.15, 298.15 and 303.15 K. A value of $C^{\circ}_{p,\mathrm{m}}$ ($\mathrm{FeCl_2}$, aq, ∞, 298.15 K) = – (256 ± 30) $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ was obtained and, from this, using $C^{\circ}_{p,\mathrm{m}}$ (HCl, aq, ∞, 298.15 K) = – 123.2 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ from Patterson *et* *al.* [2002PAT/WOO], $-(9 \pm 30)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ can be calculated for $C^{\circ}_{p,\text{m}}$ (Fe^{2+}, 298.15 K). The results are in marginal agreement.

The selected values are

$$C^{\circ}_{p,\text{m}}(\text{Fe}^{2+}, 298.15\ \text{K}) = -(23 \pm 10)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}, \text{ and}$$

$$C^{\circ}_{p,\text{m}}(\text{Fe}^{3+}, 298.15\ \text{K}) = -(108 \pm 20)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

VI.3 Peroxide oxidation of Fe^{2+} and Fe(cr)

VI.3.1 Heat of reaction of H_2O_2(aq) with Fe^{2+}

There have been several studies in which the heat of oxidation of Fe^{2+} to Fe^{3+} with aqueous peroxide

$$\text{Fe}^{2+} + \tfrac{1}{2}\,\text{H}_2\text{O}_2(\text{aq}) + \text{H}^+ \rightleftharpoons \text{Fe}^{3+} + \text{H}_2\text{O(l)} \qquad \text{(VI.23)}$$

has been reported, although Bewley [1960BEW] and Sousa-Alonsa *et al.* [1968SOU/CHA] found evidence for side reactions. As the primary interest has been to derive a value for the heat of formation of Fe^{3+} in the absence of hydrolysis, most measurements were carried out in moderately concentrated aqueous acid solutions. Results are summarized in Table VI-8.

Table VI-8: Enthalpy of Reaction (VI.23).

Reference	Aqueous medium (*m*)	Final iron (*m*)	Reaction enthalpy/kJ·mol^{-1}	
			reported	recalculated (I = 0)
[1934ROT/WIE]	17.3 HCl		– 136.5†	
[1949EVA/BAX]	1 $HClO_4$ @ + 0.1 sulfate	0.1	– 137	
[1958FON2]	0.51 $HClO_4$	0.0025	– 150.16 ± 1.00	– 151.2 ± 2.5
[1959KOE/COU]	4.36 HCl		– 131.18 ± 0.19#	
[1960BEW]	0.093 H_2SO_4	0.001	– 145.2 (– 149.5‡)	
	0.41 H_2SO_4	0.001	– 148.1 (– 148.5‡)	
[1968SOU/CHA]	0.05 H_2SO_4	0.0005	– 146.65	
	0.101 $HClO_4$	0.0005	– 145.60 ± 1.75	– 146.8 ± 2.0
[1970BER/TUM]	0.01 H_2SO_4	0.003 to 0.009	– 148.76	

@ Iron was added as the sulfate salt, 0.1 mol·L^{-1} sulfate in the final solution.

† Measured at 293.85 K.

\# Measured at 303.15 K.

‡ The value based on the first addition of iron(II) solution to the peroxide solution (see Appendix A).

As discussed in the Appendix A entries, none of the results can easily be corrected to calculate the value of the heat of the hypothetical oxidation reaction of Fe^{2+} to Fe^{3+} at $I = 0$. Studies of the enthalpy of dilution of highly charged unsymmetrical electrolytes in the absence of hydrolysis are sparse [1957LAN/MIE], [1996ARS/FER]. Further, in the case of the experiments carried out in sulfuric acid solutions, account needs to be taken of deprotonation of hydrogen sulfate and sulfate complexation/ association with the simple iron species. Therefore, the results in sulfuric acid are not used here. The two results in concentrated choride medium [1934ROT/WIE], [1959KOE/COU] were at temperatures other than 298.15 K.

The early result of Evans *et al.* [1949EVA/BAX] in perchloric acid appears to be inconsistent with the other results in similar media. The two other results in perchlorate medium, after extrapolation to $I = 0$ [1996PLY/GRE] (Appendix A), are only in marginal agreement. In the present review, for optimization calculations involving chemical thermodynamic quantities for iron species, we accept the simple average of these two results

$$\Delta_r H_m^\circ \text{ (VI.23)} = -(149.0 \pm 4.0)\ \text{kJ}\cdot\text{mol}^{-1},$$

where the uncertainty is an estimate.

After evaluation of the available cycles for iron species and optimization to ensure consistency with other thermodynamic quantities for iron species (Chapter XI), the consistent value of $\Delta_r H_m^\circ$ (VI.23) (*i.e.*, $\Delta_{ox} H(\text{Fe(II)})$ in tables in Chapter XI), is calculated to be $-(150.0 \pm 1.1)$ kJ·mol^{-1}, in good agreement with the original assessed value.

VI.3.2 Heat of reaction of H_2O_2(aq) with Fe(cr)

The heat of the oxidation of iron metal was measured by Vasil'ev *et al.* [1976VAS/RAS] in 1.05, 2.20, 3.47, and 4.87 mol·kg^{-1} $HClO_4$(sln) containing hydrogen peroxide (1.0 and 1.5 wt-%).

$$\text{Fe(cr)} + \tfrac{3}{2}\,H_2O_2\text{(aq)} + 3\,H^+ \rightleftharpoons Fe^{3+} + 3\,H_2O\text{(l)} \qquad \text{(VI.24)}$$

There are difficulties with the standard methods [1996PLY/GRE] for extrapolation of the experimental values to $I = 0$ (see Appendix A). Nevertheless, in the present review the value $\Delta_r H_m^\circ$ (VI.24) = $-(617.8 \pm 2.5)$ kJ·mol^{-1} is derived from the data of Vasil'ev *et al.* [1976VAS/RAS], and is used in the data optimization. The work of Vasil'ev *et al.* [1978VAS/VAS2] leads to a rather similar value, but the solutions used in that study contained sulfate in concentrations such that corrections for complexation would be required.

After evaluation of the available cycles for iron species and optimization to ensure consistency with other thermodynamic quantities for iron species (Chapter XI), the consistent value of $\Delta_r H_m^\circ$ (VI.24) (*i.e.*, $\Delta_{ox} H(\text{Fe,cr})$ in tables in Chapter XI), is calculated to be – (620.8 ± 1.0) kJ·mol^{-1}, in marginal agreement with the original assessed value.

VI.4 Interaction coefficients

VI.4.1 Aqueous iron(III) perchlorate

The value for $\varepsilon(\mathrm{Fe}^{3+}, \mathrm{ClO}_4^-)$ of (0.56 ± 0.03) kg·mol^{-1} at 298.15 K which was recommended in earlier TDB volumes is cited as having been derived by Ciavatta [1980CIA]. However, Ciavatta [1980CIA] refers to Biedermann [1975BIE] for this value, which in fact was based on the assumption that $\varepsilon(\mathrm{Fe}^{2+}, \mathrm{ClO}_4^-) = \varepsilon(\mathrm{Mg}^{2+}, \mathrm{ClO}_4^-) =$ 0.33 kg·mol^{-1} in a calculation of the E° value for the $\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}$ couple in [1937SCH/SHE].

It is apparent from the electrochemical data for the $\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}$ couple in perchlorate media, [1937SCH/SHE] and [2000TAG/DIA], at 298.15 K that the SIT yields a markedly non-linear dependence on the molality of perchlorate ion (*cf.* Section VI.1.2.1.1.1). Given that $\varepsilon(\mathrm{Fe}^{2+},\mathrm{Cl}^-)$ and $\varepsilon(\mathrm{M}^{2+}, \mathrm{ClO}_4^-)$ for the Fe^{2+} analogues show the conventional linear dependence over the same perchlorate concentration range, one must conclude that $\varepsilon(\mathrm{Fe}^{3+}, \mathrm{ClO}_4^-)$ is not independent of ionic strength. In keeping with this observation, the $\Delta\varepsilon$ for the first hydrolysis constant of Fe^{3+} is also nonlinear with respect to ionic strength in $\mathrm{NaClO_4}$ solutions, and this departure from linearity is most likely associated with the behaviour of $\varepsilon(\mathrm{Fe}^{3+}, \mathrm{ClO}_4^-)$ rather than that of $\varepsilon(\mathrm{FeOH}^{2+}, \mathrm{ClO}_4^-)$.

One approach to this problem is to consider analogous 3:1 electrolyte systems that are known to be less susceptible to hydrolysis. Examples are listed in Table VI-9 of $\varepsilon(\mathrm{M}^{3+}, \mathrm{ClO}_4^-)$ and $\varepsilon(\mathrm{M}^{3+},\mathrm{Cl}^-)$ values derived from application of the SIT to osmotic coefficient data limited to a total molality of unity, beyond which departures from linearity were observed. The chloride values and the differences between these coefficients are given for convenience here, and will be used in the discussion of the $\varepsilon(\mathrm{Fe}^{3+},\mathrm{Cl}^-)$ value. The order of M(III) in the table corresponds approximately to the ionic radii for the M^{3+} ions for six-fold coordination.

A first approximation would be to assign a conservative value of (0.5 ± 0.1) kg·mol^{-1} to $\varepsilon(\mathrm{Fe}^{3+}, \mathrm{ClO}_4^-)$ based on the values suggested for the small Al^{3+} and Ga^{3+} ions, but applying a broad uncertainty to cover the range of values listed in the Table VI-9. However, this value would not encompass any reasonable value derived from the electrochemical data for the $\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}$ couple (Section VI.1.2.1.1.1).

Based on the behaviour of the Fe(III)/Fe(II) potential in perchlorate medium, and assuming that $\varepsilon(\mathrm{Fe}^{2+}, \mathrm{ClO}_4^-) = (0.37 \pm 0.04)$ kg·mol^{-1} (Section VI.4.4), it has been found that using the $\mathrm{SIT_2}$ formulation (Section VI.1.2.1.1.1):

$$\varepsilon(\mathrm{Fe}^{3+}, \mathrm{ClO}_4^-) = ((0.78 \pm 0.05) - (0.41 \pm 0.05)\log_{10} I_m)\ \mathrm{kg\cdot mol^{-1}}.$$

The SIT_1 linear fit yields:

$$\varepsilon(\mathrm{Fe}^{3+}, \mathrm{ClO}_4^-) = (0.73 \pm 0.04)\ \mathrm{kg\cdot mol^{-1}}.$$

These values have been adopted in the present review.

Table VI-9: Interaction coefficients ($\mathrm{kg\cdot mol^{-1}}$) derived at 298.15 K for a series of 3:1 electrolytes arranged in order of increasing ionic radii.

M(III)	$\mathrm{M}^{3+}, \mathrm{ClO}_4^-$	$\mathrm{M}^{3+}, \mathrm{Cl}^-$	Diff.
Al	0.52 (d)	0.34 (b)	0.18
Cr		0.30 ± 0.03 (c)	
Fe		0.18 (a)	
Ga	0.50 (g)		
Lu	0.44 (e)	0.25 (f)	0.19
Gd	0.43 (e)	0.24 (f)	0.19
La	0.40 (e)	0.21 (f)	0.19

(a) See Section (VI.4.2).

(b) Analysis of osmotic data from [1941MAS], [1949ROB/STO], [1955HAR/GAR], [2002APE/KOR2] limited to $m_{\mathrm{AlCl_3}} < 1.1$. These papers are discussed in the corresponding Appendix A entries. The entries for [1999MOL/GON] and [2000RIC/BRA] discuss the reasons information in those two papers has not been used.

(c) NEA compilation, *e.g.* [2005GAM/BUG], from [1980CIA].

(d) Analysis of osmotic coefficient data from [1970KAL] limited to $m_{\mathrm{AlCl_3}} < 1.1$.

(e) Analysis of osmotic coefficient data from [1977RAR/WEB] limited to $m_{\mathrm{Ln(ClO_4)_3}} < 1.0$.

(f) Analysis of osmotic coefficient data from [1976SPE/WEB] limited to $m_{\mathrm{LnCl_3}} < 1.0$.

(g) Analysis of osmotic coefficient data from [1959ROB/STO] limited to $m_{\mathrm{Ga(ClO_4)_3}} < 1.0$.

VI.4.2 Aqueous iron(III) chloride

VI.4.2.1 Evaluation from analogy and osmotic data

Due to the complexities of hydrolysis and ion association in the iron(III) chloride system, this review first considers the possibility of using surrogate cations which are less prone to hydrolysis and complex formation with chloride ions than the Fe^{3+} ion.

Second, the conventional approach of using isopiestic and vapour-pressure measurements to derive the osmotic coefficients of $FeCl_3$ solutions is considered, although such data do not provide a useful route to deriving the corresponding ion interaction coefficients. A recent isopiestic study by Rumyantsev *et al.* (2004) [2004RUM/HAG] using four standard solutions, H_2SO_4 [1976RAR/HAB], $CaCl_2$ [1997RAR/CLE], NaCl [1985CLA/GLE] and KCl [1999ARC2] at 298.15 K was carried out to 1.676 $\mathrm{mol \cdot kg^{-1}}$. Comparisons were made of the calculated osmotic coefficients for these standards derived from these references with the tabulated values given in the earlier NEA reviews. The differences were mainly within the combined uncertainties of these smoothed data. Rumyantsev *et al.* did observe loss of HCl at higher concentrations of iron(III) chloride that limited the total concentration that could be attained. No attempt was made by these authors to correct for hydrolysis of Fe^{3+}.

The results of two earlier studies of the vapour pressure of iron(III) chloride solutions with no added HCl at 298.15 K [1956GRO], [1963SUS/PRO], which extended to high concentrations of 15.80 and 4.827 $\mathrm{mol \cdot kg^{-1}}$, respectively, have been recalculated in this review. However, only the data below 1.8 $\mathrm{mol \cdot kg^{-1}}$ were considered in the treatment to derive a value for $\varepsilon(\mathrm{Fe^{3+},Cl^-})$.

The general Eq. (B.11) for the dependence of the osmotic coefficient on the molality of $FeCl_3$ is as follows:

$$\begin{aligned}1-\phi &= \frac{A\ln(10)|z_+z_-|}{I_m\left(Ba_j\right)^3}\left[1+Ba_j\sqrt{I_m}-2\ln\left(1+Ba_j\sqrt{I_m}\right)-\frac{1}{\left(1+Ba_j\sqrt{I_m}\right)}\right]\\ &+\left(\frac{\nu_+\nu_-}{\nu_++\nu_-}\right)\ln(10)\varepsilon(\mathrm{N,X})m_{NX}\end{aligned} \qquad \text{(VI.25)}$$

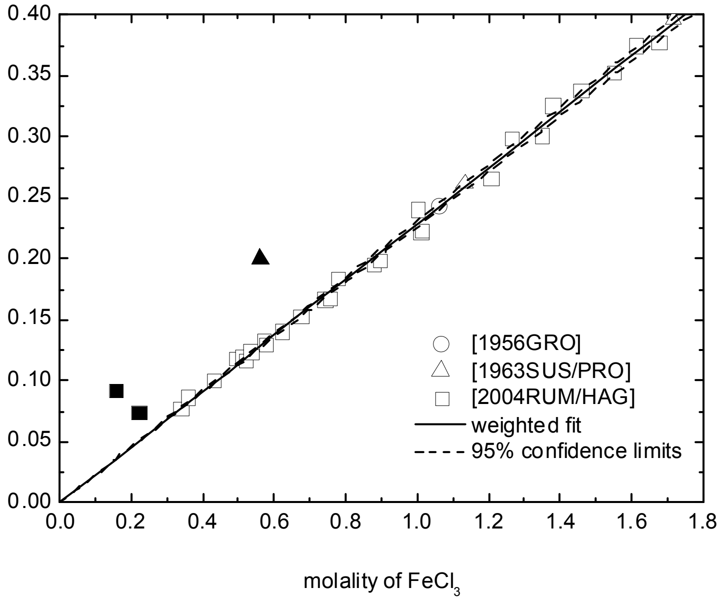
It follows for $FeCl_3$ at 298.15 K,

$$\begin{aligned}1-\phi-\frac{3.516}{I_m(3.375)}\left[1+1.5\sqrt{I_m}-2\ln(1+1.5\sqrt{I_m})-\frac{1}{\left(1+1.5\sqrt{I_m}\right)}\right]\\ =1.727\varepsilon(\mathrm{Fe^{3+},Cl^-})m_{\mathrm{FeCl_3}}\end{aligned} \qquad \text{(VI.26)}$$

The plot of the LHS of Eq. (VI.26) *vs.* $m_{\mathrm{FeCl_3}}$ is shown in Figure VI-10, where the three solid symbols represent outliers that were ignored in the linear regression. From the slope of this weighted plot, $\varepsilon(\mathrm{Fe^{3+},Cl^-})$ = (0.133 ± 0.004) (2σ) $\mathrm{kg \cdot mol^{-1}}$ without any consideration of chloride complexation of Fe^{3+}, or of hydrolysis or polymerization. The unweighted fit gave an identical slope. The NEA recommended values for $\varepsilon(\mathrm{Al^{3+},Cl^-})$ and $\varepsilon(\mathrm{Cr^{3+},Cl^-})$ are (0.33 ± 0.02) and (0.30 ± 0.03) $\mathrm{kg \cdot mol^{-1}}$, respectively, where the former should not be affected by either hydrolysis or specific chloride interactions.

Figure VI-11 shows the osmotic coefficient as a function of the $FeCl_3$ molality indicating that Eq. (VI.26) effectively represents the data from [1956GRO] and [1963SUS/PRO] to at least 3.5 $mol \cdot kg^{-1}$ (or a stoichiometric ionic strength of 21). Apelblat and Korin [2002APE/KOR], who claim to have carried out vapour-pressure measurements of saturated $FeCl_3$ solutions from 278.15 to 323.15 K, cite a solubility limit for anhydrous $FeCl_3$ of 5.90 $mol \cdot kg^{-1}$ at 298.15 K, and comment that the higher concentrations reported by [1962KAN/GRO], *i.e.*, by [1956GRO], involved either supersaturated $FeCl_3$ solutions and/or the formation of possibly four solid hydrates. However, the osmotic coefficient of 2.73 reported by Apelblat and Korin [2002APE/KOR] corresponding to an assumed 5.90 $mol \cdot kg^{-1}$ solution at 298.15 K is far higher than seems reasonable from the results depicted in Figure VI-11.

Figure VI-10: The dependence of the (negative) LHS terms in Eq. (VI.26) on the molality of iron(III) chloride at 298.15 K showing the weighted fit to the three data sets shown in the legend with the solid symbols representing values which are distinct outliers and were therefore not included in the regression. The solid line was calculated from the above equation with $\varepsilon(Fe^{3+},Cl^{-}) = (0.133 \pm 0.002)$ (2σ) $kg \cdot mol^{-1}$.



However, the osmotic data can also be analyzed by acknowledging that there is association between Fe^{3+} and Cl^{-}. The optimized values, determined in a way similar to those for iron(II) chloride (see the Appendix A entry for [2004MOO/HAG]), are

$$\log_{10} \beta_1^{\circ} (\text{FeCl}^{2+}, 298.15\ \text{K}) = (1.38 \pm 0.02)$$

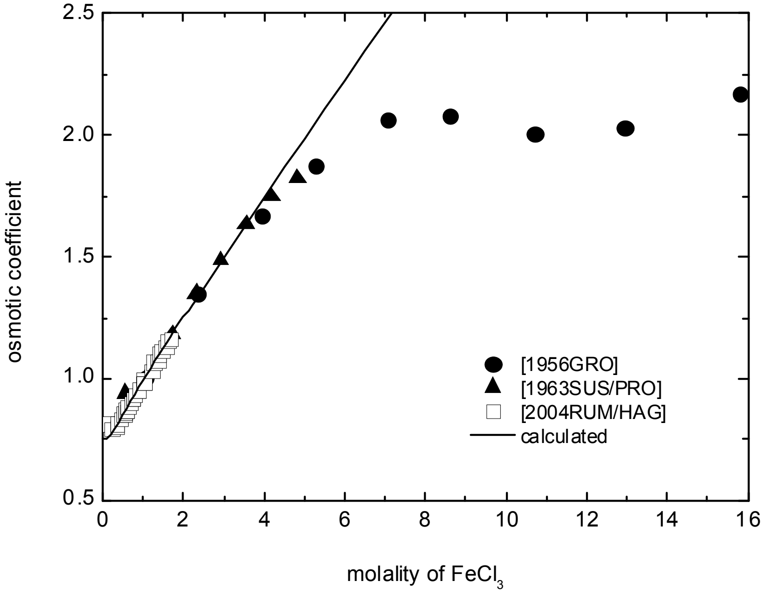
$$\varepsilon(\text{FeCl}^{2+},\text{Cl}^-) = (0.27 \pm 0.01)\ \text{kg}\cdot\text{mol}^{-1}$$

$$\varepsilon(\text{Fe}^{3+},\text{Cl}^-) = (0.50 \pm 0.10)\ \text{kg}\cdot\text{mol}^{-1}$$

and therefore,

$$\Delta\varepsilon = \varepsilon(\text{FeCl}^{2+},\text{Cl}^-) - \varepsilon(\text{Fe}^{3+},\text{Cl}^-) = -\ 0.23\ \text{kg}\cdot\text{mol}^{-1}.$$

Figure VI-11: The osmotic coefficients of iron(III) chloride solutions at 298.15 K are shown as a function of molality.



These values are similar to those derived from analysis of data on the complexation of Fe^{3+} with Cl^- (Section VIII.2.3) and the analysis of data on the electrochemical reduction of Fe^{3+} to Fe^{2+} (Section VI.1.2.1). However, both hydrolysis and the effect of formation of iron(III) species containing more than one chloride ion have been neglected.

VI.4.2.2 Evaluation from electrochemical data

As discussed in Section VIII.2.2.1, the value for the formation constant β_1° for the weak iron(II) chlorido complex, FeCl^+, at 298.15 K has a high uncertainty, and indeed, no value has been selected in the present review. For the electrochemical Fe(III)/Fe(II) data, fits have been carried out corresponding to two cases (a) $\log_{10} \beta_1^{\circ} = -\ 1.0$, as recommended in this review (~ 2% $FeCl^+$ in 1.05 m HCl) and (b) $\log_{10} \beta_1^{\circ} = -\ 0.11$, as suggested by the study of Heinrich and Seward [1990HEI/SEW] (~ 10% $FeCl^+$ in 1.05 m HCl).

With (0.17 ± 0.01) $kg \cdot mol^{-1}$ for the $\varepsilon(Fe^{2+},Cl^-)$ value one gets for SIT_1: $\varepsilon(Fe^{2+},Cl^-) - \varepsilon(Fe^{3+},Cl^-) = -(0.59 \pm 0.02)\ kg \cdot mol^{-1}$ (Section VI.1.2.1.1.2) which yields after rounding and estimation of the error:

$$\varepsilon(Fe^{3+},Cl^-) = (0.76 \pm 0.03)\ kg \cdot mol^{-1}\ (SIT_1)\ \ \text{(cases a and b).}$$

When SIT_1 analyses are applied to the data of Popoff and Kunz [1929POP/KUN] for cases a and b, no significant differences are found in the calculated E° and $\varepsilon(Fe^{3+},Cl^-)$ values.

For SIT_2 ($\varepsilon(Fe^{3+},Cl^-) = \varepsilon_1 + \varepsilon_2 \log_{10} I_m$, *cf.* Appendix B):

- case a: $\varepsilon(Fe^{2+},Cl^-) - \varepsilon_1(Fe^{3+},Cl^-) = -(0.67 \pm 0.01)\ kg \cdot mol^{-1}$

  $\varepsilon_2(Fe^{3+},Cl^-) = -(0.59 \pm 0.06)\ kg \cdot mol^{-1}$

After rounding and estimation of the error:

$$\varepsilon(Fe^{3+},Cl^-) = ((0.84 \pm 0.04) - (0.59 \pm 0.06) \log_{10} I_m)\ kg \cdot mol^{-1}\ (SIT_2)$$

- case b: $\varepsilon(Fe^{2+},Cl^-) - \varepsilon_1(Fe^{3+},Cl^-) = -(0.61 \pm 0.01)\ kg \cdot mol^{-1}$

  $\varepsilon_2(Fe^{3+},Cl^-) = -(0.50 \pm 0.03)\ kg \cdot mol^{-1}.$

After rounding and estimation of the uncertainty:

$$\varepsilon(Fe^{3+},Cl^-) = ((0.78 \pm 0.04) - (0.50 \pm 0.05) \log_{10} I_m)\ kg \cdot mol^{-1}.$$

The two SIT_2 analyses (cases a and b) lead to the same values of E°, but values for $\varepsilon_1(Fe^{3+},Cl^-)$ and $\varepsilon_2(Fe^{3+},Cl^-)$ that overlap only marginally. This illustrates the influence of association between Fe^{2+} and Cl^-, which is more important at high chloride concentrations. For the two trial $\log_{10} \beta_1^{\circ}$ values used here, – 1.0 and – 0.11 (cases a and b), the SIT_1 analyses did not show any difference in $\varepsilon(Fe^{3+},Cl^-)$.

In the present review, for consistency, the ε values based on the electrochemical measurements and the associated case (a) calculations have been adopted.

$$\varepsilon(Fe^{3+},Cl^-) = (0.76 \pm 0.03)\ kg \cdot mol^{-1}\ (SIT_1)$$

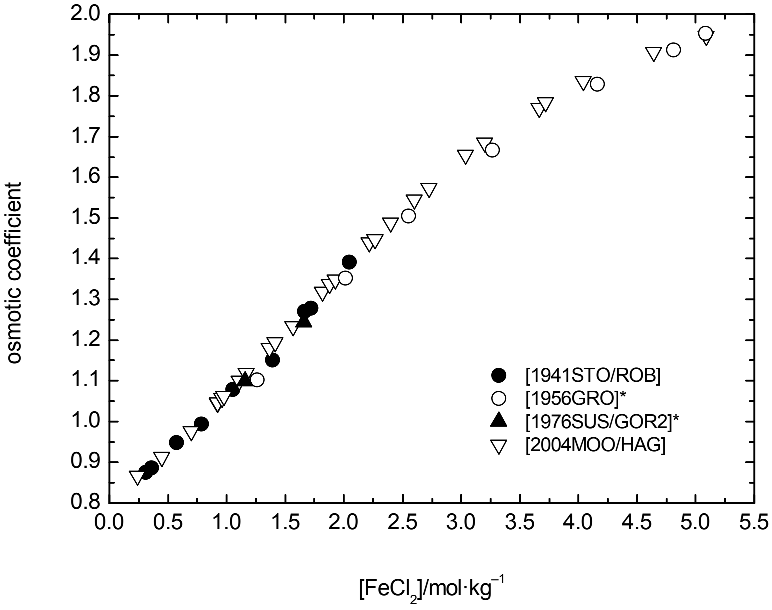
$$\varepsilon(Fe^{3+},Cl^-) = ((0.84 \pm 0.04) - (0.59 \pm 0.06) \log_{10} I_m)\ kg \cdot mol^{-1}\ (SIT_2)$$

VI.4.3 Aqueous iron(II) chloride

Goldberg *et al.* [1979GOL/NUT] carried out a critical assessment of the available vapour-pressure data for iron(II) chloride solutions citing two studies, *viz.*, [1941STO/ROB] and [1962KAN/GRO], whereby they rejected the latter results which were in fact smoothed data taken from the thesis of Groenveld [1956GRO] in which the experimental results are given. The synopsis given in Appendix A illustrates that the Goldberg *et al.* model provides a reasonable fit to all the currently available osmotic coefficient data, but is obsolete because of the abundant newer data contained in [2004MOO/HAG].

The isopiestic data of Stokes and Robinson [1941STO/ROB] were refitted by Stokes [1948STO], Guggenheim and Stokes [1958GUG/STO] and again recently by Moog *et al.* [2004MOO/HAG] using their own recent osmotic coefficient data for the standard NaCl solution used by Stokes and Robinson. These recalculated values and those of Moog *et al.* are all used by this review. The [1956GRO] and [1976SUS/GOR2] data were recalculated with different values being found than were reported in [2004MOO/HAG] and are tabulated in the individual synopses in Appendix A. The combined data set is shown in Figure VI-12.

Figure VI-12: Summary of the osmotic coefficient data *vs.* molality of $FeCl_2$ at 298.15 K where the asterisk denotes sets of values recalculated in the present review; these values differ from the recalculated values reported in [2004MOO/HAG].



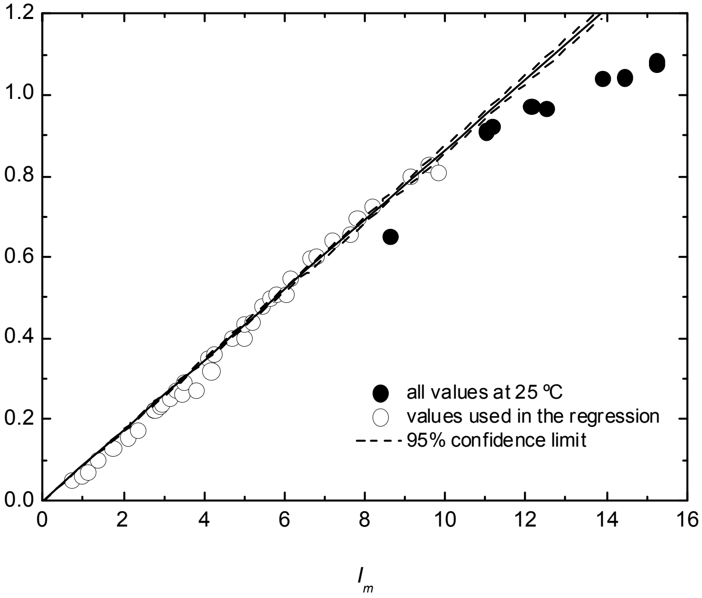
From the carefully compiled data set of [2004MOO/HAG], which includes their own and previous isopiestic and vapour-pressure measurements, Figure VI-13 was constructed of the combined data set of y *vs.* I_m where,

$$y = \phi - 1 + \frac{2A\ln(10)}{1.5^3 I_m}\left[1 + 1.5\sqrt{I_m} - \frac{1}{1.5\sqrt{I_m}} - 2\ln\left(1 + 1.5\sqrt{I_m}\right)\right] \tag{VI.27}$$

such that the slope = $\frac{2\ln(10)}{9}\varepsilon(\mathrm{Fe}^{2+},\mathrm{Cl}^-)$.

There is a clear departure from linearity above an ionic strength, I_m, of 10 such that the higher values were not included in the regression, as well as one erroneous value reported in [1976SUS/GOR2]; see Appendix A.

Figure VI-13: Plot of y from Eq. (VI.27) *vs.* ionic strength at 298.15 K where only those values represented by open symbols were included in the linear regression which is shown here as a weighted fit.



The slope of the regression is (0.0866 ± 0.0014) (2σ) such that the resulting value of $\varepsilon(\mathrm{Fe}^{2+},\mathrm{Cl}^-)$ is (0.169 ± 0.004) kg·mol^{-1}. Weights were assigned to these data based on an assessment of the experimental uncertainties. Calculations established that no correction was found to be necessary for the formation of the FeCl^+ complex due to its weakness at 298.15 K and hydrolysis of Fe^{2+} is also insignificant in these solutions, unlike in the analogous Fe^{3+} system. Indeed, the spreadsheet-based refinement of the osmotic coefficient data at 298.15 K would suggest the optimum fit is obtained with the following parameter set: $\log_{10} \beta_1^{\circ} = -(2.1 \pm 0.2)$, $\varepsilon(Fe^{2+},Cl^-) = (0.17 \pm 0.01)$ kg·mol^{-1}, $\varepsilon(FeCl^+,Cl^-) = (0.16 \pm 0.01)$ kg·mol^{-1}, although the latter interaction coefficient is not selected in this review.

The ion interaction coefficients for the corresponding (Cu^{2+},Cl^-), (Ni^{2+},Cl^-) and (Co^{2+},Cl^-) systems recommended currently by the NEA are (0.08 ± 0.01), (0.17 ± 0.02) and (0.16 ± 0.02) kg·mol^{-1}, respectively, such that the value recommended here for the iron(II) ion appears quite reasonable and strengthens the use of $\varepsilon(Ni^{2+}, ClO_4^-)$ as an analogue for $\varepsilon(Fe^{2+}, ClO_4^-)$ (see Section VI.4.4).

Finally, Groenveld [1956GRO] also measured the vapour pressures of seven $FeCl_2$ solutions at 293.15 and 298.15 K. Taking only the lowest four molalities, *i.e.* ≤ 3.267 mol·kg^{-1}, yielded $\varepsilon(Fe^{2+},Cl^-) = (0.17 \pm 0.01)$ and (0.16 ± 0.01) kg·mol^{-1}, respectively.

Therefore, this review adopts:

$$\varepsilon(Fe^{2+},Cl^-) = (0.17 \pm 0.01) \text{ kg·mol}^{-1}.$$

VI.4.4 Aqueous iron(II) perchlorate

Prior to this review there were no NEA recommended values for the ion interaction coefficients of iron(II) ion with chloride, perchlorate or nitrate ions. However, as mentioned in the discussion of the derivation of $\varepsilon(Fe^{3+}, ClO_4^-)$, Ciavatta refers to Biedermann [1975BIE] who used the assumption that $\varepsilon(Fe^{2+}, ClO_4^-) = \varepsilon(Mg^{2+}, ClO_4^-) =$ 0.33 kg·mol^{-1} in a calculation of the E° value for the Fe^{3+}/Fe^{2+} couple in [1937SCH/SHE]. In the absence of any experimental data from which to derive $\varepsilon(Fe^{2+}, ClO_4^-)$ directly, analogues must be found from which to assign a reasonable value for this interaction, which fortunately is not complicated by complexation or hydrolysis concerns. Moreover, there exists a number of analogue systems involving M^{2+} ions from which to make meaningful comparisons as shown in Table VI-10.

Table VI-10: Ion interaction coefficients, $\varepsilon(M^{2+},Cl^-)$ and $\varepsilon(M^{2+}, ClO_4^-)$ kg·mol^{-1} at 298.15 K taken from Appendix B.

M	$\varepsilon(M^{2+},Cl^-)$	$\varepsilon(M^{2+}, ClO_4^-)$
Zn		0.33 ± 0.03
Cu	0.08 ± 0.01	0.32 ± 0.02
Ni	0.17 ± 0.02	0.37 ± 0.03
Co	0.16 ± 0.02	0.34 ± 0.03
Mn	0.13 ± 0.01	
Mg	0.19 ± 0.02	0.33 ± 0.03

Consider also that the adopted value for $\varepsilon(\mathrm{Fe}^{2+},\mathrm{Cl}^{-})$ is (0.17 ± 0.01) kg·mol^{-1}, which is compatible with two first-row transition metal ions with small ionic radii. This review adopts the value of $\varepsilon(\mathrm{Ni}^{2+},\mathrm{ClO}_4^{-})$, although values between 0.34 and 0.37 could also be justified. The uncertainty is increased to embrace all the values listed in Table VI-10 with the exception of that for Cu^{2+}, v*iz*.:

$$\varepsilon(\mathrm{Fe}^{2+},\mathrm{ClO}_4^{-}) = (0.37 \pm 0.04)\ \mathrm{kg{\cdot}mol^{-1}}.$$

Chapter VII

Iron oxygen and hydrogen compounds and complexes

VII.1 Aqueous iron hydroxido complexes

VII.1.1 Aqueous Fe(II) hydroxido complexes

An early neutron diffraction study of iron(II) chloride in D_2O [1992HER/NEI2] established the octahedral configuration of the hexaaquo ion with nearest neighbour Fe-O and Fe-D distances of (2.12 ± 0.02) and (2.75 ± 0.05) Å.

There have been relatively few studies made of the hydrolysis of iron(II) compared to those of iron(III) hydrolysis, mainly due to the experimental difficulties of maintaining reducing conditions that preclude the formation of even small levels of iron(III), which hydrolyses at much lower pH (< 3). Equally difficult is the problem that iron(II) hydroxo phases precipitate after less than 1% of the total aqueous iron(II), has hydrolyzed within the concentration ranges that allow classic potentiometric and spectrophotometric measurements to be made. These experimental issues have dictated that with only one dubious exception, the hydrolysis of iron(II) to form higher-order hydroxido species have only been quantified from solubility studies where as in the case of the iron(III) system, there is again the difficulty in attaining equilibrium at ambient conditions for well developed crystalline phases. The difficulties with the solubility studies of the iron(II) system are compounded by the need to carefully control the redox conditions and in the case of magnetite, which has been the most extensively studied phase, the often undetected presence of maghemite (γ-Fe_2O_3) can bias the results. The available hydrolysis constants are summarized in Table VII-1.

Table VII-1: Experimental equilibrium data (logarithmic values) for the hydrolysis of Fe(II) in acidic and basic solutions.

Method	Medium	I_m	t / °C	$\log_{10}{}^{*}\beta_{n,m}$ reported	Reference
$Fe^{2+} + H_2O(l) \rightleftharpoons FeOH^{+} + H^{+}$					
gl	$NaClO_4$	1.052	25.0	– 9.5 ± 0.2	[1953HED]
pot/gl	0	variable	25.0	– 7.93 ± 0.01	[1956GAY/WOO]
	KCl	0.5	25.0	– 7.17	
gl	$NaClO_4$	1.016	20.0	– 6.95 ± 0.11	[1963BOL/ARV]
		0.516	25.0	– 6.72 ± 0.04	
		0.530	25.0	– 6.76 ± 0.04	
		2.062	25.0	– 6.70 ± 0.04	
		0.516	35.0	– 6.50 ± 0.03	
		0.516	40.0	– 6.36 ± 0.02	
		0.516	25.0	– 6.77 ± 0.08	
		0.530	40.0	– 6.29 ± 0.05	
coul	NaCl	0.513	25.0	– 9.5 (I = 0)	[1967TAK/POS]
			50.0	– 9.0 (I = 0)	
			75.0	– 8.5 (I = 0)	
sp	$NaClO_4$	2.213	25.0?	– 8.03 ± 0.01	[1970EHR/LEI2]
sol	HCl/KOH	≈ 0	50.0	– 8.58	[1970SWE/BAE] (a)
			100.0	– 7.41	
			150.0	– 6.54	
			200.0	– 5.87	
			260.0	– 5.25	
pot	HCl	0.0097	25.0	– 9.58 ± 0.08	[1971MES]
gl	NaCl	0.072	25.0	– 9.12 ± 0.02	[1978JOH/BAU]
		0.120	25.0	– 8.98 ± 0.08	
		0.094	25.0	– 8.85 ± 0.03	
sol	HCl/NaOH	≈ 0	100.0	– 8.78 ± 0.35	[1980TRE/LEB]
			150.0	– 8.09 ± 0.25	
			200.0	– 7.56 ± 0.20	
			250.0	– 7.12 ± 0.20	
			300.0	– 6.76 ± 0.23	
$Fe^{2+} + 2\,H_2O(l) \rightleftharpoons Fe(OH)_2(aq) + 2\,H^{+}$					
sol	HCl/KOH	≈ 0	50.0	– 18.94	[1970SWE/BAE]
			100.0	– 16.40	
			150.0	– 14.49	
			200.0	– 13.01	

(Continued next page)

Table VII-1 (continued)

Method	Medium	I_m	t / °C	$\log_{10} {}^*\beta_{n,m}$ reported	Reference
			260.0	– 11.63	
sol	HCl/NaOH	≈ 0	100.0	– 17.15 ± 0.14	[1980TRE/LEB]
			150.0	– 15.44 ± 0.14	
			200.0	– 14.09 ± 0.10	
			250.0	– 12.99 ± 0.10	
			300.0	– 12.09 ± 0.10	
$FeOH^+ + 2\ H_2O(l) \rightleftharpoons Fe(OH)_3^- + 2\ H^+$					
sp	$NaClO_4$	2.213	25.0?	– 25.58 ± 0.03	[1970EHR/LEI2]
$Fe^{2+} + 3\ H_2O(l) \rightleftharpoons Fe(OH)_3^- + 3\ H^+$					
sol	HCl/NaOH	≈ 0	100.0	– 28.11 ± 0.26	[1980TRE/LEB]
			150.0	– 25.63 ± 0.26	
			200.0	– 23.68 ± 0.19	
			250.0	– 22.10 ± 0.19	
			300.0	– 20.80 ± 0.19	

(a) the hydrolysis constants attributed to [1970SWE/BAE] were obtained from their fitting equations of the corresponding solubility constants reproduced here at the five main temperatures investigated.

VII.1.1.1 The first hydrolysis constant

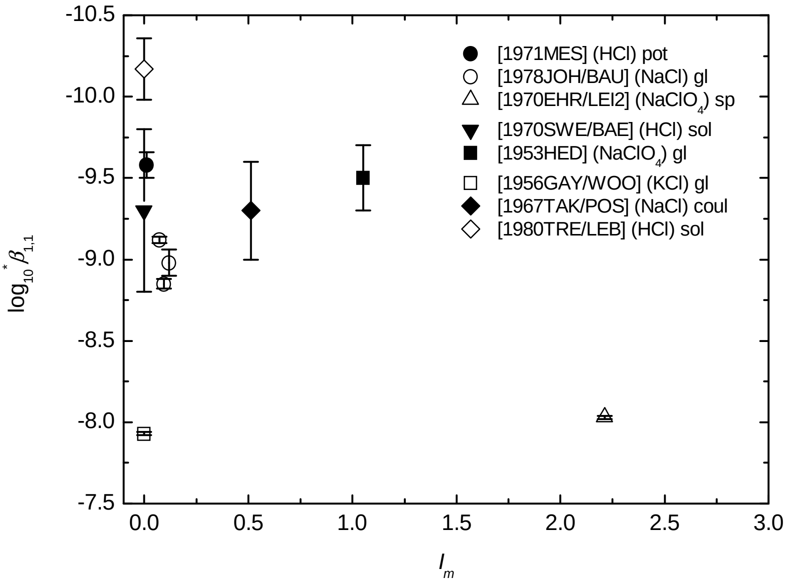
The predominant equilibrium that could be studied by classic homogeneous techniques was the first hydrolysis step:

$$Fe^{2+} + H_2O(l) \rightleftharpoons FeOH^+ + H^+ \tag{VII.1}$$

where the resulting $\log_{10} {}^*\beta_{1,1}$ values were obtained in a variety of media and are shown in Figure VII-1.

It is apparent that the experimental uncertainties reported by these investigators, with the exception of the solubility value obtained by extrapolation from high-temperature magnetite solubility measurements [1970SWE/BAE] and [1980TRE/LEB] which were at least made under a H_2 atmosphere, are statistically based and are far too low. Moreover, given that even trace impurities of iron(III) will lead to higher apparent $\log_{10} {}^*\beta_{1,1}$ values, the conservative approach is considered by taking the $\log_{10} {}^*\beta_{1,1}$ values in dilute HCl (I = 0.0097 [1971MES]) and NaCl (I = ≤ 0.12 [1978JOH/BAU]) and applying only the Debye-Hückel correction $\{2D + \log_{10} {}^*\beta_{1,1}\}$ to yield $\log_{10} {}^*\beta^\circ_{1,1}$ = – (9.49 ± 0.16) (*cf.* [1976BAE/MES] recommend a value of – 9.5[1]), and – (8.84 ± 0.10) from the three titrations reported by [1978JOH/BAU]. The recommended conservative value based on these two studies alone is: $\log_{10} {}^*\beta^\circ_{1,1}$ = – (9.1 ± 0.4) at 298.15 K. The disparity between the various values simply highlights the experimental difficulties inherent in this system. Given the sparse and scattered nature of these data, there can be no estimate of the $\varepsilon(\mathrm{FeOH}^+, \mathrm{X}^-)$ value at this time.

Figure VII-1: Plot of the logarithm of the first hydrolysis constant for Fe^{2+} at 298.15 K as a function of ionic strength where the data (*) in [1971MES] and [1978JOH/BAU] were selected for regression using only the SIT Debye-Hűckel term. Not included in this figure are the data from [1963BOL/ARV] that exhibit ${}^*\beta_{1,1}$ values which are a factor of *ca*. two orders of magnitude higher than even those of [1956GAY/WOO], indicative of the effects of Fe(III) contamination.



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[1] Baes and Mesmer [1976BAE/MES] quote a $\log_{10} {}^*\beta^\circ_{1,1}$ value of – 9.5 [1967TAK/POS] as providing confirmation of the earlier [1971MES] value, but considering the undisclosed details of the study by Tagashi and Posey, including the activity coefficient calculations, which appear not to have been implemented, and the uncertainty as to the validity of the fitting equation quoted by these authors, this review considers the value of $-\log_{10} {}^*\beta^\circ_{1,1}$ = (9.3 ± 0.3) at 0.513 m ionic strength as being tentative at best.

Considering the difficulties associated with measuring the concentration of $FeOH^+$, which is generally a minor Fe(II)-containing species in solution, and therefore in obtaining a unique UV-visible spectrum for this species, the cumulative hydrolysis constant, $({}^*K^{\circ}_{2,1}\,{}^*K^{\circ}_{3,1})$, for the equilibrium, $FeOH^+ + 2\,H_2O(l) \rightleftharpoons Fe(OH)_3^- + 2\,H^+$, of $-(25.58 \pm 0.03)$ at 298.15 K proposed by [1970EHR/LEI2] should be considered suspect. Nevertheless, combining the solubility constants for magnetite, $\log_{10}{}^*\beta^{\circ}_{s,0}$ and $\log_{10}{}^*\beta^{\circ}_{s,3}$, with the recommended first hydrolysis constant, $\log_{10}{}^*\beta^{\circ}_{1,1}$, gives a $({}^*K^{\circ}_{2,1}\,{}^*K^{\circ}_{3,1}) = -(25.2 \pm 0.5)$, which is in remarkably good agreement, but this is probably fortuitous.

VII.1.2 Solubility of iron(II) oxide/hydroxide phases

Commonly the earlier solubility studies involved fine-grained iron(II) hydroxide and were hampered by the use of poorly characterized (or uncharacterized), often amorphous, solid phases, *e.g.*, [1953LEU/KOL] and [1956GAY/WOO]. Leussing and Kolthoff catalogue eleven solubility products determined prior to 1953 for iron(II) hydroxide in water measured by a variety of techniques with values ranging from 4.5×10^{-21} to 7×10^{-13} M^2 which add little to our knowledge of the chemistry of iron(II) in aqueous solution other than underscoring the need to use a well-characterized solid if reliable thermodynamic quantities are to be obtained.

As is the case for the Fe(III) solid phases, the well-crystallized phases, predominantly magnetite, are slow to dissolve at ambient temperatures. Moreover, careful control of the redox conditions is required for the iron(II) system. Most, if not all, of the low-temperature preparation methods for magnetite (α-Fe_3O_4, an inverse spinel), for example, yield mainly maghemite (γ-Fe_2O_3) [2000WES/PAL], which cannot be differentiated by XRD from magnetite and is very slow to convert to magnetite at ambient conditions. Moreover, it was recently demonstrated [2000WES/PAL] that in acidic to near neutral solutions, a reversible transformation equilibrium, which is independent of the redox state of the system,

$$\alpha\text{-}Fe_3O_4 + 2\,H^+ \rightleftharpoons Fe^{2+} + \alpha\text{-}Fe_2O_3 + H_2O(l) \qquad \text{(VII.2)}$$

can persist for an indefinite period, and thereby control the concentration of Fe^{2+} in solution below those expected for the thermodynamic solubility of magnetite according to Eq. (VII.3), even under strongly reducing conditions up to temperatures of at least 473.15 K. Therefore, considerable care must be taken in carrying out solubility measurements for magnetite and the solubility constants at 298.15 K must be estimated by extrapolation of high-temperature solubility data, which are quite disparate at neutral to high pH.

The general hydrolysis equilibrium for magnetite can be represented as:

$$\tfrac{1}{3}\,Fe_3O_4(cr) + (2-b)\,H^+ + \tfrac{1}{3}\,H_2(g) \rightleftharpoons Fe(OH)_b^{(2-b)+} + (\tfrac{4}{3}-b)\,H_2O(l) \qquad \text{(VII.3)}$$

There has been a number of high-temperature solubility experimental investigations of magnetite [1970SWE/BAE], [1971HEL], [1977CHO/EUG], [1978CRE/SUS], [1980TRE/LEB], [1993DIN/ISH], [1995ZIE/JON], [2000MAN], and [2004SIM/PET].

The available solubility constants for iron(II)-containing solids are summarized in Table VII-2, although results of studies at more extreme conditions where in particular, ion pairing is a significant factor, have been excluded, *e.g.*, [1971HEL], [1977CHO/EUG], [1978CRE/SUS], [2004SIM/PET]. Moreover, a reanalysis of the two major data sets, [1970SWE/BAE] and [1980TRE/LEB], by Thornton and Walker [1987THO/WAL] and [1989WAL/THO], although useful, is not considered further here. The limited experimental data presented in [1993DIN/ISH] for an unconstrained study of a commercially "pure" magnetite at 423 K provide no useful information and these results are also not included in Table VII-2.

Table VII-2: Experimental equilibrium data (logarithmic values) for the solubility of magnetite in acidic and basic solutions.

Solid Phase	Medium	I_m	t / °C	n	$\log_{10}{}^{*}\beta_{s,n}$ reported	Reference
$Fe(OH)_2$(am)	NaCl	0	25	0	12.9 ± 0.2	[1953LEU/KOL]
$Fe(OH)_2$(cr?)	NaOH	0	25	3	– 19.1	[1956GAY/WOO]
$Fe(OH)_2$(cr?)	HCl	0	25	0	10.9	[1995ZIE/JON] [2004WES/ZIE]
α-Fe_3O_4	HCl/NaOH	0	25 (a)	0	12.02	[1970SWE/BAE]
				1	2.7	
				2	– 8.5	
				3	– 17.42 (c)	
α-Fe_3O_4	NaOH	~ 0	150	3	– 17.8 ± 0.9	[1976KAN/GRA]
			200		– 17.6 ± 0.7	
			250		– 16.9 ± 0.6	
			300		– 16.8 ± 0.7	
α-Fe_3O_4	HCl/NaOH	0	100	0	8.23 ± 0.08	[1980TRE/LEB] (b)
			150		6.94 ± 0.06	
			200		5.92 ± 0.05	
			250		5.10 ± 0.05	
			300		4.42 ± 0.05	

(a) Extrapolated values of $\log_{10}{}^{*}\beta_{s,n}$ from results in the range 323.15 to 573.15 K.

(b) The $\log_{10}{}^{*}\beta_{s,n}$ values for $n > 0$ were reported in terms of the corresponding hydrolysis constants.

(c) This value was later shown [1980TRE/LEB] to be compromised by the concomitant formation of $Fe(OH)_4^-$.

In their study of magnetite solubility over the range 294.15 to 561.15 K, Ziemniak *et al.* [1995ZIE/JON] used basic sodium phosphate and ammonia solutions to fix the pH. They claim to have identified 14 aqueous iron(II) and iron(III) species in their data treatment, although they incorporated solubility constants from Tremaine and LeBlanc [1980TRE/LEB] to anchor the speciation for the uncomplexed iron(II) species. This study also supports the findings of Tremaine and LeBlanc that significant quantities of Fe(II) and Fe(III) species exist under near neutral to basic pH conditions even under the reducing conditions that prevailed in their experiments, as well as in those of Sweeton and Baes [1970SWE/BAE] who did not recognize this problem in their study. However, the complexity of the phosphate-buffered system introduces too many uncertainties in the solubility constants derived for them and for the ammonia-buffered system. Their contention [1995ZIE/JON] that the stability of amine complexes of transition metal ions increase with increasing temperature is false, so that for these reasons these results are not considered further by this review. Finally, Ziemniak *et al.* [1995ZIE/JON] propose that iron(II) hydroxide is the stable phase relative to magnetite at p_{H_2} = 1 atm up to the transformation temperature of 389 K.

For crystalline magnetite, the solubility constants of Tremaine and LeBlanc [1980TRE/LEB] for formation of $Fe(OH)_b^{2-b}$, $b = 0 - 3$ according to Eq. (VII.3) were combined with those of Sweeton and Baes [1970SWE/BAE] for $b = 0 - 2$, with additional results from [1976KAN/GRA] in basic solutions where $Fe(OH)_3^-$ is assumed to be the only iron(II) species in solution. As mentioned in the synopsis of the Sweeton and Baes study, pH is perhaps the least well known, but most important, variable in these investigations and was only estimated by iterative calculations that depend on the speciation of the iron in solution. The effects of adsorption, impurities, and other possible side reactions complicate the calculation of pH for the near neutral to moderately basic pH range in particular where the lowest concentrations of iron exist in solution. The following generalized equation was used to fit the solubility constants, *viz.*, using standard weighted least-squares procedures in all cases:

$$\log_{10} \beta^{o}_{x,y} = a + b/T + c \log_{10} T \qquad \text{(VII.4)}$$

VII.1.2.1 First solubility constant of magnetite (iron(II) system)

$$\tfrac{1}{3} Fe_3O_4(cr) + 2 H^+ + \tfrac{1}{3} H_2(g) \rightleftharpoons Fe^{2+} + \tfrac{4}{3} H_2O(l) \qquad \text{(VII.5)}$$

The $\log_{10} {}^{*}\beta^{o}_{s,0}$ values for Reaction (VII.5), [1970SWE/BAE] and [1980TRE/LEB], were fitted in a number of ways utilizing generalized Eq. (VII.4) based on the following criteria:

Fit 1: Assuming that $\Delta_r C^{o}_{p,m}$ (298.15 K) = constant with no other constraints.

Fit 2: Assuming that $\Delta_r C^{o}_{p,m}$ (298.15 K) = 0 with no other constraints.

Fit 3: Assuming that $S^{o}_{m}(Fe^{2+}$, 298.15 K) = – 101.01 J·K^{-1}·mol^{-1}, which is the entropy for Fe^{2+} recommended initially during the preparation of this review (note the value for S°_{m} (Fe^{2+}, 298.15 K) finally selected in this review is slightly different, *viz.*, – (102.18 ± 2.78) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, but the value – 101.01 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ is well within the indicated uncertainty). Note that in both solubility studies, [1970SWE/BAE] and [1980TRE/LEB], the entropy term was also fixed before fitting their data.

Fit 4: Assuming that S°_{m} (Fe^{2+}, 298.15 K) = – 101.01 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ and $C^{\circ}_{p,\mathrm{m}}$ (Fe^{2+}, 298.15 K) = – 22 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ [1988HOV], which is also well within the uncertainty of the value finally recommended by this review, *viz.*, – (23 ± 10) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$.

The parameters associated with these fits, which are shown in Figure VII-2, are given in Table VII-3.

Figure VII-2: Temperature dependence of $\log_{10}{}^{*}\beta^{\circ}_{\mathrm{s},0}$ using the four approaches outlined above to fit the data in [1970SWE/BAE] and [1980TRE/LEB].

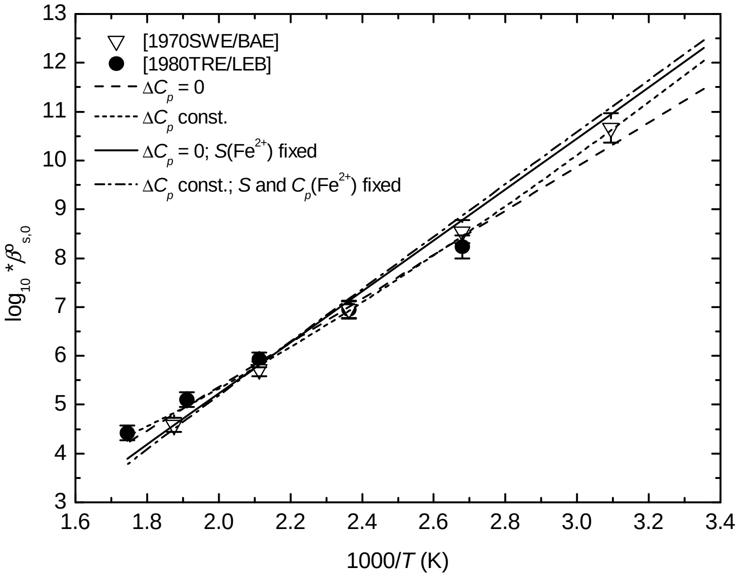


Table VII-3: Parameters of Eq. (VII.4) for the first solubility constant with the fixed values shown in italics (the number of significant figures in this and subsequent tables of fitting parameters is maintained to reproduce the fits).

Fit	*a*	*b*	*c*
1	– 56.003 ± 27.562	7771.7 ± 1723.3	16.964 ± 8.932
2	– 3.658 ± 0.375	4511.1 ± 172.7	
3	*– 5.2218*	5223.8 ± 44.1	
4	*2.4746*	4928.6 ± 54.1	*– 2.6460*

The remaining thermodynamic properties at 298.15 K were determined as follows:

$$\Delta_{\mathrm{r}}G^{\circ}_{\mathrm{m}} = \Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}(\mathrm{Fe}^{2+}) + (4/3)\,\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}(\mathrm{H_2O, l}) - (1/3)\,\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}(\mathrm{Fe_3O_4, cr}) = -RT\ln{}^{*}\beta^{\circ}_{\mathrm{s},0}$$

$$\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}(\mathrm{Fe}^{2+}) = \Delta_{\mathrm{r}}G^{\circ}_{\mathrm{m}} - (4/3)(-\,237140) + (1/3)(-\,1012720)\ \{\mathrm{J\cdot mol^{-1}}\}$$

$$\Delta_{\mathrm{r}}H^{\circ}_{\mathrm{m}} = \Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{Fe}^{2+}) + (4/3)\,\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{H_2O, l}) - (1/3)\,\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{Fe_3O_4, cr})$$

$$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{Fe}^{2+}) = \Delta_{\mathrm{r}}H^{\circ}_{\mathrm{m}} - (4/3)\,\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{H_2O, l}) + (1/3)\,\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{Fe_3O_4, cr})$$

$$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{Fe}^{2+}) = \Delta_{\mathrm{r}}H^{\circ}_{\mathrm{m}} - (4/3)(-\,285830) + (1/3)(-\,1115780)\ \{\mathrm{J\cdot mol^{-1}}\}$$

$$\Delta_{\mathrm{r}}S^{\circ}_{\mathrm{m}}(\mathrm{Fe}^{2+}) = -\,(\Delta_{\mathrm{r}}G^{\circ}_{\mathrm{m}} - \Delta_{\mathrm{r}}H^{\circ}_{\mathrm{m}})/298.15$$

$$S^{\circ}_{\mathrm{m}}(\mathrm{Fe}^{2+}) = \Delta_{\mathrm{r}}S^{\circ}_{\mathrm{m}} - (4/3)\,S^{\circ}_{\mathrm{m}}(\mathrm{H_2O, l}) + (1/3)\,S^{\circ}_{\mathrm{m}}(\mathrm{Fe_3O_4, cr}) + (1/3)\,S^{\circ}_{\mathrm{m}}(\mathrm{H_2, g})$$

$$S^{\circ}_{\mathrm{m}}(\mathrm{Fe}^{2+}) = \Delta_{\mathrm{r}}S^{\circ}_{\mathrm{m}} - (4/3)(69.950) + (1/3)(145.89) + (1/3)(130.68)\ \{\mathrm{J\cdot K^{-1}\cdot mol^{-1}}\}$$

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{Fe}^{2+}) = \Delta_{\mathrm{r}}C^{\circ}_{p,\mathrm{m}} - (4/3)\,C^{\circ}_{p,\mathrm{m}}(\mathrm{H_2O, l}) + (1/3)\,C^{\circ}_{p,\mathrm{m}}(\mathrm{H_2, g}) + (1/3)\,C^{\circ}_{p,\mathrm{m}}(\mathrm{Fe_3O_4, cr})$$

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{Fe}^{2+}) = \Delta_{\mathrm{r}}C^{\circ}_{p,\mathrm{m}} - (4/3)(75.351) + (1/3)(28.836) + (1/3)(150.78)\ \{\mathrm{J\cdot K^{-1}\cdot mol^{-1}}\}$$

These calculated thermodynamic quantities for Fe^{2+} are given in Table VII-4.

Table VII-4: Thermodynamic quantities for Fe^{2+} at 298.15 K with the fixed values shown in italics as discussed earlier in this section.

Fit	$\log_{10}{}^{*}\beta^{\circ}_{\mathrm{s},0}$	$\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}$ /kJ·mol⁻¹	$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ /kJ·mol⁻¹	S°_{m} /J·K⁻¹·mol⁻¹	$C^{\circ}_{p,\mathrm{m}}$ /J·K⁻¹·mol⁻¹
1	12	– 90	– 98	– 130	48
2	11.5	– 87	– 77	– 71	0
3	12.3	– 91.6	– 90.8	*– 101.0*	0
4	12.5	– 92.5	– 91.7	*– 101.0*	*– 22*

Considering the length of the extrapolation and the uncertainty of the data, the most constrained fit (4) is adopted here leading to the corresponding values listed in Table VII-4 being those preferred. Parker and Khodakovskii, [1995PAR/KHO] proposed the following thermodynamic properties for aqueous Fe^{2+} at 298.15 K: $\Delta_f G_m^o(Fe^{2+}$, 298.15 K) = – (90.5 ± 1.0) kJ·mol^{-1}; $\Delta_f H_m^o(Fe^{2+}$, 298.15 K) = – (90.0 ± 0.5) kJ·mol^{-1}; $S_m^o(Fe^{2+}$, 298.15 K) = – (101.6 ± 3.7) J·K^{-1}·mol^{-1}, whereas Wagman *et al.* [1982WAG/EVA] proposed: $\Delta_f G_m^o(Fe^{2+}$, 298.15 K) = – 78.90 kJ·mol^{-1}; $\Delta_f H_m^o(Fe^{2+}$, 298.15 K) = – 89.1 kJ·mol^{-1}; $S_m^o(Fe^{2+}$, 298.15 K) = – 137.7 J·K^{-1}·mol^{-1}.

VII.1.2.2 Second solubility constant of magnetite (iron(II) system)

$$\tfrac{1}{3}Fe_3O_4(cr) + H^+ + \tfrac{1}{3}H_2(g) \rightleftharpoons FeOH^+ + \tfrac{1}{3}H_2O(l) \qquad (VII.6)$$

The $\log_{10} {}^*\beta_{s,1}^o$ values for Reaction (VII.6) were fitted in three ways utilizing Eq. (VII.4) based on the following criteria:

Fit 1: Assuming that $\Delta_r C_{p,m}^o$(298.15 K) = 0 with no other constraints.

Fit 2: Using the $\log_{10} {}^*\beta_{s,1}^o$ value at 298.15 K equal to 3.20 in combination with the corresponding value of $\log_{10} {}^*\beta_{s,0}^o$ as reported above for Fit 3 in Table VII-4 to give $\log_{10} {}^*\beta_{1,1}^o$ = – 9.1 which is compatible with the independent hydrolysis data and a $\Delta_r C_{p,m}^o$(298.15 K) = 0 for Reaction (VII.6).

Fit 3: Same as for Fit 2, except using $\log_{10} {}^*\beta_{s,0}^o$ as reported above for Fit 4 in Table VII-4 at 298.15 K.

The parameters for the three fitting options corresponding to Eq. (VII.4) are listed in Table VII-5 with the resulting thermodynamic quantities being given in Table VII-6. The three fits of $\log_{10} {}^*\beta_{s,1}^o$ as a function of the reciprocal temperature (K) are illustrated in Figure VII-3. The more highly constrained Fit (3) is again preferred leading to the proposed thermodynamic properties of $FeOH^+$ at 298.15 K in Table VII-6.

Wagman *et al.* [1982WAG/EVA] proposed: $\Delta_f G_m^o(FeOH^+$, 298.15 K) = – 277.4 kJ·mol^{-1}; $\Delta_f H_m^o(FeOH^+$, 298.15 K) = – 324.7 kJ·mol^{-1}; $S_m^o(FeOH^+$, 298.15 K) = – 29 J·K^{-1}·mol^{-1}.

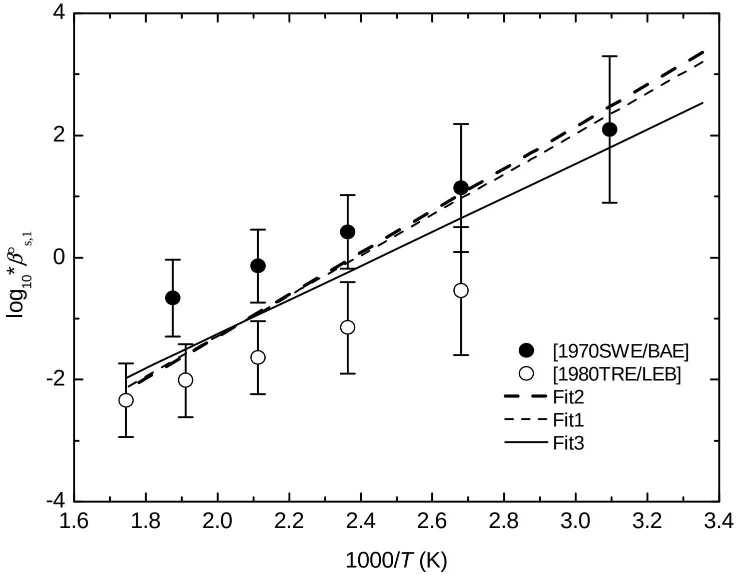
Table VII-5: Parameters of Eq. (VII.4) for the second solubility constant.

Fit	*a*	*b*
1	– 6.848 ± 1.717	2795.35 ± 791.21
2	– 7.917 ± 0.663	3314.3 ± 197.6
3	– 8.170 ± 0.672	3437.1 ± 200.4

Table VII-6: Thermodynamic quantities for $FeOH^+$ at 298.15 K with the fixed values shown in italics.

Fit	$\log_{10}{}^*\beta^\circ_{s,1}$	$\Delta_f G^\circ_m$ / $kJ\cdot mol^{-1}$	$\Delta_f H^\circ_m$ / $kJ\cdot mol^{-1}$	S°_m / $J\cdot K^{-1}\cdot mol^{-1}$
1	2.5	– 273	– 330	– 62
2	*3.20*	– 277	– 340	– 83
3	*3.36*	– 278	– 343	– 88

Figure VII-3: Temperature dependence of $\log_{10}{}^*\beta^\circ_{s,1}$ using the three approaches outlined to fit the data in [1970SWE/BAE] and [1980TRE/LEB].



VII.1.2.3 Third solubility constant of magnetite (iron(II) system)

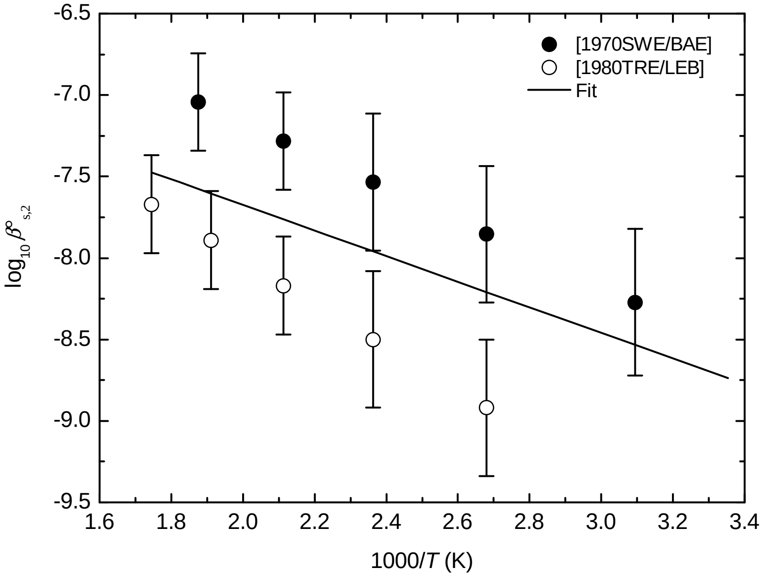
$$\tfrac{1}{3}\,Fe_3O_4(cr) + \tfrac{1}{3}\,H_2(g) + \tfrac{2}{3}\,H_2O(l) \rightleftharpoons Fe(OH)_2(aq) \qquad (VII.7)$$

The results for $\log_{10}\beta^\circ_{s,2}$ for Reaction (VII.7) from [1970SWE/BAE] and [1980TRE/LEB] were combined in a weighted, but unrestrained fit using the linear version of Eq. (VII.4). The parameters for this fit are: $a = -(6.700 \pm 0.911)$ and $b = -(786.38 \pm 412.73)$, which produced the straight line in Figure VII-4 and a $\log_{10}{}^*\beta^\circ_{s,2}$ at 298.15 K = $-(8.7 \pm 1.1)$ and the thermodynamic parameters for $Fe(OH)_2(aq)$: $\Delta_f G^\circ_m$ ($Fe(OH)_2$, aq, 298.15 K) = – 446 $kJ\cdot mol^{-1}$; $\Delta_f H^\circ_m$ ($Fe(OH)_2$, aq, 298.15 K) = – 547 $kJ\cdot mol^{-1}$; S°_m ($Fe(OH)_2$, aq, 298.15 K) = 22 $J\cdot K^{-1}\cdot mol^{-1}$. Wagman *et al.*

[1982WAG/EVA] provide no estimates of the thermodynamic properties of $Fe(OH)_2(aq)$.

The value, $\log_{10}{}^{*}\beta^{o}_{s,2}$ at 298.15 K = – (8.7 ± 1.1) when combined with $\log_{10}{}^{*}\beta^{o}_{s,0}$ at 298.15 K = – (12.5 ± 0.2) yields $\log_{10}{}^{*}\beta^{o}_{2,1}$ = – (21.2 ± 1.1). There are no other hydrolysis results with which to compare this value.

Figure VII-4: Temperature dependence of $\log_{10}{}^{*}\beta^{o}_{s,2}$ using the simple unconstrained linear fit to the data in [1970SWE/BAE] and [1980TRE/LEB].



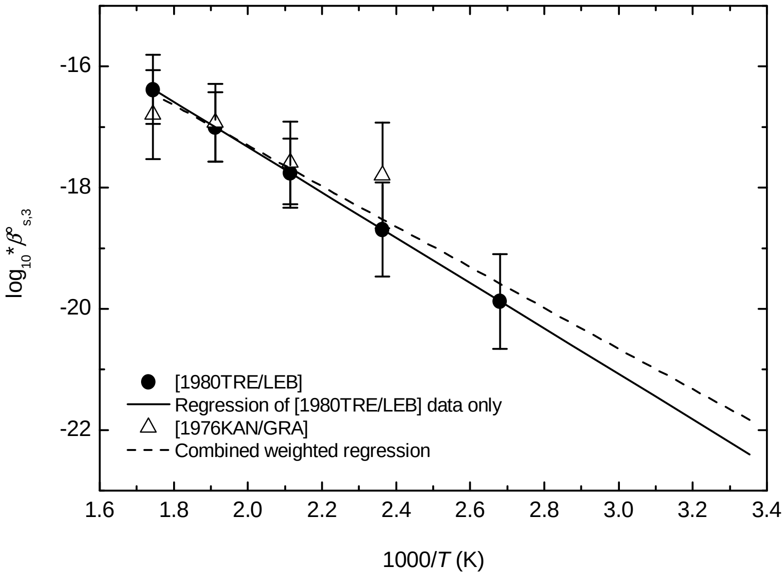
VII.1.2.4 Fourth solubility constant of magnetite (iron(II) system)

$$\tfrac{1}{3}\,Fe_3O_4(cr) + \tfrac{1}{3}\,H_2(g) + \tfrac{5}{3}\,H_2O(l) \rightleftharpoons Fe(OH)_3^- + H^+ \qquad (VII.8)$$

As mentioned previously, the results from the Sweeton and Baes [1970SWE/BAE] study at high pH are neglected here due to the unrecognized and dominant presence of iron(III) in aqueous solution in their experiments. The simple weighted linear fit of the $\log_{10}{}^{*}\beta^{o}_{s,3}$ values for Reaction (VII.8) reported in [1976KAN/GRA] and [1980TRE/LEB] is shown in Figure VII-5, where the experimental uncertainties have been increased considerably, and yielded the following parameters for Eq. (VII.4): a = – (10.612 ± 0.683) and b = – (3347.82 ± 330.08). The extrapolated value of $\log_{10}{}^{*}\beta^{o}_{s,3}$ at 298.15 K is – (21.84 ± 0.12) which in turn when combined with the proposed value of $\log_{10}{}^{*}\beta^{o}_{s,0}$ corresponds to $\log_{10}{}^{*}\beta^{o}_{3,1}$ = – (34.3 ± 0.2). The thermodynamic parameters for $Fe(OH)_3^-$: $\Delta_f G^{o}_{m}(Fe(OH)_3^-)$ = – 608 $kJ\cdot mol^{-1}$;

$\Delta_f H_m^\circ(\text{Fe(OH)}_3^-) = -784\ \text{kJ}\cdot\text{mol}^{-1}$; $S_m^\circ(\text{Fe(OH)}_3^-) = 6\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. Wagman *et al.* [1982WAG/EVA] provide only an estimate of $\Delta_f G_m^\circ(\text{Fe(OH)}_3^-) = -614.9.\ \text{kJ}\cdot\text{mol}^{-1}$.

Figure VII-5: Temperature dependence of $\log_{10}{}^{*}\beta_{s,3}^{\circ}$ using the simple unconstrained linear fit to the data in [1976KAN/GRA] and [1980TRE/LEB].



VII.1.2.5 The solubility of other iron(II) containing phases

The solubility data for FeS were summarized by Pohl [1962POH], and there was a later experimental study of the solubility of troilite, FeS, at 298.15 K [1976TEW/CAM]. Pyrite solubility was studied from 523.15 to 623.15 K by Ohmoto *et al.* [1994OHM/HAY] (also see Section IX.1.1.1).

The solubility of FeCO_3 was reported at 298.15 K [1992BRU/WER]. Preis and Gamsjäger [2002PRE/GAM] reviewed the available solubility results for siderite, including those of [1992BRU/WER] to derive a $\Delta_f H^\circ$ value of $-(752.0 \pm 1.2)$ kJ·mol^{-1}. The solubility of siderite was later studied in NaCl solutions at 298.15 K [2002SIL/LIU] (*cf.* Section X.1.2.1.2).

Ziemniak and Tunison [2003ZIE/TUN] report the solubility of maricite, $\text{NaFe(PO}_4\text{)}$ under hydrothermal conditions.

VII.1.3 Fe(III) Hydrolysis

The hydrolysis equilibria are represented by the generalized equation:

$$m\,\mathrm{Fe}^{3+} + n\,\mathrm{H_2O(l)} \rightleftharpoons \mathrm{Fe}_m(\mathrm{OH})_n^{3m-n} + n\,\mathrm{H}^+$$

for which the existence of the following aqueous (n,m) species has been reported: (1,1); (2,1); (3,1); (4,1); (2,2); and (4,3). Due to the insolubility of the iron(III) hydroxide/oxide solid phases, the hydrolysis constants for the (3,1) and (4,1) species are available only from solubility studies and are therefore not known with accuracy, mainly because these solids are generally not crystalline at low temperatures and the rates of dissolution are very slow, but also because of the typical problems of extracting solubility constants for multi-hydrolyzed metal species in solution for highly insoluble metal oxides/hydroxides. Baes and Mesmer [1976BAE/MES] reported a value for ${}^*\beta^{\circ}_{4,3}$ based on a paper by Schlyter [1962SCH2], which in turn cited the unpublished experimental work of Biedermann, and only one more recent study by Khoe *et al.* [1986KHO/BRO] provided hydrolysis constants in sodium nitrate and chloride media, but detection of this species appears suspect to this review (see section below).

In contrast to the limited and fragmented data available for the hydrolysis of iron(II), there were a large number of studies reported for the corresponding iron(III) system, beginning in the nineteenth century, *e.g.*, [1896GOO], with particular activity in the middle of the twentieth century. The reported hydrolysis constants are summarized in Table VII-7[1]. Reasons for exclusion of the results of several other studies [1951SID/VOS], [1959PER], [1971HEM/RIC], [1973DAN/CHI], [1973WHI], [1975KNI/SYL], [1976DOU/DEB], [1992KUM/NAK], [1994DAN/RIG] are discussed in Appendix A. Experimental problems associated with these investigations include the propensity of Fe^{3+} to hydrolyze even at low pH such that the free hydrogen concentration is high compared to that of the iron(III) species and can lead to large liquid-junction potentials for potentiometric studies and will represent a significant fraction of the ionic strength at low ionic strengths. Moreover, for spectrophotometric studies, very low pH solutions are required to obtain the spectrum of unhydrolyzed Fe^{3+}. There is also the added problem of colloid formation. The latter is associated with, or is a consequence of, the formation of a dimer (2,2) even at millimolar concentrations of

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[1] The article by Perera and Hefter [2003PER/HEF], which reports results of combined UV-visible spectrophotometric and pH-potentiometric titrations on iron(III)-cyanide and -hydroxide solutions in (mainly) 1 M $\mathrm{NaClO_4}$ at (25.00 ± 0.05) °C, was only discovered after the first draft of the present review had been completed and comments refereed. This ambitious study claimed to have identified the first six mononuclear hydroxidoiron(III) species in solution and the corresponding hydrolysis constants were determined. However, the technical difficulties encountered in investigating extremely low iron(III) concentrations ($2 - 10 \times 10^{-6}$ M) appear to have compromised these results so that not including them will not affect quantitatively the values selected in the current review.

iron(III) such that both effects limit severely conditions under which $\mathrm{Fe(OH)}_2^+$ is an important species. Consequently, the hydrolysis constant for the formation of this species is still poorly known. Hydrolysis also promotes the formation of carbonato complexes unless CO_2 is rigorously excluded due to the direct rapid addition of CO_2(aq) to the Fe–OH bond. Strong complexation with common anions, such as chloride and sulfate, can also bias the interpretation of hydrolysis data.

Table VII-7: Experimental equilibrium data (logarithmic values) for the hydrolysis of Fe(III) in acidic and basic solutions.

Method	Medium	I_m	T/K	$\log_{10}{}^*\beta_{n,m}$ reported	Reference
$Fe^{3+} + H_2O(l) \rightleftharpoons FeOH^{2+} + H^+$					
gl	HCl	0.0017	298.15	– 2.75	[1938LAM/JAC]
		0.0019	298.15	– 2.73	
pot	KNO_3/KCl	0.53M	298.15	– 2.76 ± 0.00	[1941BRO]
sp	$NaClO_4$	0.047	298.15	– 2.53	[1949OLS/SIM]
pot	$NaClO_4$	3.50	298.15	– 2.98 ± 0.05	[1953HED2]
sp	$NaClO_4$	0.0147	298.15	– 2.372	[1955MIL/VOS]
		0.0401	298.15	– 2.438	
		0.0904	298.15	– 2.496	
		1.081	298.15	– 2.768	
sp	$NaClO_4$	0.102	298.15	– 2.54	[1955MIL/VOS] at one pH
		0.203	298.15	– 2.62	
		0.305	298.15	– 2.66	
		0.618	298.15	– 2.72	
		1.049	298.15	– 2.78	
		2.206	298.15	– 2.78	
		3.493	298.15	– 2.83	
sp	$NaClO_4$	0.0117	291.15	– 2.548	[1957MIL]
		0.0217	291.15	– 2.600	
		0.0318	291.15	– 2.628	
		1.049	291.15	– 2.939	
		0.0117	298.15	– 2.371	
		0.0217	298.15	– 2.420	
		0.0318	298.15	– 2.452	
		1.049	298.15	– 2.765	
		0.0117	305.15	– 2.191	
		0.0217	305.15	– 2.247	
		0.0318	305.15	– 2.279	

(Continued next page)

Table VII-7 (continued)

Method	Medium	I_m	T/K	$\log_{10} {}^*\beta_{n,m}$ reported	Reference
		1.049	305.15	– 2.586	
sol	$HClO_4$	varied	298.15	– 2.5 ± 0.1	[1973HAS/MIS]
sp	$NaClO_4$	0.10	298.15	– 2.61 ± 0.04	[1977SAP/PAT]
		0.10	306.15	– 2.45 ± 0.04	
		0.10	313.15	– 2.31 ± 0.04	
		0.10	328.15	– 2.05 ± 0.04	
		0.10	343.15	– 1.81 ± 0.04	
		0.10	353.15	– 1.63 ± 0.04	
		0.51	298.15	– 2.75 ± 0.04	
		0.51	298.15	– 2.75 ± 0.04	
		0.51	306.15	– 2.61 ± 0.04	
		0.51	313.15	– 2.57 ± 0.04	
		0.51	328.15	– 2.32 ± 0.04	
		0.51	343.15	– 2.06 ± 0.04	
		0.51	353.15	– 1.79 ± 0.04	
		1.05	298.15	– 2.81 ± 0.04	
		1.05	306.15	– 2.69 ± 0.04	
		1.05	313.15	– 2.56 ± 0.04	
		1.05	328.15	– 2.31 ± 0.04	
		1.05	343.15	– 2.05 ± 0.04	
		1.05	353.15	– 1.90 ± 0.04	
		2.07	298.15	– 2.87 ± 0.04	
		2.07	306.15	– 2.74 ± 0.04	
		2.07	313.15	– 2.47 ± 0.04	
		2.07	328.15	– 2.61 ± 0.04	
		2.07	343.15	– 2.12 ± 0.04	
		2.07	353.15	– 1.94 ± 0.04	
		2.51	298.15	– 2.86 ± 0.04	
		2.51	306.15	– 2.74 ± 0.04	
		2.51	313.15	– 2.61 ± 0.04	
		2.51	328.15	– 2.36 ± 0.04	
		2.51	343.15	– 2.13 ± 0.04	
		2.51	353.15	– 1.97 ± 0.04	
		3.05	298.15	– 2.88 ± 0.04	
		3.05	306.15	– 2.75 ± 0.04	
		3.05	313.15	– 2.61 ± 0.04	
		3.05	328.15	– 2.39 ± 0.04	
		3.05	343.15	– 2.15 ± 0.04	

(Continued next page)

Table VII-7 (continued)

Method	Medium	I_m	T/K	$\log_{10}{}^*\beta_{n,m}$ reported	Reference
		3.05	353.15	– 2.00 ± 0.04	
sp	$NaClO_4$	0.0201	298.15	– 2.42 ± 0.03	[1979ZOT/KOT]
		0.0503	298.15	– 2.45 ± 0.04	
		0.101	298.15	– 2.57 ± 0.05	
		0.513	298.15	– 2.68 ± 0.06	
		2.213	298.15	– 2.84 ± 0.08	
		0.0503	323.15	– 1.90 ± 0.06	
		0.101	323.15	– 1.99 ± 0.02	
		0.513	323.15	– 2.22 ± 0.06	
		2.220	323.15	– 2.30 ± 0.05	
		0.101	353.15	– 1.41 ± 0.03	
		0.513	353.15	– 1.61 ± 0.05	
		2.209	353.15	– 1.75 ± 0.04	
sp	$NaClO_4$	0.101	353.15	– 1.45 ± 0.04	[1980ZOT/KOT]
		0.513	353.15	– 1.53 ± 0.05	
		1.050	353.15	– 1.67 ± 0.06	
		2.213	353.15	– 1.63 ± 0.05	
		0.101	383.15	– 0.97 ± 0.04	
		0.511	383.15	– 1.08 ± 0.04	
		1.042	383.15	– 1.20 ± 0.05	
		2.178	383.15	– 1.26 ± 0.06	
		0.507	413.15	– 0.71 ± 0.04	
		1.028	413.15	– 0.79 ± 0.04	
		2.128	413.15	– 0.83 ± 0.06	
		0.502	443.15	– 0.39 ± 0.07	
		1.009	443.15	– 0.50 ± 0.06	
		2.064	443.15	– 0.60 ± 0.06	
		0.986	473.15	– 0.23 ± 0.08	
		1.982	473.15	– 0.32 ± 0.07	
pot	$NaClO_4$	1.05	298.15	– 2.71 ± 0.02	[1986KHO/BRO]
	KNO_3	1.05	298.15	– 2.75 ± 0.04	
				– 2.98 ± 0.06 (a)	
	KCl	1.03	298.15	– 3.20 ± 0.07	
				– 3.44 ± 0.08 (a)	
pot	$NaClO_4$	0.513	298.15	– 2.70 ± 0.02	[1990SAL/VAS]
		1.05	298.15	– 2.80 ± 0.02	
		2.21	298.15	– 2.91 ± 0.02	
		3.50	298.15	– 2.98 ± 0.02	

(Continued next page)

Table VII-7 (continued)

Method	Medium	I_m	T/K	$\log_{10} {}^*\beta_{n,m}$ reported	Reference
pot	$NaClO_4$	0.01	298.15	– 2.37 ± 0.04	[2000BYR/LUO]
		0.0501	298.15	– 2.45 ± 0.02	
		0.101	298.15	– 2.54 ± 0.04	
		0.253	298.15	– 2.65 ± 0.02	
		0.408	298.15	– 2.67 ± 0.02	
		0.724	298.15	– 2.73 ± 0.02	
		1.05	298.15	– 2.77 ± 0.02	
		2.21	298.15	– 2.70 ± 0.03	
		3.49	298.15	– 2.80 ± 0.02	
		4.94	298.15	– 2.79 ± 0.02	
		6.56	298.15	– 2.78 ± 0.02	
		8.42	298.15	– 2.73 ± 0.03	
		0.750	278.15	– 3.30 ± 0.03	
		0.751	283.15	– 3.11 ± 0.03	
		0.752	298.15	– 2.70 ± 0.02	
		0.753	313.15	– 2.37 ± 0.03	
		0.754	329.15	– 2.04 ± 0.03	
pot/sp	$NaClO_4$	0.101	298.15	– 2.55 ± 0.04	[2007STE]
		0.512	298.15	– 2.68 ± 0.03	
		1.08	298.15	– 2.74 ± 0.03	
		3.49	298.15	– 2.77 ± 0.03	
$Fe^{3+} + 2\,H_2O(l) \rightleftharpoons Fe(OH)_2^+ + 2\,H^+$					
pot	$NaClO_4$	3.50	298.15	– 6.18 ± 0.09	[1953HED2]
pot	$NaClO_4$	3.05	298.15	– 4.42 ± 0.21	[1977SAP/PAT]
		3.05	328.15	– 3.08 ± 0.14	
pot	$NaClO_4$	1.05	298.15	– 6.25 ± 0.03	[1986KHO/BRO]
	KNO_3	1.05	298.15	– 6.57 ± 0.11	
				– 6.41 ± 0.08 (a)	
	KCl	1.03	298.15	– 6.70 ± 0.09	
				– 6.56 ± 0.05 (a)	
pot	$NaClO_4$	0.513	298.15	$\leq$– 5.70	[1990SAL/VAS]
		1.05	298.15	– 5.8 ± 0.1	
		2.21	298.15	– 6.0 ± 0.1	
		3.50	298.15	– 6.2 ± 0.1	
sp	$NaClO_4$	0.101	298.15	– 6.34 ± 0.13	[2007STE]
		0.512	298.15	– 6.78 ± 0.03	

(Continued next page)

Table VII-7 (continued)

Method	Medium	I_m	T/K	$\log_{10}{}^*\beta_{n,m}$ reported	Reference
$2\,Fe^{3+} + 2\,H_2O(l) \rightleftharpoons Fe_2(OH)_2^{4+} + 2\,H^+$					
pot	$NaClO_4$	3.500	298.15	– 2.85 ± 0.08	[1953HED2]
sp	$NaClO_4$	0.101	298.15	2.23 $^{(b)}$	[1955MIL/VOS]
		0.202	298.15	2.42 $^{(b)}$	
		0.304	298.15	2.52 $^{(b)}$	
		0.405	298.15	2.60 $^{(b)}$	
		1.08	298.15	– 6.94 ± 0.02	
		0.617	298.15	2.71 $^{(b)}$	
		1.049	298.15	2.87 $^{(b)}$	
		2.206	298.15	3.11 $^{(b)}$	
		3.493	298.15	3.27 $^{(b)}$	
mag.	$NaClO_4$	3.503	288.15	– 2.42 ± 0.03	[1955MUL/SEL]
		3.503	298.15	– 2.07 ± 0.05	
		3.503	308.15	– 1.92 ± 0.09	
		3.503	318.15	– 1.72 ± 0.05	
		3.503	324.15	– 1.53 ± 0.10	
sp	$NaClO_4$	0.104	291.15	2.43 $^{(b)}$	[1957MIL]
		0.206	291.15	2.63 $^{(b)}$	
		0.308	291.15	2.71 $^{(b)}$	
		1.052	291.15	3.01 $^{(b)}$	
		0.104	298.15	2.35 $^{(b)}$	
		0.206	298.15	2.51 $^{(b)}$	
		0.308	298.15	2.60 $^{(b)}$	
		1.052	298.15	2.89 $^{(b)}$	
		0.104	305.15	2.23 $^{(b)}$	
		0.206	305.15	2.39 $^{(b)}$	
		0.308	305.15	2.49 $^{(b)}$	
		1.052	305.15	2.73 $^{(b)}$	
mag	$NaClO_4$	3.50	298.15	– 1.80 ± 0.16	[1973VER/RAN]
pot	$NaClO_4$	3.05	298.15	– 3.16 ± 0.12	[1977SAP/PAT]
		3.05	328.15	– 2.69 ± 0.31	
		3.05	353.15	– 2.40 ± 0.16	
pot	$NaClO_4$	1.05	298.15	– 3.12 ± 0.01	[1986KHO/BRO]
	KNO_3	1.05	298.15	– 3.14 ± 0.03	
				– 3.03 ± 0.02 $^{(a)}$	
	KCl	1.03	298.15	– 4.03 ± 0.11	
				– 3.76 ± 0.02 $^{(a)}$	

(Continued next page)

Table VII-7 (continued)

Method	Medium	I_m	T/K	$\log_{10} {}^*\beta_{n,m}$ reported	Reference
pot	$NaClO_4$	0.513	298.15	-2.84 ± 0.02	[1990SAL/VAS]
		1.05	298.15	-2.83 ± 0.02	
		2.21	298.15	-2.79 ± 0.02	
		3.49	298.15	-2.84 ± 0.02	
pot	$NaClO_4$	3.50	298.15	-2.81 ± 0.02	[2001CIA/TOM3] (d)
pot	$NaClO_4$	0.101	298.15	-2.93 ± 0.01	[2007STE]
		0.512	298.15	-2.89 ± 0.01	
		1.08	298.15	-2.87 ± 0.01	
		3.49	298.15	-2.74 ± 0.01	
$3\,Fe^{3+} + 4\,H_2O(l) \rightleftharpoons Fe_3(OH)_4^{5+} + 4\,H^+$					
cond/pot	$NaClO_4$	3.49	298.15	-5.64 ± 0.27 [c]	[1962SCH2]
pot	KNO_3	1.05	298.15	-6.94 ± 0.11 (a)	[1986KHO/BRO]
	KCl	1.03	298.15	-7.55 ± 0.13 (a)	
pot	$NaClO_4$	3.50	298.15	-6.01 ± 0.18	[2001CIA/TOM3] (d)
$3\,Fe^{3+} + 5\,H_2O(l) \rightleftharpoons Fe_3(OH)_5^{4+}$					
pot	$NaClO_4$	3.50	298.15	-8.24 ± 0.09	[2001CIA/TOM3] (d)

(a) This speciation scheme [1986KHO/BRO] includes the formation of the $Fe_3(OH)_4^{5+}$ species.

(b) These constants were reported for the simple dimerization equilibrium: $2FeOH^{2+} \rightleftharpoons Fe_2(OH)_2^{4+}$.

(c) This value (converted to molal units) was quoted by Schlyter [1962SCH2] and attributed to unpublished conductance titrations and glass-electrode pH measurements by G. Biedermann in 1959; this value was also cited by Baes and Mesmer [1976BAE/MES].

(d) This potentiometric study by the Sillén school was discovered after completion of the first draft of the current review and it is essentially an expansion of a much earlier investigation of the title complexes in 3 M $NaClO_4$ at 298.15 K over a wider range of pH, and metal and ligand concentrations [1969CIA/NUN]. The authors proposed four models based on their treatment of the combined datasets utilizing the fitting routine SUPERQUAD [1985GAN/SAB] which obviously was unavailable when their first study was completed. The results listed above stem from their model B3, which the authors favoured although their choice is somewhat questionable. In fitting their results it must be noted that the first two hydrolysis constants of iron(III) were considered to be well established and thus were fixed as follows: $\log_{10} {}^*\beta_{110} = -2.98$ and $\log_{10} {}^*\beta_{210} = -6.18$.

VII.1.3.1 The first hydrolysis constant

The first hydrolysis constant for the equilibrium,

$$Fe^{3+} + H_2O(l) \rightleftharpoons FeOH^{2+} + H^+ \qquad (VII.9)$$

was the most extensively studied. The SIT treatment of *all* these data obtained in $NaClO_4$ solutions at 298.15 K according to the equation:

$$\log_{10} {}^*\beta_{1,1} + 4D - \log_{10} a_w = \log_{10} {}^*\beta^\circ_{1,1} - \Delta\varepsilon\, I_m$$

is plotted in Figure VII-6 for those data at 298.15 K. First, the results indicated with (*) were rejected as outliers and experimental uncertainties were applied to the remaining data commensurate with the experimental method applied. The recent data set of [2000BYR/LUO] also appears to be the most reliable so that the larger number of experimental points and the relatively low experimental uncertainly allows this study to have a higher weight. Moreover, as shown in the synopsis [2000BYR/LUO], a good fit can be obtained to $I_m = 3.5$. However, it is clear that $\Delta\varepsilon$ is not a linear function (SIT$_1$) of I_m over virtually the entire measured range such that an alternative treatment can be assumed, *i.e.*, $\Delta\varepsilon = \Delta\varepsilon_1 + \Delta\varepsilon_2 \log_{10} I_m$, SIT$_2$. This restricted data set and the resulting weighted fits are shown in Figure VII-7. In order to reconcile the $\Delta\varepsilon$ to be recommended for this equilibrium with those of other systems where they are generally independent of I_m albeit over restricted ranges, this fit is shown in Figure VII-6 as well as one (designated, for convenience, in this Section only, as SIT$_3$) with the $\log_{10} {}^*\beta^{\circ}_{1,1}$ fixed from the three-term fit. The reasoning here is that the three-term fit should yield a more accurate value of $\log_{10} {}^*\beta^{\circ}_{1,1}$, which is more important than obtaining the most accurate ion interaction parameters for the equilibrium.

Figure VII-6: Plot of all the available values of $\log_{10} {}^*\beta_{1,1} + 4D - \log_{10} a_w$ *vs.* I_m in NaClO$_4$ media for the first hydrolysis constant of Fe^{3+} at 298.15 K where the lines represent the fits to the limited data set represented in Figure VII-7.

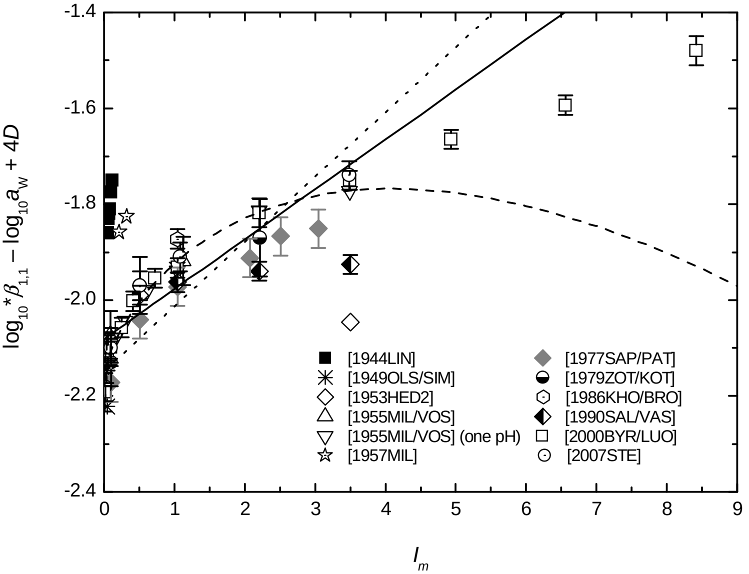
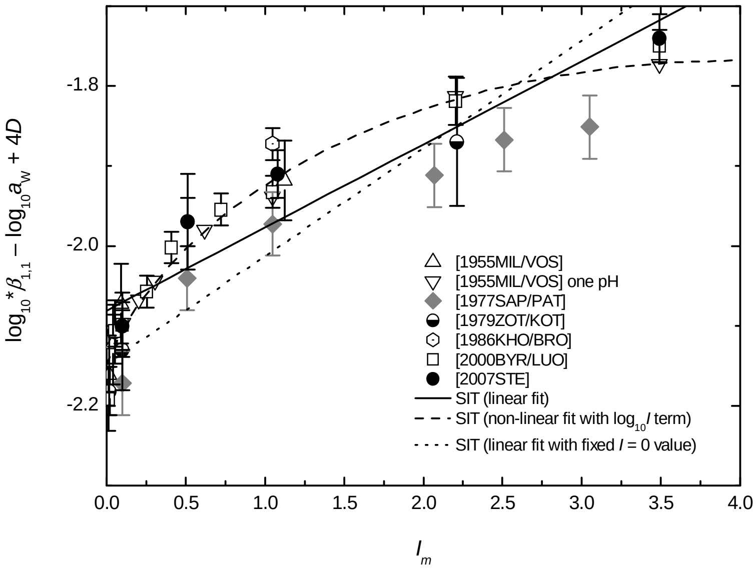


Figure VII-7: Plot of the limited data set ($I_m > 3.5$) of $\log_{10} {}^*\beta_{1,1} + 4D - \log_{10} a_w$ *vs.* I_m in $NaClO_4$ medium for the first hydrolysis constant of Fe^{3+} at 298.15 K.



The three-term (SIT_2) fit yielded: $\log_{10} {}^*\beta^{\circ}_{1,1} = -(2.15 \pm 0.02)$; $\Delta\varepsilon_1 = -(0.22 \pm 0.03)$ kg·mol^{-1}; $\Delta\varepsilon_2 = (0.21 \pm 0.05)$ kg·mol^{-1}, with $\Delta\varepsilon = \varepsilon(FeOH^{2+}, ClO_4^-) + \varepsilon(H^+, ClO_4^-) - \varepsilon(Fe^{3+}, ClO_4^-)$

$$\begin{aligned}\varepsilon(FeOH^{2+}, ClO_4^-) &= (-(0.22 \pm 0.03) + (0.21 \pm 0.05)\log_{10} I_m) - (0.14 \pm 0.02) \\ &\quad + ((0.78 \pm 0.05) - (0.41 \pm 0.05)\log_{10} I_m)\ \text{kg}\cdot\text{mol}^{-1} \\ &= ((0.42 \pm 0.06) - (0.20 \pm 0.07)\log_{10} I_m)\ \text{kg}\cdot\text{mol}^{-1}.\end{aligned}$$

However, as mentioned above, the majority of $\Delta\varepsilon$ values reported by the NEA are independent of I_m so that a forced linear two-term fit (SIT_1) produced the values: $\log_{10} {}^*\beta^{\circ}_{1,1} = -(2.08 \pm 0.02)$; $\Delta\varepsilon = -(0.10 \pm 0.02)$ kg·mol^{-1} (2σ), such that:

$$\begin{aligned}\varepsilon(FeOH^{2+}, ClO_4^-) &= -(0.10 \pm 0.02) - (0.14 \pm 0.02) + (0.73 \pm 0.04) \\ &= (0.49 \pm 0.05)\ \text{kg}\cdot\text{mol}^{-1}.\end{aligned}$$

Finally an attempt to utilize the SIT_2 fit to take advantage of the more accurate SIT_2 $\log_{10} {}^*\beta^{\circ}_{1,1}$ value, $-(2.15 \pm 0.03)$, by fixing this value to a forced two-term linear I_m fit (SIT_3) produced $\Delta\varepsilon = -(0.13 \pm 0.02)$ kg·mol^{-1} such that

$$\varepsilon(\mathrm{FeOH^{2+}, ClO_4^-}) = -(0.13 \pm 0.02) - (0.14 \pm 0.02) + (0.73 \pm 0.04)$$
$$= (0.46 \pm 0.05)\ \mathrm{kg \cdot mol^{-1}}.$$

It must also be remembered that for the Fe^{3+} ion, which hydrolyzes at relatively low pH, the low ionic strength data have larger than usual uncertainties. Nevertheless, as a compromise to the known curvature of $\varepsilon(\mathrm{Fe^{3+}, ClO_4^-})$, which is readily attributed completely to this small highly charged cation, this final treatment appears to be a reasonable compromise to providing a realistic value of $\log_{10} {}^*\beta^{\circ}_{1,1}$ while establishing an identical value of $\Delta\varepsilon$ to that obtained from the two-term SIT_1 fit (see Figure VII-7). These fits are shown in Figure VII-6 to illustrate that the limit of $I_m = 4$ indeed applies to their utility.

For comparison, the previously reported $\log_{10} {}^*\beta^{\circ}_{1,1}$ value by Baes and Mesmer [1976BAE/MES] is – 2.19 at 298.15 K. Interestingly, using the whole ionic strength range (*i.e.*, $I_m = 8.42\ \mathrm{mol \cdot kg^{-1}}$), the corresponding parameters are: $\log_{10} {}^*\beta^{\circ}_{1,1} = -(2.11 \pm 0.02)$; $\Delta\varepsilon_1 = -(0.16 \pm 0.03)\ \mathrm{kg \cdot mol^{-1}}$; $\Delta\varepsilon_2 = (0.08 \pm 0.01)\ \mathrm{kg \cdot mol^{-1}}$. Finally, using the conventional $\Delta\varepsilon$, which is independent of ionic strength for the entire data set in Figure VII-6, a weighted linear regression yielded: $\log_{10} {}^*\beta^{\circ}_{1,1} = -(2.06 \pm 0.02)$; $\Delta\varepsilon = -(0.075 \pm 0.007)\ \mathrm{kg \cdot mol^{-1}}$.

In summary, the selected value from the SIT_2 fit is assigned a larger uncertainty:

$$\log_{10} {}^*\beta^{\circ}_{1,1}(\mathrm{FeOH^{2+}}, 298.15\ \mathrm{K}) = -(2.15 \pm 0.03)$$

with

$$\varepsilon(\mathrm{FeOH^{2+}, ClO_4^-}) = ((0.42 \pm 0.06) - (0.20 \pm 0.07) \log_{10} I_m)\ \mathrm{kg \cdot mol^{-1}}$$

or, from the two-term linear fit (SIT_3)

$$\varepsilon(\mathrm{FeOH^{2+}, ClO_4^-}) = (0.46 \pm 0.05)\ \mathrm{kg \cdot mol^{-1}}.$$

VII.1.3.1.1 Temperature dependence of the first hydrolysis constant of iron(III)

From the $\log_{10} {}^*\beta^{\circ}_{n,m}$ values summarized in Table VII-7 as a function of temperature, only values from those studies selected for use at 298.15 K in the previous section, and which also contained results at other temperatures, were considered for the determination of the temperature dependence of the first hydrolysis constant. Two versions of the SIT were applied, *viz.*, with the usual linear $\log_{10} {}^*\beta^{\circ}_{n,m}$ *vs.* I_m least-squares fit giving $\Delta\varepsilon_1$ as the slope and with the non-linear version involving ($\Delta\varepsilon_1 + \Delta\varepsilon_2 \log_{10} I_m$). Table VII-8 also lists the results of application of the SIT where the uncertainties (2σ) are those obtained from the weighted least-squares fitting procedure.

Table VII-8: Parameters for equilibrium constants (logarithmic values) for the hydrolysis of Fe(III) as a function of temperature in aqueous $NaClO_4$.

Nr. of parameters	T/K	$\log_{10} {}^*\beta^{\circ}_{n,m}$	$\Delta\varepsilon_1$	$\Delta\varepsilon_2$
$Fe^{3+} + H_2O(l) \rightleftharpoons FeOH^{2+} + H^+$				
2	298.15	– 2.08 ± 0.00 (a)	– 0.10 ± 0.02	
3		– 2.15 ± 0.00 (a)	– 0.22 ± 0.04	0.21 ± 0.08
2	306.15 (b)	– 1.97 ± 0.05	– 0.10 ± 0.01	
3		– 2.03 ± 0.05	– 0.19 ± 0.02	0.18 ± 0.04
2	313.15 (c)	– 1.77 ± 0.08	– 0.09 ± 0.02	
3		– 1.96 ± 0.08	– 0.34 ± 0.16	0.42 ± 0.27
2	323.15 (d)	– 1.54 ± 0.10	– 0.12 ± 0.00	
3		– 1.55 ± 0.10	– 0.13 ± 0.01	0.03 ± 0.02
2	328.15 (b)	– 1.60 ± 0.08	– 0.09 ± 0.04	
3		– 1.56 ± 0.08	– 0.04 ± 0.19	– 0.09 ± 0.34
2	343.15 (b)	– 1.31 ± 0.05	– 0.11 ± 0.02	
3		– 1.39 ± 0.05	– 0.22 ± 0.05	0.20 ± 0.08
2	353.15 (b)	– 1.08 ± 0.05	– 0.09 ± 0.02	
3		– 1.18 ± 0.05	– 0.23 ± 0.03	0.25 ± 0.06
2	353.15 (e)	– 0.92 ± 0.10	– 0.14 ± 0.03	
3		– 1.00 ± 0.10	– 0.29 ± 0.08	0.37 ± 0.19
$2\,FeOH^{2+} \rightleftharpoons Fe_2(OH)_2^{4+}$				
2	291.15 (f)	1.57 ± 0.03	0.18 ± 0.05	
2	298.15 (f)	1.46 ± 0.04	0.21 ± 0.07	
2	305.15 (f)	1.34 ± 0.03	0.27 ± 0.06	

(a) These constants were assigned zero uncertainties to increase their weight to coincide with the selected values at 298.15 K. Obtained from fitting to the constants from Milburn and Vosburgh [1955MIL/VOS], Sapoeszko *et al*. [1977SAP/PAT], Zotov and Kotova [1979ZOT/KOT], Khoe *et al*. [1986KHO/BRO], Byrne *et al*. [2000BYR/LUO] and Stefansson [2007STE].

(b) Obtained from fitting to the constants from Sapoeszko *et al*. [1977SAP/PAT].

(c) Obtained from fitting to the constants from Sapoeszko *et al*. [1977SAP/PAT], and one data point from Byrne *et al*. [2000BYR/LUO].

(d) Obtained from fitting to the constants from Zotov and Kotova [1979ZOT/KOT].

(e) Obtained from fitting to the constants from Zotov and Kotova [1979ZOT/KOT], [1980ZOT/KOT].

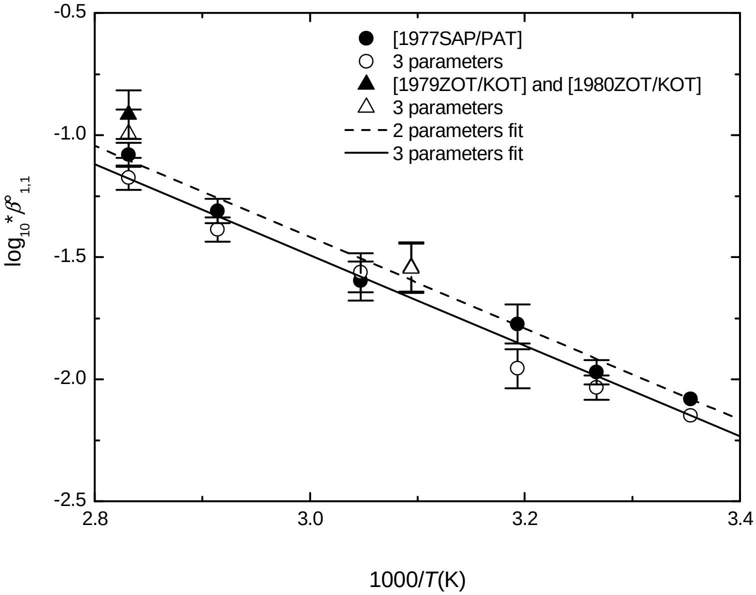
(f) Obtained from fitting to the constants from Milburn [1957MIL].

For the first hydrolysis constant the results were plentiful and provided the basis for application of the SIT over the temperature range, 298.15 to 353.15 K. Results were also available from [1980ZOT/KOT] at temperatures in excess of 373.15 K, but these were ignored in order to avoid the need for pressure corrections and because the focus is to obtain thermodynamic quantities for 298.15 K. The uncertainties used in these fits (illustrated by the error bars in Figure VII-8) were changed from the statistical values for the eight data sets listed in Table VII-8 with the uncertainty of the 298.15 K value being set to 0.00 to anchor the fit to maintain consistency with the corresponding Gibbs-energy values. From the two versions of the SIT, the weighted linear plots in Figure VII-8 yielded a temperature-independent value of $\Delta_r H^o_{1,1}$ ((VII.9), 298.15 K) that is selected in the present review:

$$\Delta_r H^o_{1,1}\ ((\text{VII.9}),\ 298.15\ \text{K}) = (36 \pm 3)\ \text{kJ}\cdot\text{mol}^{-1}.$$

The corresponding $\Delta_r G^o_{1,1}$ ((VII.9), 298.15 K) values for the two- and three-parameter fits are (11.9 ± 0.1) and (12.3 ± 0.1) $\text{kJ}\cdot\text{mol}^{-1}$, respectively, resulting in $\Delta_r S^o_{1,1}$ ((VII.9), 298.15 K) values of (80 ± 9) and (78 ± 10) $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

Figure VII-8: Temperature dependence of $\log_{10}{}^*\beta^o_{1,1}$ based on the two SIT extrapolations.

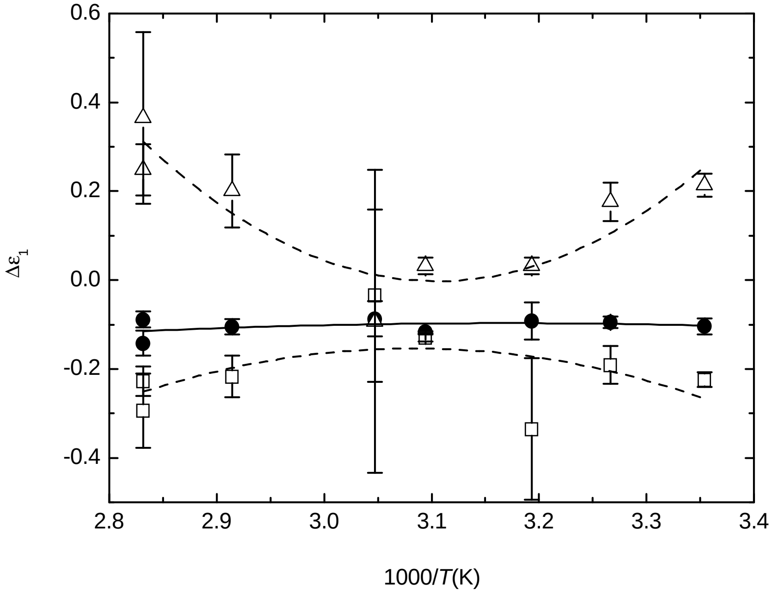


The apparent value of 0 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for $\Delta_r C^o_p$ for formation of the first hydrolysis species over the range of 55 K is not surprising, and is analogous to that found for the first hydrolysis reaction of Al^{3+} over a somewhat larger temperature interval [1993PAL/WES].

Arnek and Schlyter [1968ARN/SCH2] recalculated earlier calorimetric data from [1962SCH2], which had originally been treated graphically, and with the hydrolysis constants of Hedström [1953HED2] recommended $\Delta_r H_{1,1}$(3 M $NaClO_4$, 298.15 K) = (46 ± 8) $kJ\cdot mol^{-1}$ and a corresponding entropy of reaction of (96 ± 25) $J\cdot K^{-1}\cdot mol^{-1}$.

Figure VII-9 is presented merely to show that the $\Delta\varepsilon_i$ values listed in Table VII-8 are of a reasonable magnitude and follow smooth and minor trends with temperature, indicating that the application of the SIT has produced meaningful extrapolations of $\log_{10}{}^*\beta_{1,1}$ to infinite dilution.

Figure VII-9: Plot of $\Delta\varepsilon_i$ values as a function of reciprocal temperature in kelvin where ● represents the $\Delta\varepsilon$ values for the two-parameter fit, whereas ○ and Δ represent $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$ for the three-parameter fit. The curves are provided simply as a visual aid to follow their trends with temperature.



VII.1.3.2 The second hydrolysis constant

The second hydrolysis constant for the equilibrium,

$$Fe^{3+} + 2\,H_2O(l) \rightleftharpoons Fe(OH)_2^+ + 2\,H^+ \qquad (VII.10)$$

was the most poorly studied of the three main hydrolysis equilibria due to the presence of the dimerization equilibrium and the onset of precipitation of generally fine amorphous iron(III) hydroxide phase/s. In Table VII-7 there are only three studies listed where $\log_{10}{}^{*}\beta_{2,1}$ (VII.10) values are reported and of these it is immediately apparent that those from [1977SAP/PAT] are in sharp disagreement with those of the remaining two studies. Application of the SIT according to the equation:

$$\log_{10}{}^{*}\beta_{2,1}\,(\mathrm{VII.10}) + 6D - 2\log_{10}a_{\mathrm{w}} = \log_{10}{}^{*}\beta^{\circ}_{2,1}\,(\mathrm{VII.10}) - \Delta\varepsilon\, I_m$$

to the five $\log_{10}{}^{*}\beta_{2,1}$ (VII.10) values ([1977SAP/PAT], [1986KHO/BRO], [1990SAL/VAS]) derived from potentiometry at 298.15 K is illustrated in Figure VII-10. This weighted linear regression produced the values: $\log_{10}{}^{*}\beta^{\circ}_{2,1}$ (VII.10) = – (4.8 ± 0.4) (2σ) and $\Delta\varepsilon$ = – (0.08 ± 0.17) $\mathrm{kg{\cdot}mol^{-1}}$. The non-linear behaviour of $\varepsilon(\mathrm{Fe^{3+}}, \mathrm{ClO_4^-})$ as a function of ionic strength is presumably lost in the large uncertainty associated with the $\log_{10}{}^{*}\beta_{2,1}$ (VII.10) values, if indeed it is assumed that all of the non-linear dependence observed in the SIT treatment of the first hydrolysis constant can be ascribed to this term. It is difficult to reject the significantly lower values of $\log_{10}{}^{*}\beta_{2,1}$ (VII.10) that were based on a spectrophotometric study [2007STE] out of hand other than the fact that the reported adsorption maxima are very similar in magnitude and wavelength, *viz.*, for $\mathrm{Fe^{3+}}$ $\lambda_{\max}$ = 240 nm (ε = 380 – 420 $\mathrm{m^2{\cdot}mol^{-1}}$); $\mathrm{FeOH^{+}}$: $\lambda_{\max}$ = 205 nm (ε = 460 – 480 $\mathrm{m^2{\cdot}mol^{-1}}$) and $\lambda_{\max}$ = 297 nm (ε = 200 – 210 $\mathrm{m^2{\cdot}mol^{-1}}$); $\mathrm{Fe(OH)_2^+}$: $\lambda_{\max}$ = 242 nm (ε = 430 $\mathrm{m^2{\cdot}mol^{-1}}$) with a $\lambda_{\mathrm{shoulder}}$ = 339 nm (ε = 180 $\mathrm{m^2{\cdot}mol^{-1}}$). This makes the assignment of the absorbance for the $\mathrm{Fe(OH)_2^+}$ ion tenuous despite the large number of measurements made and the low concentrations of total iron(III) employed. More independent data for this minor species, which only becomes significant at pH values where colloids are readily formed, are needed and this is a problem common to other trivalent hydrolysable metal ions, such as $\mathrm{Al^{3+}}$ for example.

The value

$$\log_{10}{}^{*}\beta^{\circ}_{2,1}\,(\mathrm{VII.10}) = -\,(4.8 \pm 0.4)$$

is selected in the present review.

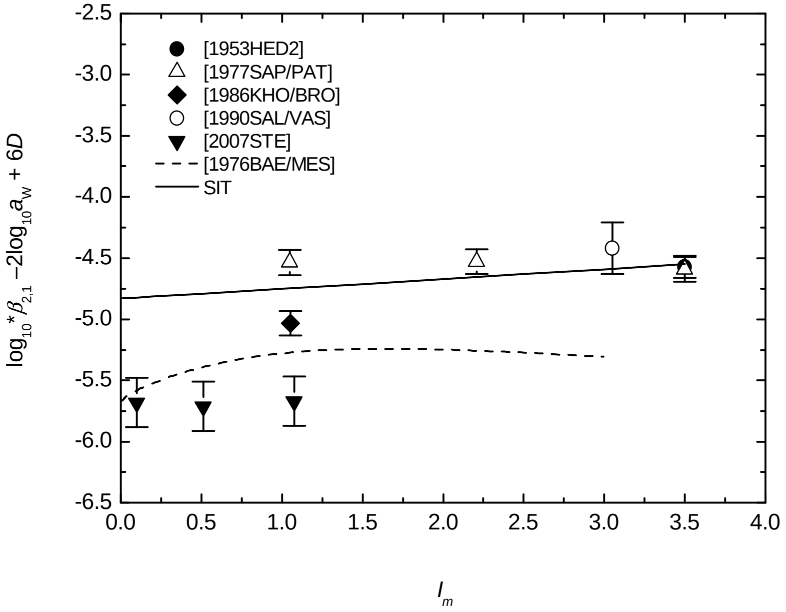
Using:

$$\Delta\varepsilon = \varepsilon(\mathrm{Fe(OH)_2^+}, \mathrm{ClO_4^-}) + 2\varepsilon(\mathrm{H^+}, \mathrm{ClO_4^-}) - \varepsilon(\mathrm{Fe^{3+}}, \mathrm{ClO_4^-})$$

$$\varepsilon(\mathrm{Fe(OH)_2^+}, \mathrm{ClO_4^-}) = -\,(0.08 \pm 0.17) - 2(0.14 \pm 0.02) + (0.73 \pm 0.04)$$

$$= (0.37 \pm 0.18)\ \mathrm{kg{\cdot}mol^{-1}}.$$

Figure VII-10: Plot of $\log_{10}{}^{*}\beta_{2,1}$ (VII.10) + 6D – 2$\log_{10} a_w$ *vs.* I_m in $NaClO_4$ medium for the second hydrolysis constant of Fe^{3+} at 298.15 K including a dashed curve generated from the fit created by Baes and Mesmer ([1976BAE/MES], Table 10.18) of the unspecified data available at that time.



VII.1.3.2.1 Temperature dependence of the second and higher hydrolysis constants of iron(III)

No acceptable studies of the second hydrolysis constant for iron(III) were found for temperatures other than 298.15 K.

VII.1.3.3 The hydrolysis equilibrium for the formation of the dimer

Baes and Mesmer [1976BAE/MES] summarized the kinetic data available at that time from pressure-jump and stopped-flow experiments for the decomposition of the $Fe_2(OH)_2^{4+}$ dimer that gave a consistent set of rate constants which corresponded to a two-term rate law:

$$\frac{-\mathrm{d}[Fe_2(OH)_2^{4+}]}{\mathrm{d}t} = (k_1 + k_2[H^+])[Fe_2(OH)_2^{4+}]$$

The combined studies extended from 287.45 to 307.95 K with $k_1 = (0.4 \pm 0.2)\ s^{-1}$ and $k_2 = (3.1 \pm 0.4)\ M^{-1}\cdot s^{-1}$ at 298.15 K. However, around that time Vértes *et al.*

[1973VER/RAN] used Mössbauer spectroscopy to interrogate the Fe(II)/Fe(III) electron-exchange reaction and reported rate constants for dimer decomposition in the range (0.8 to 1.7) × 10^{-3} s^{-1} at 298.15 K in 1 M ClO_4^-, SO_4^{2-}, NO_3^- and Cl^- at pH (2.25 ± 0.05) where the acid-catalyzed path can be neglected. Interestingly, these authors claim that their k_1 values, which are at least a factor of 200 smaller than those reported by Baes and Mesmer, correspond to the true decomposition step, whereas the previous two spectrophotometric studies in fact resulted from the rapid initial protonation of the dimer. However, this contention by Vértes *et al.* implies half-lives for the formation of the dimer (considered as a condensation step involving two $FeOH^{2+}$ cations) on the order of hours at 298.15 K at pH > 2 which is not consistent with the results of many investigations of this equilibrium. However, the rate constant for the formation of the dimer is still *ca.* 1 × 10^{-3} s^{-1} under these conditions, implying a half-life of *ca.* ten minutes such that titrations must be carried out very slowly, preferably with small increments of titrant (to avoid localized precipitation) to achieve equilibrium throughout the whole titration.

Thermodynamic results for the dimerization equilibrium, $2\,FeOH^{2+} \rightleftharpoons Fe_2(OH)_2^{4+}$, are presented in Table VII-7 and are indicated by asterisks. This equilibrium was studied by spectrophotometry, [1955MIL/VOS] [1957MIL], and by potentiometry [1953HED2]. The dimerization constant within the SIT is represented as:

$$\log_{10} K_{2,2} - 8D = \log_{10} K^{o}_{2,2} - \Delta\varepsilon\, I_m$$

However, to reduce the large $|\Delta z^2|$ associated with this equilibrium and to eliminate the need to rely on each author's choice of the $\beta_{1,1}$, the dimerization constants were converted here to the combined equilibrium constant using the $\beta_{1,1}$ values derived in this review. The combined or overall formation equilibrium is,

$$2\,Fe^{3+} + 2\,H_2O(l) \rightleftharpoons Fe_2(OH)_2^{4+} + 2\,H^+ \qquad (VII.11)$$

and can be conveniently represented by the following SIT expression for which $\Delta z^2 = 0$:

$$\log_{10} {}^*\beta_{2,2}\,(VII.11) - 2\log_{10} a_w = \log_{10} {}^*\beta^{o}_{2,2}\,(VII.11) - \Delta\varepsilon\, I_m.$$

Figure VII-11 presents a plot of the left-hand side of the above equation *vs.* I_m where the uncertainties shown were assigned during the data reduction process, because in all cases the reported uncertainties appear to be over optimistic, representing the goodness of fit rather than real experimental uncertainties.

The weighted linear fit to all the data shown in Figure VII-11 yields: $\log_{10} {}^*\beta^{o}_{2,2}$ (VII.11) = – (2.82 ± 0.07); $\Delta\varepsilon$ = – (0.14 ± 0.05) kg·mol^{-1} (2σ). As with the linear plot in Figure VII-10, any potential curvature imposed by the non-linear $\varepsilon(Fe^{3+}, ClO_4^-)$ term is masked by the scatter of the data. For comparison of the result of this fit, the previously reported $\log_{10} {}^*\beta^{o}_{2,2}$ (VII.11) value by Baes and Mesmer is – 2.95 [1976BAE/MES] at 298.15 K based on a smaller data set. Therefore this review accepts:

$$\log_{10} {}^{*}\beta^{\circ}_{2,2}\,(\text{VII.11}) = -\,(2.82 \pm 0.07).$$

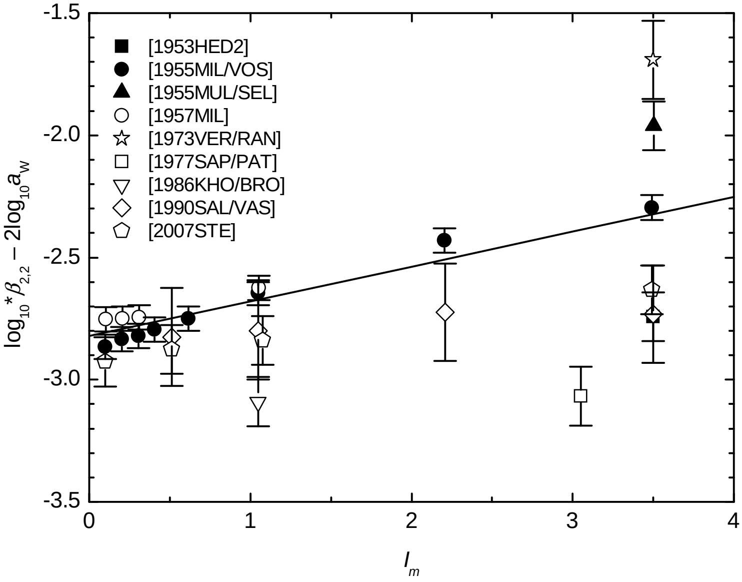
Using:

$$\Delta\varepsilon = \varepsilon(\mathrm{Fe_2(OH)_2^{4+}}, \mathrm{ClO_4^-}) + 2\varepsilon(\mathrm{H^+}, \mathrm{ClO_4^-}) - 2\varepsilon(\mathrm{Fe^{3+}}, \mathrm{ClO_4^-})$$

$$\varepsilon(\mathrm{Fe_2(OH)_2^{4+}}, \mathrm{ClO_4^-}) = -\,(0.14 \pm 0.05) - 2(0.14 \pm 0.02) + 2(0.73 \pm 0.04)$$

$$= (1.04 \pm 0.10)\ \mathrm{kg{\cdot}mol^{-1}}$$

Figure VII-11: Plot of $\log_{10} {}^{*}\beta_{2,2}\,(\text{VII.11}) - 2\log_{10} a_{\mathrm{w}}$ *vs.* I_m in $\mathrm{NaClO_4}$ medium for the formation constant of $\mathrm{Fe_2(OH)_2^{4+}}$ at 298.15 K.



VII.1.3.3.1 Temperature dependence of the equilibrium formation of the dimer.

For the formation of the dimer, $\mathrm{Fe_2(OH)_2^{4+}}$, there are two isolated values of $\log_{10}{}^{*}\beta^{\circ}_{2,2}\,(\text{VII.11})$ at $I_m = 3.05$ ($\mathrm{NaClO_4}$) at 328.15 and 353.15 K [1977SAP/PAT], and five values at $I_m = 3.50$ ($\mathrm{NaClO_4}$) from 288.15 to 324.15 K [1955MUL/SEL], but only Milburn [1957MIL] provided $\log_{10}\beta^{\circ}_{2,2}\,(\text{VII.11})$ constants as a function of ionic strength (0.104 to 1.05) at three, albeit relatively low, temperatures, *viz.*, 291.15, 298.15 and 305.15 K. These dimerization constants were subjected to a SIT analysis which produced the values shown in Table VII-8; we note that the plots of these limited results are linear in I_m. Taking the corresponding smoothed values of $\log_{10}{}^{*}\beta_{1,1}$ as a function of temperature (Figure VII-8), the $\log_{10}{}^{*}\beta^{\circ}_{2,2}\,(\text{VII.11})$ values at 291.15, 298.15 and

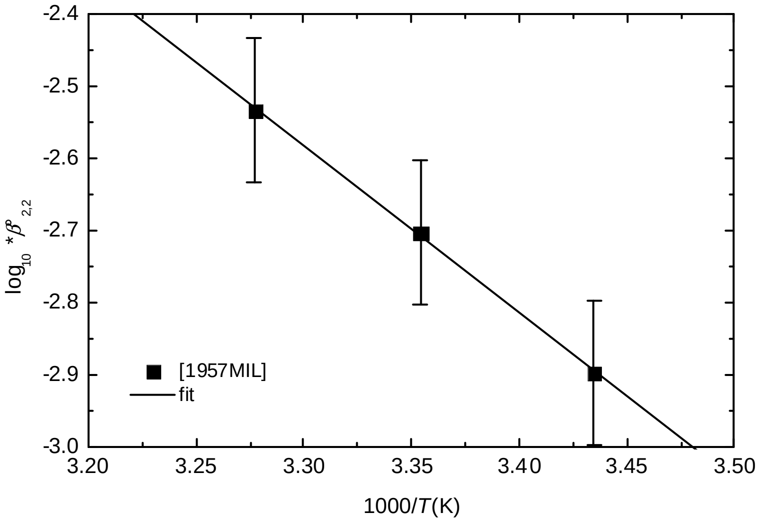
305.15 K are estimated as – 2.90, – 2.70 and – 2.53, respectively, with an uncertainty of ± 0.10 (1σ). A plot of $\log_{10} {}^*\beta^{o}_{2,2}$ (VII.11) as a function of the reciprocal temperature in kelvin is shown in Figure VII-12 from which the selected value

$$\Delta_r H^{o}_{2,2}\,((\text{VII.11}), 298.15\ \text{K}) = (44 \pm 3)\ \text{kJ}\cdot\text{mol}^{-1}$$

is estimated (2σ uncertainty). The smoothed $\log_{10} {}^*\beta^{o}_{2,2}$ (VII.11) value at 298.15 K obtained from the van't Hoff equation is – 2.71 in keeping with the value of – 2.82 (Section VII.1.3.3) derived from all the $\log_{10} {}^*\beta_{2,2}$ (VII.11) data for 298.15 K (Table VII-7). Furthermore, a van't Hoff plot of the $\log_{10} {}^*\beta_{2,2}$ (VII.11) results from [1955MUL/SEL] at $I_m = 3.50$ ($NaClO_4$) yielded a very similar value for $\Delta_r H_{2,2}$ (VII.11) of (42 ± 8) kJ·mol^{-1} (2σ); we note that despite the high charges involved, for this reaction $\Delta z^2 = 0$.

Arnek and Schlyter [1968ARN/SCH2] recommended $\Delta_r H$ ((VII.11), 3 M $NaClO_4$, 298.15 K) = (42 ± 2) kJ·mol^{-1} and a corresponding entropy of reaction of (84 ± 5) J·K^{-1}·mol^{-1}.

Figure VII-12: Plot of the $\log_{10} {}^*\beta^{o}_{2,2}$ (VII.11) values as a function of the reciprocal temperature (kelvin).



VII.1.3.4 The hydrolysis equilibrium for the formation of the trimer

The trimer, $Fe_3(OH)_4^{5+}$, has been reported in only very limited studies, [1962SCH2] and [1986KHO/BRO] where it was postulated to occur as a minor species before precipitation occurs [1976BAE/MES]. Most significantly, in the latter study the trimer was not identified in their data treatment in 1 M $NaClO_4$ solution, whereas they reported $\log_{10} {}^*\beta_{4,3}$ values of $-(6.94 \pm 0.11)$ and $-(7.55 \pm 0.13)$ in 1 M KNO_3 and KCl, respectively. The same pH and iron(III) concentration ranges were covered in all three media leading this review to speculate that if this species exists at all, it may well incorporate an anion from the medium in its structure, although chloride would be expected to bond more strongly than nitrate. Consequently, in selecting hydrolysis constants for the other, well-established species from the data of Khoe *et al.* [1986KHO/BRO], the scheme was chosen in which the (4,3) species was excluded.

VII.1.3.5 Other hydrolysis equilibria

For the formation of the neutral $Fe(OH)_3(aq)$ species according to the equilibrium:

$$Fe^{3+} + 3\ H_2O(l) \rightleftharpoons Fe(OH)_3(aq) + 3\ H^+ \qquad (VII.12)$$

only one reference [2007STE], which deals with a solubility study of fine-grained ferrihydrite (see solubility section), provides a provisional maximum value of $\log_{10} {}^*\beta^{\circ}_{3,1}$ (VII.12) ≤ -14, which is given here without any corroboration, and will be a difficult constant to determine in the future.

The hydrolysis constant for the formation of the tetrahedral $Fe(OH)_4^-$ anion according to the equilibrium

$$Fe^{3+} + 4\ H_2O(l) \rightleftharpoons Fe(OH)_4^- + 4\ H^+ \qquad (VII.13)$$

could only be estimated based on solubility experiments with metastable ferrihydrite [2007STE] that provided a provisional value of $\log_{10} {}^*\beta^{\circ}_{4,1}$ (VII.13)= $-(21.5 \pm 0.5)$, which in turn leads to $\Delta_r G^{\circ}_m$ (VII.13) = (123 ± 3) $kJ\cdot mol^{-1}$ at 298.15 K.

VII.1.4 Solubility of Fe(III) Phases

Many early solubility products for "ferric hydroxide", such as those compiled by Evans and Pryor [1949EVA/PRY], are concentration-based values, $K_s = c_{Fe^{3+}} c_{OH^-}{}^3$, for uncharacterized, freshly precipitated material, uncorrected for either hydrolysis or ion-solution interaction. They therefore tend to overestimate K_s severely (by up to four or five orders of magnitude); values cited by [1949EVA/PRY] range from $10^{-34.5}$ to $10^{-37.9}$. Cooper [1937COO] re-evaluated data from Kriukov and Awsejewitsch [1933KRI/AWS] and obtained a best estimate of $10^{-38.6}$ for the activity product of freshly precipitated "$Fe(OH)_3$". This agrees with a turbidimetric value of $10^{-(38.6 \pm 0.4)}$, also for freshly precipitated material and corrected for speciation and activity [1964PLA].

Comparable solubility products for ferrihydrite have been obtained in studies of natural systems. For example, a solubility study using an edta complexation technique on three nearly neutral soil specimens, likely containing ferrihydrite as the saturating phase, gave an average activity-based solubility product of $10^{-(39.3 \pm 0.4)}$

[1982NOR/LIN]. The complex speciation involved in this study makes a full evaluation difficult. Solution analysis of polluted stream waters and mine tailings containing schwertmannite ($Fe_8O_8(OH)_{8-2x}(SO_4)x\cdot nH_2O(s)$ where $1.74 \le x \le 1.86$ and $8.17 \le n \le 8.62$) and/or ferrihydrite [1999YU/HEO] yielded a bracketed value of $a_{Fe^{3+}}a_{OH^-}{}^3 = 10^{-(38.7 \pm 0.5)}$ at 288.15 K.

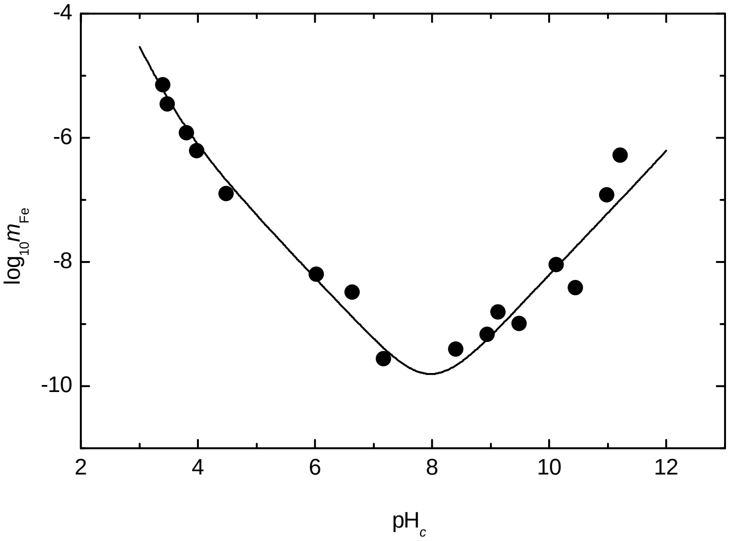
It has long been recognized that the apparent solubility of precipitated "$Fe(OH)_3$" declines with aging, and that of a solid mixture is governed by the least stable component. Gayer and Woontner [1956GAY/WOO] studied "ferric hydroxide" precipitates, but with aging conditions severe enough (several weeks near 373.15 K) that their specimens were probably altered to hematite and/or goethite. A series of comparative measurements on "active" and "inactive" precipitated iron(III) hydroxide and synthetic goethite in 3 M perchlorate medium [1957BIE/SCH], [1961LEN/BUS], [1963SCH/MIC] is relevant to the relative stability of ferrihydrites and is therefore discussed in Section VII.2.15.2.

Kinetic factors may rationalize the thermodynamically inexplicable activity correlation obtained by Fox [1988FOX] for synthetic and natural "colloidal ferric hydroxide" specimens:

$$a_{Fe^{3+}}(a_{OH^-})^{2.35} = 10^{-31.7}.$$

Stefansson [2007STE] measured the solubility of 2-line ferrihydrite at 0.01 M ($NaClO_4$) ionic strength at 298.15 K. The results are only shown in a plot of $\log_{10} m_{Fe}$ *vs.* "pH" which is reproduced in Figure VII-13. In this case study, 2-line ferrihydrite was acknowledged as not being a stable crystalline phase, but the author reported that no physical change occurred to the solid during the course of the experiments. Therefore, it is possible that hydrolysis constants derived from the solubility constants may be of value, particularly in alkaline media where no other low-temperature data are available. It must also be acknowledged that the activity coefficients and water activity corrections have been ignored considering the low ionic strength (0.01 M). The solubility profile in Figure VII-13 (solid curve) was based on the following solubility constants deduced from [2007STE]: $\log_{10} {}^*\beta^{\circ}_{s,0} = 3.5$, $\log_{10} {}^*\beta^{\circ}_{s,1} = 1.3$, $\log_{10} {}^*\beta^{\circ}_{s,2} = -2.3$, $\log_{10} \beta^{\circ}_{s,3} = \le -11$ and $\log_{10} {}^*\beta^{\circ}_{s,4} = -(18.2 \pm 0.5)$. These solubility constants led to the following hydrolysis constants: $\log_{10} {}^*\beta^{\circ}_{1,1} = -2$, $\log_{10} {}^*\beta^{\circ}_{2,1} = -6$, $\log_{10} {}^*\beta_{3,1} \le -14$, and $\log_{10} {}^*\beta^{\circ}_{4,1} = -21.5$. The value of $\log_{10} {}^*\beta^{\circ}_{1,1}$ is within reasonable agreement with that obtained by other techniques, *viz.*, between -2.09 and -2.15, especially considering how few solubility data points are available at low pH_c, and the inherent unreliability of solubility measurements of metastable solid phases. However, the value of ${}^*\beta^{\circ}_{2,1}$ is an order of magnitude smaller than the one calculated from the combined data of Hedström [1953HED2] and Salvatore and Vasca [1990SAL/VAS].

Figure VII-13: Solubility dependence of ferrihydrite *vs.* pH_c at 298.15 K reproduced digitally from the Figure 3 in [2007STE].



A similar case was presented earlier by Liu and Millero [1999LIU/MIL] who also used a metastable iron(III) phase, $\mathrm{Fe(OH)_3(am)}$, to measure the solubility at 298.15 K as a function of pH and ionic strength. Although the pH range did not extend to low pH where $\mathrm{Fe^{3+}}$ is the dominant iron(III) species in solution, they were able to determine solubility products involving $\mathrm{FeOH^{2+}}$, $\mathrm{Fe(OH)_2^+}$ and $\mathrm{Fe(OH)_4^-}$ with the $\mathrm{Fe(OH)_3(aq)}$ species being too insignificant to detect in the data analysis, which is shown in the synopsis [1999LIU/MIL]. The absence of detectable $\mathrm{Fe(OH)_3(aq)}$ in solution is consistent with the finding for ferrihydrite [2007STE], but somewhat surprising considering that this species has a wide pH stability field at high temperatures. Using the same logic as applied above for the [2007STE] solubility data and applying the SIT resulted for the hydrolysis equilibria,

$$\mathrm{FeOH^{2+} + H_2O(l) \rightleftharpoons Fe(OH)_2^+ + H^+} \qquad \text{(VII.14)}$$

$$\mathrm{Fe(OH)_2^+ + 2\,H_2O(l) \rightleftharpoons Fe(OH)_4^- + 2\,H^+} \qquad \text{(VII.15)}$$

resulted in the following quantities: $\log_{10} {}^*K^{\circ}_{2,1} = -(3.3 \pm 0.2)$ and $\Delta\varepsilon = (0.00 \pm 0.08)$ $\mathrm{kg{\cdot}mol^{-1}}$, and $\log_{10} {}^*\beta^{\circ}_{4,1} / {}^*\beta^{\circ}_{2,1} = -(17.38 \pm 0.16)$ and $\Delta\varepsilon = -(0.17 \pm 0.07)$ $\mathrm{kg{\cdot}mol^{-1}}$. Combining these results with those recommended for the first hydrolysis constant, *viz.*, $\log_{10} {}^*\beta^{\circ}_{1,1} = -(2.15 \pm 0.03)$ and $\Delta\varepsilon = -(0.13 \pm 0.03)$ $\mathrm{kg{\cdot}mol^{-1}}$, yields $\log_{10} {}^*\beta^{\circ}_{2,1} = -(5.45 \pm 0.20)$ and $\Delta\varepsilon = -(0.13 \pm 0.09)$ $\mathrm{kg{\cdot}mol^{-1}}$, which are within the combined uncertainties of the (rounded) recommended values of $\log_{10} {}^*\beta^{\circ}_{2,1} = -(4.8 \pm 0.4)$ and

$\Delta\varepsilon = -(0.1 \pm 0.2)$ kg·mol^{-1}. Similarly, Eq. (VII.15) can be converted to the fourth hydrolysis constant: $\log_{10} {}^{*}\beta^{\circ}_{4,1} = -(19.5 \pm 0.2)$ and $\Delta\varepsilon = -(0.17 \pm 0.11)$ kg·mol^{-1} (*cf.*, $\log_{10} {}^{*}\beta^{\circ}_{4,1}$ of $-(20.8 \pm 2.9)$ discussed below and obtained for crystalline hematite at high temperatures, *i.e.*, ≥ 333.15 K, and $\log_{10} {}^{*}\beta^{\circ}_{4,1} = -21.5$ obtained for ferrihydrite). Clearly these results support the hypothesis that reasonable hydrolysis equilibrium constants can be obtained from solubility studies of relatively long-lived metastable phases at ambient temperatures, probably with more precision than can be obtained by extrapolation of solubility results obtained for stable crystalline phases at high temperatures.

Berner [1969BER] conducted batch solubility experiments with “fine-grained” hematite and goethite in 0.12 mol·kg^{-1} HCl at 358.15 K according to the equilibria:

$$\tfrac{1}{2}\,\mathrm{Fe_2O_3(cr)} + 3\,\mathrm{H^+} \rightleftharpoons \mathrm{Fe^{3+}} + 1\tfrac{1}{2}\,\mathrm{H_2O(l)} \qquad \text{(VII.16)}$$

$$\mathrm{FeOOH(cr)} + 3\,\mathrm{H^+} \rightleftharpoons \mathrm{Fe^{3+}} + 2\,\mathrm{H_2O(l)} \qquad \text{(VII.17)}$$

with two attempted reversal experiments for hematite that approached the solubilities obtained from undersaturation after 150 days with rocking. There are unanswered questions regarding the degree of crystallinity and particle size of the solid phases such that mean solubilities of 5.09×10^{-4} and 1.17×10^{-3} mol·kg^{-1}, respectively, must be viewed with caution.

Taylor and Owen [1997TAY/OWE] attempted to measure the equilibrium solubilities of well-characterized crystalline hematite and maghemite in batch experiments at 298.15 K in dilute nitric acid solutions where equilibrium (VII.16) is dominant. After correction for the first hydrolysis constant, application of SIT produced $\log_{10} {}^{*}\beta^{\circ}_{s,0}$ values for hematite and maghemite of (0.62 ± 0.42) and (1.87 ± 0.20), respectively, corresponding to $\Delta_r G$ ((VII.16), 298.15 K) values of $-(0.7 \pm 0.3)$ and $-(2.0 \pm 0.2)$ kJ·mol^{-1}, respectively. These and some earlier studies on maghemite solubility are discussed further in Section VII.2.4.2.

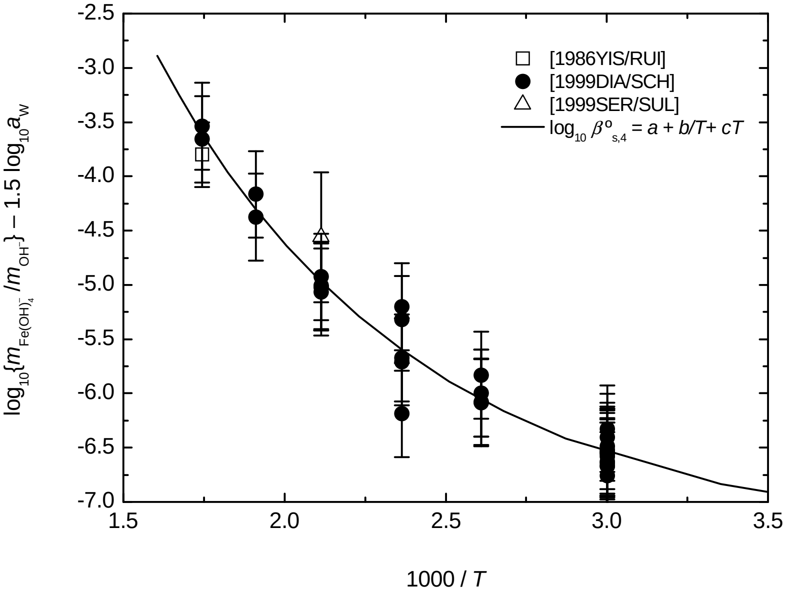
Hsu and Marion [1985HSU/MAR] also used a batch technique at 298.15 K to measure the solubility of crystalline goethite, which was formed *in situ*, with equilibration times exceeding twelve years. Some samples also contained lepidocrocite but these data were not analyzed. Application of the SIT gave a value of $\log_{10} {}^{*}\beta^{\circ}_{s,0}$ for goethite of (2.17 ± 0.10). This appears to be a careful study, although the uncertainty is unrealistically small and no confirming data are available; however, the solubility is higher than expected from the thermodynamic data evaluation for goethite in Section VII.2.9 (see also Section VII.2.16).

One of the most comprehensive solubility studies of well-characterized crystalline hematite in alkaline solution was carried out by Diakonov *et al.* [1999DIA/SCH] from 333.15 to 573.15 K under conditions where the $\mathrm{Fe(OH)_4^-}$ anion is assumed to dominate the speciation of Fe(III) in solution. The dissolution equilibrium can be written conveniently in the basic form:

$$\frac{1}{2}\ Fe_2O_3(cr) + 1\frac{1}{2}\ H_2O(l) + OH^- \rightleftharpoons Fe(OH)_4^- \qquad (VII.18)$$

which eliminates the Debye-Hückel term in fitting the solubility constants. In order to extrapolate these data, which were generally obtained at relatively low ionic strengths ($\leq$ 0.2001 $mol\cdot kg^{-1}(H_2O)$), to 298.15 K this form of the equilibrium should provide the most conservative (more linear) approach. From the results of Diakonov *et al.* and taking the activities of water for NaCl solutions from Archer [1992ARC], a plot of $\log_{10}\{m_{Fe(OH)_4^-}/m_{OH^-}\}+1.5\log_{10}a_W$, which is equivalent to $\log_{10}\beta^{\circ}_{s,4}$, *vs.* 1/*T* (kelvin), shown in Figure VII-14, provides a simple extrapolation to T = 298.15 K.

Figure VII-14: Solubility data mainly from [1999DIA/SCH] for crystalline hematite in basic solutions as a function of reciprocal temperature (K).



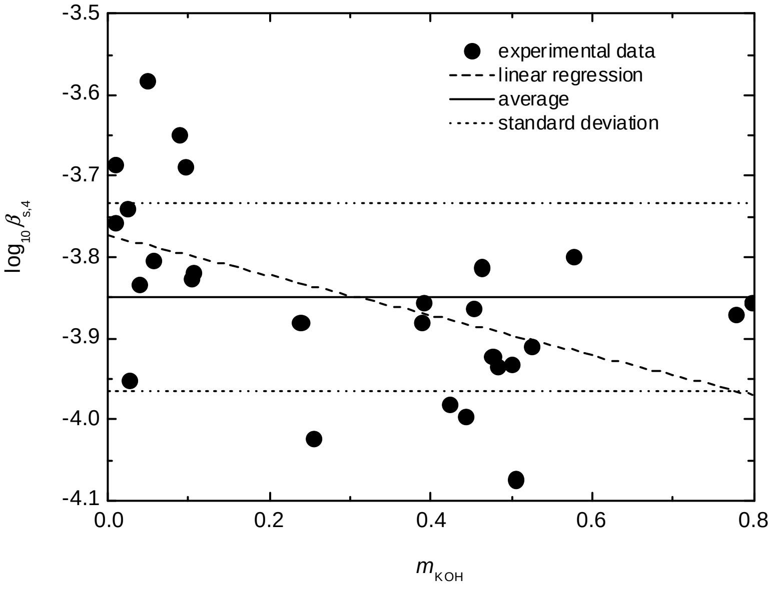
The scatter in the data at each temperature exceeds any isothermal trends due to the assumption of ignoring the differences in the activity coefficients of OH^- and $Fe(OH)_4^-$. Moreover, the agreement with the earlier comprehensive data set at 573.15 K [1986YIS/RUI] is quite satisfactory (see next paragraph), although the more limited study of the same equilibrium by Sergeeva *et al.* [1999SER/SUL] at 473.15 K showed less satisfactory agreement, but within the combined expanded uncertainty limits. The degree of curvature in this plot is surprising when compared to analogous plots for the corresponding aluminium system and considering the isocoulombic nature of the equilibrium. Nevertheless, the simple fitting equation

$$\log_{10} \beta^{\circ}_{s,4} = a + b/(T/\mathrm{K}) + c(T/\mathrm{K}) \qquad \text{(VII.19)}$$

yielded the parameters: $a = -(14.81 \pm 2.26)$, $b = (878.0 \pm 464.0)$ and $c = (0.01688 \pm 0.00267)$. This fit gives a 298.15 K value for $\log_{10} \beta^{\circ}_{s,4}$ of $-(6.8 \pm 2.9)$ which would correspond to a value of $\log_{10} {}^{*}\beta^{\circ}_{4,1}$ of $-(21.4 \pm 2.9)$ when combined with $\log_{10} \beta^{\circ}_{s,0} = (0.6 \pm 0.4)$ [1997TAY/OWE], *cf.*, the provisional value from [2007STE] of $\log_{10} {}^{*}\beta^{\circ}_{4,1} = -(21.5 \pm 0.5)$.

Regardless of how the solubility data from [1986YIS/RUI] in Figure VII-15 are extrapolated to infinite dilution, the $\log_{10} \beta^{\circ}_{s,4}$ value for the equilibrium, ½ Fe_2O_3(cr) + OH^- + 1½ H_2O(l) $\rightleftharpoons$ $Fe(OH)_4^-$, is $-(3.8 \pm 0.1)$ at 573.15 K, which is in reasonable agreement with the solubility data in [1999DIA/SCH] (see their value plotted in Figure VII-14).

Figure VII-15: Solubility data from [1986YIS/RUI] for crystalline hematite in KOH solutions at 573.15 K as a function of hydroxide ion molality.



The solubility products obtained from studies where the solid phase was clearly identified as being crystalline and was well characterized throughout the study are summarized in Table VII-9.

Baron and Palmer [1996BAR/PAL] studied the solubility of jarosite from 276.15 to 308.15 K in acidic solutions where the dissolution equilibrium may be represented as:

$$\mathrm{KFe_3(SO_4)_2(OH)_6(s) + 6\,H^+ \rightleftharpoons K^+ + 3\,Fe^{3+} + 2\,SO_4^{2-} + 6\,H_2O(l)} \qquad \text{(VII.20)}$$

although their analysis of the synthetic solid phase gave an approximate formula, $\mathrm{K_{0.98}(H_3O)_{0.02}Fe_{2.79}(SO_4)_2(OH)_{5.37}{\cdot}0.63H_2O}$. A re-evaluated $\log_{10}{}^*\beta_\mathrm{s}$ value at 298.15 K of − 9.8 is suggested that is quite different from the values of *ca.* − 11.1 proposed by the original authors. However, the uncertainties in the stoichiometry of jarosite, as well as particle size and crystallinity variations, and more importantly the more recent detailed experimental and simulation results for jarosite dissolution [2006SMI/HUD] that provide sound evidence that this reaction is incongruent even in acidic solutions, render these estimates of $\log_{10}{}^*\beta_\mathrm{s}$ as being speculative at best. As an illustration of this point, the same can be said of studies of ferrihydrite [2007STE] and schwertmannite [1999YU/HEO], discussed above.

Table VII-9: Solubility products of crystalline iron(III) oxy/hydroxides.

Equilibrium	T/K	$\log_{10}{}^*\beta^{\mathrm{o}}_{\mathrm{s},n}$	Reference
$\frac{1}{2}\,\alpha\text{-}\mathrm{Fe_2O_3} + 3\,\mathrm{H^+} \rightleftharpoons \mathrm{Fe^{3+}} + 1\frac{1}{2}\,\mathrm{H_2O(l)}$	473.15	− 4.54 ± 0.36	[1999SER/SUL]
$\frac{1}{2}\,\alpha\text{-}\mathrm{Fe_2O_3} + 2\,\mathrm{H^+} \rightleftharpoons \mathrm{FeOH^{2+}} + \frac{1}{2}\,\mathrm{H_2O(l)}$	473.15	− 3.88 ± 0.36	
$\frac{1}{2}\,\alpha\text{-}\mathrm{Fe_2O_3} + 2\frac{1}{2}\,\mathrm{H_2O(l)} \rightleftharpoons \mathrm{Fe(OH)_4^-} + \mathrm{H^+}$	473.15	− 15.9 ± 0.2	
$\alpha\text{-}\mathrm{FeOOH} + 3\,\mathrm{H^+} \rightleftharpoons \mathrm{Fe^{3+}} + 2\,\mathrm{H_2O(l)}$	298.15	2.2 ± 0.1	[1985HSU/MAR]
$\frac{1}{2}\,\alpha\text{-}\mathrm{Fe_2O_3} + 3\,\mathrm{H^+} \rightleftharpoons \mathrm{Fe^{3+}} + 1\frac{1}{2}\,\mathrm{H_2O(l)}$	298.15	0.79 ± 0.35	[1997TAY/OWE]
$\frac{1}{2}\,\gamma\text{-}\mathrm{Fe_2O_3} + 3\,\mathrm{H^+} \rightleftharpoons \mathrm{Fe^{3+}} + 1\frac{1}{2}\,\mathrm{H_2O(l)}$	298.15	2.06 ± 0.25	
$\frac{1}{2}\,\alpha\text{-}\mathrm{Fe_2O_3} + 2\frac{1}{2}\,\mathrm{H_2O(l)} \rightleftharpoons \mathrm{Fe(OH)_4^-} + \mathrm{H^+}$	573.15	− 15.2 ± 0.1	[1986YIS/RUI]
$\frac{1}{2}\,\alpha\text{-}\mathrm{Fe_2O_3} + 2\frac{1}{2}\,\mathrm{H_2O(l)} \rightleftharpoons \mathrm{Fe(OH)_4^-} + \mathrm{H^+}$	298.15 (a)	− 20.8 ± 2.9	[1999DIA/SCH]
$\frac{1}{2}\,\alpha\text{-}\mathrm{Fe_2O_3} + 3\,\mathrm{H^+} \rightleftharpoons \mathrm{Fe^{3+}} + 1\frac{1}{2}\,\mathrm{H_2O(l)}$	298.15	0.15	[2004WES/ZIE] (b)
$\frac{1}{2}\,\alpha\text{-}\mathrm{Fe_2O_3} + 2\,\mathrm{H^+} \rightleftharpoons \mathrm{FeOH^{2+}} + \frac{1}{2}\,\mathrm{H_2O(l)}$		− 2.1	

(a) extrapolated from data taken over the range 333.15 − 573.15 K

(b) obtained from a fit of existing data at that time

The solubilities of other phases studied include $\mathrm{Fe(OH)_{2.70}Cl_{0.30}}$ at 298.15 K [1966BIE/CHO], hydrous iron(III) oxide [1976BYR/KES], [1988FOX], [1989COR/GIO], [1993KUM/SUZ], [1999LIU/MIL], as well as microcrystalline goethite [1985HSU/MAR].

As a general interest matter, which is only on the periphery of relevance to this review, Tamaura and Katsura [1983TAM/ITO] provide kinetic experimental evidence for the transformation of γ-FeOOH to stoichiometric $\mathrm{Fe_3O_4}$ ($\mathrm{Fe^{2+}} + 2\,\gamma\text{-}\mathrm{FeOOH(s)} \rightarrow \mathrm{Fe_3O_4(s)} + 2\,\mathrm{H^+}$) at 298.15 K. The mechanism involves the initial rapid adsorption of

Fe^{2+} ion onto lepidocrocite surfaces under slightly to strongly basic conditions followed by the slow insertion of the Fe(II) into the structure. It is surprising that this process could be monitored at room temperature and certainly increasing temperature will increase the surface adsorption constant and the rate of interconversion. This process provides a plausible general mechanism for the formation of mixed-metal ferrites.

VII.2 Iron oxides and oxyhydroxides

The Fe-O-H_2O system includes several metastable solid phases, plus some that are stable only at elevated temperature and/or pressure. Some of the metastable phases transform exceedingly slowly under ambient conditions. The only thermodynamically stable solid oxides near 298.15 K and atmospheric pressure appear to be magnetite (Fe_3O_4) and hematite (α-Fe_2O_3), although goethite (α-FeOOH) is only marginally metastable with respect to Reaction (VII.21).

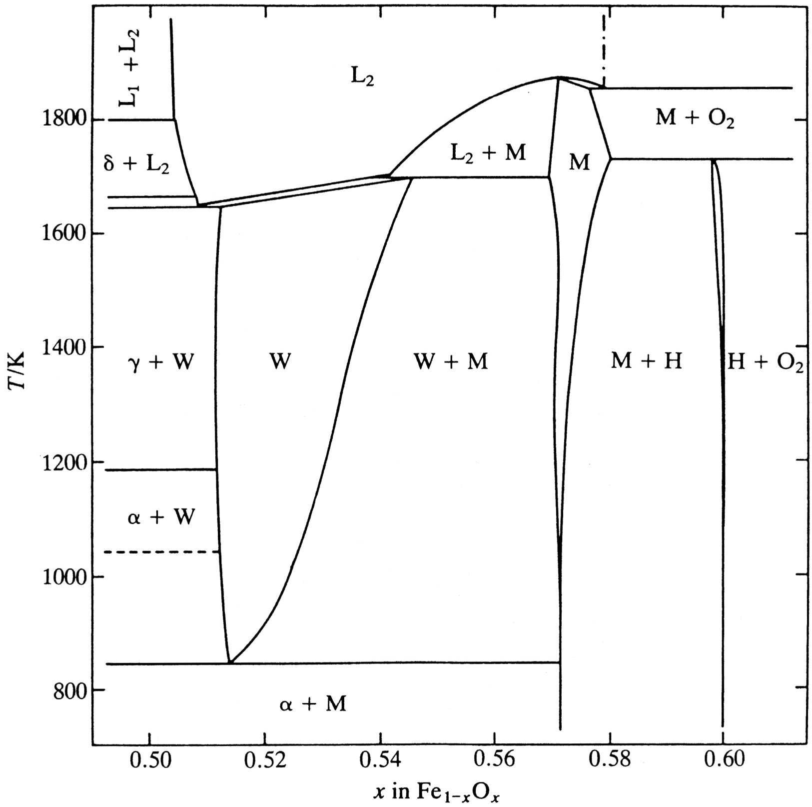
$$\alpha\text{-FeOOH} \rightleftharpoons \tfrac{1}{2}\,\alpha\text{-Fe}_2\text{O}_3 + \tfrac{1}{2}\,\text{H}_2\text{O(l)} \qquad \text{(VII.21)}$$

Magnetite, hematite, and the high-temperature phase wüstite ($Fe_{1-x}O$) are the only stable oxides in the Fe-O phase diagram at ambient pressure (Figure VII-16). They are therefore the only oxides that are readily prepared in a highly crystalline form, though care is needed with control of redox conditions and (for wüstite) quenching to ambient temperature. Well-crystallized mineral specimens of goethite and lepidocrocite (γ-FeOOH) are rare, while the best synthetic specimens of these and the less-common oxyhydroxides rarely exceed 1 μm in the longest crystal dimension and commonly have specific surface areas exceeding $10\ m^2 \cdot g^{-1}$. The coherently scattering crystalline domains in ferrihydrite (“ferric hydroxide”; see Sections VII.2.14 and VII.2.15) are typically only 1 to 6 nm in diameter, with specific surface areas exceeding $200\ m^2 \cdot g^{-1}$. Therefore, thermodynamic measurements on Fe-O-H solids are often significantly influenced by surface energy effects and adsorbed water (see Section VII.2.1). Several reviews present crystallographic details of at least the commoner Fe-O-H solids, *e.g.*, [1987TAY], [1988EGG/SCH], [1991WAY].

Unfortunately, some of the technically important oxyhydroxides are among the most difficult to define from a structural and thermodynamic viewpoint. In particular, ferrihydrite often controls iron solubility in natural waters, and its sorption properties are important in the transport and retention of many nutrients and contaminants, including several important radionuclides, in rock fractures and soils (*e.g.*, [1998JAM/DUT], [2009LEE/BAI], [2009HIE/RIE] and references therein).

Studies of phase transformations between iron oxides and oxyhydroxides date back at least to the 1830s (references cited in [1934WEL/BAU]). A century later, the commoner phases and many of their synthetic routes and transformation pathways had been identified [1934WEL/BAU], though detailed characterization awaited later developments in physicochemical instrumentation and computing methods. Several uncommon phases have also been discovered and characterized relatively recently. Standardized procedures for preparing pure, synthetic samples of many of these phases are now well-established [2000SCH/COR], and these form the basis for several recent thermodynamic measurements on metastable oxides and oxyhydroxides. Any study that does not clearly establish phase identity, particle size or surface area, and water content, as well as chemical purity, is evidently of limited value. A monograph by Cornell and Schwertmann provides a thorough grounding in many scientific and technological aspects of the iron oxides [1996COR/SCH].

Figure VII-16: Phase diagram of the $Fe_{1-x}O_x$ condensed system in the FeO to Fe_2O_3 region (from [1993GRO/STO]). H = Hematite, L = Liquid, M = Magnetite, W = Wüstite, α, β, δ refer to modifications of Fe(cr). Copyright (1993) with permission from Elsevier.



Langmuir [1969LAN] compiled solubility and thermodynamic data for solids in the $Fe–O_2–H_2O–CO_2$ system, including several Fe(III) oxides and oxyhydroxides, and compared their relative stability in terms of their solubility products, Reaction (VII.22).

$$\tfrac{1}{2}\,Fe_2O_3\cdot xH_2O(s) + {}^{(3-x)}\!/_2\; H_2O(l) \rightleftharpoons Fe^{3+} + 3\,OH^- \qquad \text{(VII.22)}$$

$$K_{s,0} = a_{Fe^{3+}}\,(a_{OH^-})^3 \text{ (assuming unit activity of water)}$$

Other solubility equilibria, such as Reaction (VII.23), can be treated in the same way.

$$\tfrac{1}{2}\,Fe_2O_3\cdot xH_2O(s) + 3\,H^+ \rightleftharpoons Fe^{3+} + {}^{(3+x)}\!/_2\; H_2O(l) \qquad \text{(VII.23)}$$

$${}^{*}K\,\text{(VII.23)} = a_{Fe^{3+}}/(a_{H^+})^3 = K_{s,0}/K_w^3$$

This approach is particularly helpful for comparing the stability of phases with variable water content. It is important, of course, to employ appropriate hydrolysis constants and activity corrections to calculate $a_{Fe^{3+}}$ for any given combination of iron concentration, pH, concentrations of complexing anions, and ionic strength.

Another useful reaction for comparing the stability of different Fe(III) oxides and oxyhydroxides is the conversion to hematite, Reaction (VII.24) (Reaction (VII.21) is an example).

$$Fe_2O_3\cdot xH_2O(s) \rightleftharpoons \alpha\text{-}Fe_2O_3 + x\,H_2O(\text{l or g}) \qquad \text{(VII.24)}$$

This is important for many of the thermodynamic measurements discussed below, because enthalpy data and solubilities for metastable Fe–O–H phases are often measured relative to α-Fe_2O_3. Reliable thermodynamic data for hematite are therefore a prerequisite for calculating many of the thermodynamic properties for other Fe–O–H phases.

To quantify the relative stability of the different phases, Langmuir [1969LAN] calculated $\log_{10} K_{s,0}$ values ranging from – (41.9 ± 0.4) for hematite to − (37.1 ± 0.6) for freshly precipitated, amorphous "$Fe(OH)_3$". In a related experimental study, Langmuir and Whittemore observed a range of $\log_{10} K_{s,0}$ values from − 43.3 to − 37.1 for synthetic precipitates and from – 43.5 to – 37.1 for natural well waters [1971LAN/WHI], with values as low as – 44.2 for goethite in a related study [1974WHI/LAN]). Overall, published values of $\log_{10} K_{s,0}$ extend from about − 44 to − 35. Extremely low solubilities ($\log_{10} K_{s,0} < -42$), however, can usually be traced to erroneous values for the Gibbs energy of formation of aqueous Fe^{2+} and Fe^{3+}, while extremely high values typically refer to freshly precipitated colloids, uncorrected for ionic activities and/or cation hydrolysis and complexation. The range of 4.8 orders of magnitude in Langmuir's calculated solubility products [1969LAN] corresponds to a span of about 27 $kJ\cdot mol^{-1}$ in the value of $\Delta_r G_m^o$ ((VII.23), 298.15 K), or about 320 $kJ\cdot mol^{-1}$ in the value of $\Delta_r G_m^o$ ((VII.25), 298.15 K).

$$6\,Fe_2O_3\cdot xH_2O(s) \rightleftharpoons 4\,Fe_3O_4(cr) + 6x\,H_2O(l) + O_2(g) \qquad \text{(VII.25)}$$

These findings suggest that the Eh values (Chapter II, Section II.1.7.5) for different metastable $Fe_3O_4/Fe_2O_3 \cdot xH_2O$ phase boundaries, at a given pH, could be up to ~ 830 mV more positive than the stable $Fe_3O_4/\alpha\text{-}Fe_2O_3$ boundary. Gibbs-energy values obtained for various solid iron(III) oxyhydroxides from the current evaluation lead to significantly smaller values for these ranges of metastable conditions (see Section VII.2.16).

VII.2.1 Particle size and surface hydration

Surface thermodynamic properties are beyond the normal scope of an NEA-TDB review, but this section is necessary because of their profound effect on apparent bulk properties of finely divided iron oxides and oxyhydroxides. This field is currently very active, with many important publications since 2002, and a detailed, independent review would be premature. This section is therefore limited to a brief historical perspective and a summary of important, recent progress.

The role of small particle size, and the correspondingly large surface contribution to thermodynamic properties of iron oxyhydroxides, was recognized in the 1930s by Fricke and co-workers [1934FRI/ACK], [1935FRI/KLE], [1937FRI/ZER], and received further attention from Ferrier in the 1960s [1964FER], [1965FER], [1966FER], [1968FER]. Based on these earlier studies, Langmuir discussed the effect of particle size on the relative stability of goethite and hematite, but the findings are marred by the limited accuracy of data then available [1971LAN].

Diakonov and co-workers reviewed available thermodynamic data on several Fe-O-H solids. Using limited data on sample surface areas, they extracted surface-area-corrected enthalpies of formation for goethite [1994DIA/KHO], maghemite [1998DIA], and lepidocrocite [1998DIA2]. These values are largely superseded, however, by more recent experimental studies [2003MAJ/GRE], [2005MAZ/NAV], [2007MAZ/NAV], [2007MAJ/MAZ]. In particular, surface-area-dependent calorimetric measurements have permitted more precise estimation of ideal, zero-surface-area, enthalpies of formation, as well as the surface enthalpies for relaxed (hydrated) surfaces, for goethite [2005MAZ/NAV], lepidocrocite [2007MAJ/MAZ], and akaganéite [2006MAZ/DEO].

Calorimetric measurements of water adsorption on goethite and hematite provided adsorption enthalpies and surface densities for a distribution of chemisorption sites, as well as yielding surface energies for H_2O-free surfaces of goethite and hematite [2007MAZ/NAV]. The adsorption calorimetry for hematite was strongly dependent on sample preparation conditions, in particular the firing temperature. Results demonstrated a crossover in relative stability with changing particle size, but in the opposite sense to Langmuir's suggested relationship [1971LAN], the more stable phase being goethite when very finely divided and hematite when well crystallized.

The contribution of adsorbed water to the heat capacity and entropy of fine-grained oxides and oxyhydroxides is also important, but has been investigated in less detail than the enthalpic contribution [1962VIC], [2003MAJ/LAN], [2005LAN].

Majzlan *et al.* explored various ways of correcting heat capacity and entropy values for excess water content in maghemite, goethite, and lepidocrocite [2003MAJ/LAN]. They considered hexagonal ice and zeolitic water to represent two limiting possibilities for describing the partially ordered state of the excess water. Using a combination of Debye and Einstein functions, they obtained very similar values for $C^{\circ}_{p,\mathrm{m}}$ (H_2O, 298.15 K) of 41.28 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ for ice and 41.37 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ for zeolitic water, and used the former value to correct their $C^{\circ}_{p,\mathrm{m}}$ data for maghemite, goethite, and lepidocrocite [2003MAJ/LAN]. This correction is similar to the value of 41.49 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ obtained by linear regression and extrapolation of the pooled $C^{\circ}_{p,\mathrm{m}}$ data for hexagonal ice at 201.34 to 268.39 K from [1936GIA/STO] and [1974HAI/MAT].

Lang [2005LAN] reported low-temperature heat-capacity measurements on a synthetic akaganéite sample, $\beta\text{-FeOOH}\cdot x\mathrm{H_2O}\cdot 0.0096\mathrm{HCl}$, after partial dehydration (x = 0.551) and rehydration (x = 0.652). The results (differences in heat capacities) indicated a gradual transition in the H_2O contribution to $C^{\circ}_{p,\mathrm{m}}$ from ice-like values below 150 K to liquid-like values at 273 K. Lang cited similar, unpublished findings for adsorbed water on TiO_2 surfaces. Note, however, that the akaganéite measurements refer only to the most labile fraction of the water content; also, the total water content was distributed in unknown proportions between surface and internal ("tunnel") sites of the akaganéite.

In the current review, we accept the heat-capacity and entropy corrections applied for maghemite, goethite, and lepidocrocite by Majzlan *et al.* [2003MAJ/LAN], but apply a conservative 10% uncertainty to the corrections. Further details are provided in the sections dealing with the individual solid phases and in Appendix A.

Further understanding of the heat-capacity and entropy contributions from adsorbed water will necessitate a long series of painstaking, low-temperature $C_{p,\mathrm{m}}$ measurements on several different Fe-O-H phases as a function of particle size and water content, with the same careful attention to preparation and characterization shown in the recent studies cited above. The influence of adsorbed water on heat capacity and entropy above 298.15 K is also problematic.

VII.2.2 Hematite, $\alpha\text{-}Fe_2O_3$

This widespread ore-forming mineral has been known since ancient times. The Greek name *haematitis* used by Theophrastus (~ 315 B.C.) perhaps refers to red jasper (a form of iron-stained silica), but Pliny's (77 A.D.) *hæmatites* was apparently hematite [1956CAL/RIC]. Hematite is isostructural with corundum ($\alpha\text{-}Al_2O_3$), hexagonal, space group: $R\bar{3}c$, Z = 6, with unit cell dimensions a_0 = 5.0367, c_0 = 13.7550 Å [2003MAJ/GRE]). The structure, as deduced by Pauling and Hendricks [1925PAU/HEN] and refined by Blake *et al.* [1966BLA/HES], consists of a hexagonal close-packed O sublattice with Fe occupying two-thirds of the octahedral sites in an ordered manner. Face-sharing pairs of FeO_6 octahedra are further linked by edge-sharing into gibbsite-like sheets in the *ab* plane. Hematite is essentially stoichiometric up to about 1300 K, then shows a small homogeneity range on the oxygen-deficient side up to the temperature for decomposition to magnetite, reported as (1665 ± 2) K in air [1946DAR/GUR]; see Figure VII-16.

Hematite is antiferromagnetic with a weak, superimposed ferromagnetic component ([1962AHA/FRE], and references therein). DTA measurements revealed three transition points at 243, 948 and 998 K [1962AHA/FRE]. The first was identified as the Morin transition, at which the sublattice magnetization rotates by 90° and the weak ferromagnetism increases abruptly. The weak ferromagnetism vanishes at the second transition, and the final transition appears to be the true Néel point [1960PAU]. The two highest transition points correspond to reported enthalpic anomalies near 950 and 1050 K [1951COU/KIN], but detailed heat-capacity measurements show a single, major λ-type transition peaking at 955 K ([1975GRO/SAM]; see Section VII.2.2.2).

VII.2.2.1 Enthalpy of formation of hematite

Hematite is an unreactive substance, which makes reaction enthalpies difficult to determine. Complete dissolution, or formation by combustion, are hard to achieve, and approach to equilibrium in both low-temperature solubility and high-temperature solid-state electrochemical experiments is slow.

Calorimetric determinations

The first determination of $\Delta_f H_m^\circ$ (Fe_2O_3, α, 298 K) appears to be Le Châtelier's value of $-$ 811.1 $kJ \cdot mol^{-1}$ [1895CHA], based on relative heats of combustion of different iron oxides admixed with charcoal, combined with the dissolution-based value (see Section VII.2.7.2.1) for $\Delta_f H_m^\circ$ (Fe_3O_4, α, 298 K) of Berthelot [1881BER]. Both this and Mixter's value of $\Delta_f H_m^\circ$ (Fe_2O_3, α, ~ 298 K) = $-$ 804 $kJ \cdot mol^{-1}$, from heats of fusion of Fe(cr) and α-Fe_2O_3 in Na_2O_2 [1913MIX], are markedly less negative than more recent determinations. The value of $\Delta_f H_m^\circ$ (Fe_2O_3, α, ~ 298 K) = $-$ 826.7 $kJ \cdot mol^{-1}$, obtained from combustion calorimetry measurements by Roth [1929ROT], appears to be more accurate, but this study too was marred by the need for substantial corrections for incomplete reactions. A later dissolution-calorimetry study from the same laboratory, after recalculation, yields a value of $\Delta_f H_m^\circ$ (Fe_2O_3, α, 298.15 K) = $-(813.66 \pm 1.74)$ $kJ \cdot mol^{-1}$ [1934ROT/WIE].

While many studies on other Fe(III) oxides are based on comparative calorimetric measurements with α-Fe_2O_3, as discussed elsewhere in Chapter VII, there appears to be only one other calorimetric study that can yield a value for $\Delta_f H_m^\circ$ (Fe_2O_3, α, 298.15 K) by using a simple Fe-O thermochemical cycle. This is a series of drop-calorimetric measurements on iron oxides, including well-crystallized magnetite and hematite, in molten sodium molybdate[1], a technique developed by Navrotsky and co-workers to overcome the problem of incomplete dissolution of hematite and other refractory oxides in more conventional media [1998LAB/NAV], [2005MAZ/NAV]. Their data (molar values from Tables 4 and 5 of [1998LAB/NAV]) yield $\Delta_r H_m^o = -(477.6 \pm 6.9)$ kJ·mol^{-1} (temperature-drop calorimetry) and $-(471.2 \pm 20.9)$ kJ·mol^{-1} (drop-solution calorimetry) for the oxidation of magnetite to hematite, Eq. (VII.26).

$$4\ Fe_3O_4(cr) + O_2(g) \rightleftharpoons 6\ \alpha\text{-}Fe_2O_3 \qquad \text{(VII.26)}$$

These values are markedly less negative than those derived from the best available high-temperature equilibrium measurements (see below), perhaps because no special effort seems to have been made to eliminate surface oxidation of the magnetite specimens [1998LAB/NAV].

Determinations from Fe_3O_4(cr)-Fe_2O_3(cr, α) equilibrium

Tigerschiöld derived standard enthalpy values for iron oxides from high-temperature gas-solid equilibrium data [1923TIG]. Previous researchers were unable to measure the reversible equilibrium between magnetite and hematite in CO-CO_2 and H_2-H_2O atmospheres, presumably because the equilibrium fractions of CO and H_2, respectively, would be very low. Tigerschiöld's calculation is therefore based on measurements of the equilibrium dissociation pressure of hematite at 1373 and 1473 K by Sosman and Hostetter [1916SOS/HOS] (*cf.* Eq. (VII.26)).

Because the data did not yield an invariant p_{O_2} at constant T (see Appendix A), Tigerschiöld obtained a range of values for $\Delta_f H_m^o$ (Fe_2O_3, α, 298 K): -824.7 to -828.2 kJ·mol^{-1}. This is nevertheless closer to current values than most of the calorimetric determinations discussed above (see also [1948RIC/JEF]).

In and around the 1960s, several studies were published on the magnetite-hematite equilibrium, based on manometric and/or mass-spectrometric p_{O_2} measurements and largely restricted to temperatures above 1300 K (*e.g.*, [1961SAL], [1962TRE/KHO], [1967KOM/OLE], [1969KOD/KUS], [1971CHI/TSV]). At such temperatures, both magnetite and hematite depart significantly from ideal stoichiometry, making it difficult to obtain an accurate value for $\Delta_f H_m^o$ (Fe_2O_3, α, 298.15 K) by third-law calculation, though detailed solid-solution data and analyses are available (*e.g.*, [1957SMI], [1961SAL], [1967KOM/OLE]). Nevertheless, the uncertainty in the calorimetric data used in the third-law calculation is relatively large when using data obtained at such high temperatures. It is doubtful that inclusion of data from these studies would improve on enthalpy estimates from solid-state electrochemical

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[1] The sodium molybdate composition was not specified by [1998LAB/NAV]; later work from the same laboratory used the composition $3Na_2O \cdot 4MoO_3$ [2005MAZ/NAV].

measurements, described below, though even they are restricted to temperatures above about 1000 K. Equilibration at somewhat lower temperatures is feasible in hydrothermal systems, but this introduces added complications of pressure correction and the need to devise novel sensors (*e.g.*, [1978CHO]). Equilibration is possible at much lower temperatures (~ 500 K) in the presence of stable, complexing anions such as acetate [1993PAL/DRU].

Even with the most careful solid-state electrochemical measurements on the magnetite-hematite equilibrium, variation between different studies is greater than normally expected, with discrepancies of as much as 20 mV, much worse than the normal reproducibility of studies of this kind. However, this is partly due to the magnifying effect of the reaction stoichiometry, Eq. (VII.27), and discrepancies in the Gibbs energy for this reaction nearly all lie within a span of 1 $\mathrm{kJ\cdot mol(Fe)^{-1}}$, as shown in Figure VII-17, which is similar to Figure 11 of [1988NEI].

$$\tfrac{1}{3}\,\mathrm{Fe_3O_4(cr)} + \tfrac{1}{12}\,\mathrm{O_2(g)} \rightleftharpoons \tfrac{1}{2}\,\alpha\text{-}\mathrm{Fe_2O_3} \qquad \text{(VII.27)}$$

The residual discrepancies seem to be due to difficulty in attaining equilibrium, possibly related to slight differences in composition, structure (cation site occupancy), degree of sintering, and particle size of the solids used in different studies. It is somewhat disturbing that the divergence between different studies increases with decreasing temperature, perhaps reflecting an increasing degree of difficulty in attaining equilibrium.

Figure VII-17 is based on third-law calculations, using the S°_{m} and $C^{\circ}_{p,\mathrm{m}}$ -T relationships for $\mathrm{Fe_3O_4(cr)}$ and α-$\mathrm{Fe_2O_3}$ obtained in this review (Sections VII.2.2.2, VII.2.2.3 and VII.2.7.1); the *y*-axis represents the experimental $\Delta_{\mathrm{r}}G^{\circ}_{\mathrm{m}}(T)$ values or relationships for Reaction (VII.27), from 12 different studies, relative to that obtained with $\Delta_{\mathrm{r}}H^{\circ}_{\mathrm{m}} = -41.223\ \mathrm{kJ\cdot mol^{-1}}$, which is the average value obtained with data from [1988NEI]. Reference cell-potential data from [1986HOL/NEI] for Ni-NiO and from [1988NEI] for Fe-wüstite and Cu-$\mathrm{Cu_2O}$ were used to transform electrochemical data from the various sources to oxygen chemical potentials.[1] Most of the sources cited by [1988NEI] are included in the figure. The relationship from Myers and Eugster [1983MYE/EUG], who used a hybrid electrochemical/gas-equilibrium technique, is omitted because the internal consistency of that study has been questioned by O'Neill [1988NEI]. Data from the $\mathrm{H_2}$-$\mathrm{H_2O}$ study of [1972RAU] are omitted because it seems unlikely that magnetite-hematite equilibrium was attained at the relatively low experimental temperatures (~ 800 K). Data from [1979FIT], which agree closely with those of [1969BRY/SME], are not included. Sources shown on Figure VII-17 that were

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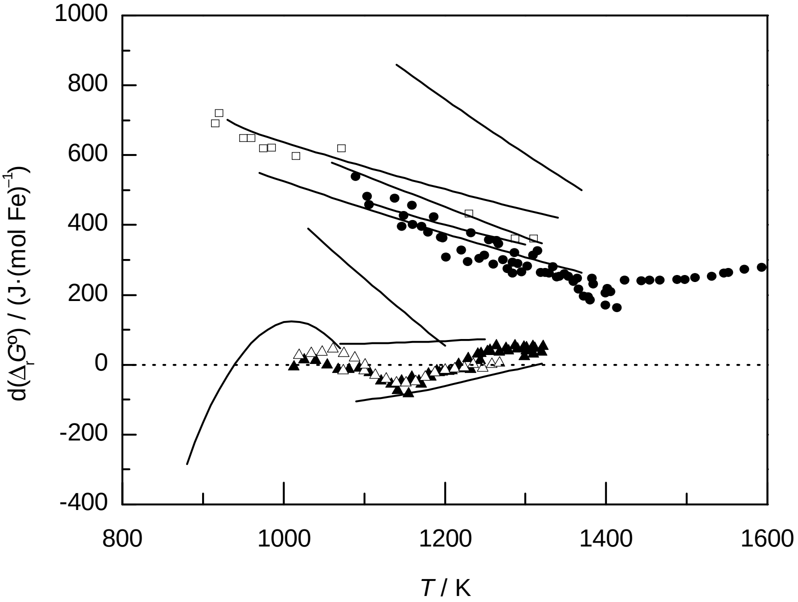
[1] This is not quite consistent with the NEA database for NiO [2005GAM/BUG], but was found to give better overall internal consistency.

not included by [1988NEI] are [1972RAO/TAR] and the mass-spectrometric study of [1971CHI/TSV].

Figure VII-17: Compilation of high-temperature equilibrium data for the magnetite-hematite buffer. Open squares [1972RAO/TAR], filled circles [1985JAC], open triangles [1988NEI] with Ni-NiO reference, filled triangles [1988NEI] with Cu-Cu_2O reference. Approximately straight lines represent correlations from (top to bottom): [1981SCH/KUS], [1972SAI/NIS], [1969BRY/SME], [1980KAT/MAT], [1968CHA/FLE], [1971CHI/TSV], [1969MOR/SAT], [1961BLU/WHI]. The strongly curved line represents the correlation from [1978CHO]. The horizontal line at $d(\Delta_r G^o_m) = 0$ represents $\Delta_r H^o_m = -41.223$ kJ·mol^{-1} for the reaction $\frac{1}{3}Fe_3O_4(cr) + \frac{1}{12}O_2(g) \rightarrow \frac{1}{2}\alpha\text{-}Fe_2O_3$.



O'Neill's experimental procedure [1988NEI], which was devised to obtain reference potentials with which to calibrate other equilibrium measurements, was especially meticulous (see Appendix A). He pointed out that his study is the only one to show the expected deviation from a near-linear *E*-*T* relationship, arising from the significant equilibrium solubility of hematite in magnetite above ~ 1150 K (though the magnitude of this deviation is greater than expected). Hemingway [1990HEM] argued that this is convincing evidence that O'Neill's data represent true equilibrium between well-crystallized magnetite and hematite, where other studies had narrowly failed;

Hemingway accordingly obtained a value of $\Delta_f H_m^o$ (Fe$_2$O$_3$, α, 298.15 K) = − (826.23 ± 1.25) kJ·mol^{-1}, about 1.6 kJ·mol^{-1} more negative than several previous evaluations he cites. With the $C_{p,m}^o$ -T relationships used in the current review, there is minimal variation of the calculated $\Delta_r H_m^o$ with T for O'Neill's study, as compared with most other works cited. We therefore accept that measurements reported in [1988NEI] probably represent true equilibrium between magnetite and hematite, but with reservations about the cause of the break in the E–T relationship. A value of $\Delta_r H_m^o$ = − (41.22 ± 1.20) kJ·mol^{-1} is suggested for Reaction (VII.27); this includes the estimated uncertainty in the thermal data used in the third-law calculation, which greatly exceeds the precision limits of O'Neill's data, and indeed exceeds the variability of all the high-temperature equilibrium data from other sources depicted in Figure VII-17. Combining this reaction enthalpy with $\Delta_f H_m^o$ (Fe$_3$O$_4$, cr, 298.15 K) = − (1115.78 ± 1.60) kJ·mol^{-1} (Section VII.2.7.2.2), we obtain a selected value of

$$\Delta_f H_m^o (\text{Fe}_2\text{O}_3, \alpha, 298.15\ \text{K}) = -(826.29 \pm 2.63)\ \text{kJ}\cdot\text{mol}^{-1}.$$

This value is very close to Hemingway's [1990HEM] recommendation of − (826.23 ± 1.25) kJ·mol^{-1}, discussed above, but with a larger uncertainty; this may overstate the uncertainty in $C_{p,m}^o$ data, especially those for (Fe$_3$O$_4$,cr) in the vicinity of the Curie transition (between 700 and 1050 K, see Section VII.2.7.1.5).

VII.2.2.2 Heat capacity of hematite

This assessment is based primarily on adiabatic $C_{p,m}^o$ measurements from [1959GRO/WES3] and [1975GRO/SAM], and drop-calorimetric enthalpy ($[\Delta_{298.15\text{K}}^{T} H_m^o]$) measurements from [1951COU/KIN]. Data for specular hematite from [1926PAR/KEL] were included initially; though in fair agreement with [1959GRO/WES3], they generated relatively large residuals to preliminary fitted curves, especially near 90 K, and were omitted from the final fitting. Twenty-one $C_{p,m}^o$ measurements by Krupka (personal communication to J.L. Haas) have apparently not been published; three other studies cited in Haas's unpublished review appear to be relatively inaccurate [1992HAA/HEM]. One of these three studies [1972REZ/FIL] is discussed in Appendix A.

The $C_{p,m}^o$ data from [1959GRO/WES3], [1975GRO/SAM], and [1926PAR/KEL] are plotted in Figure VII-18, together with fitted curves from the current review, plus a constant value of $C_{p,m}^o$ = (142.1 ± 0.4) J·K^{-1}·mol^{-1} for T > 1050 K based on enthalpy data from [1951COU/KIN]. While there is only one major anomaly, at the Néel transition near 955 K, a total of nine empirical expressions was used to describe the data, as summarized in Table VII-10. In these expressions, A, B…G are all curve-fitting parameters, including the exponent B in the first equation. While a single polynomial expression gives a reasonable fit from about 100 to 800 K, the more complex treatment gave better tracking of minor anomalies or artifacts in the data near 13 and 35 K (combined entropy contribution ~ 0.03 J·K^{-1}·mol^{-1}), as well as the "pronounced broad bump" near 500 K [1975GRO/SAM], and also reduced the slight biases in the fitted curves near their temperature limits. Residuals from the final fit, expressed as $\delta(C^{\circ}_{p,\mathrm{m}}/T)$, are shown in Figure VII-19. The data from [1959GRO/WES3] and [1975GRO/SAM] were treated separately to obtain functions below and above 298.15 K, respectively, because the former data have significantly higher precision and there is a minor mismatch in the overlap region (301.92 to 345.42 K).

Of the nine $C^{\circ}_{p,\mathrm{m}}(T)$ functions summarized in Table VII-10, only those for $298.15 < T < 775$ K and for $T > 1050$ K are recommended. The functions for $T < 298.15$ K were used only to evaluate S°_{m}(298.15 K) and $C^{\circ}_{p,\mathrm{m}}$(298.15 K) as described below. The two functions describing the Néel transition region (775 - 1050 K) require some coefficients to be expressed with seven or more significant figures, and are therefore not recommended for routine computation. More robust fits can be obtained with exponential expressions of the following type, which give both $C^{\circ}_{p,\mathrm{m}}$ and $C^{\circ}_{p,\mathrm{m}}/T$ in easily integrated forms.

$$C^{\circ}_{p,\mathrm{m}}(T) = \mathrm{A} + \mathrm{B}\,T\exp(\mathrm{C}T)$$

Figure VII-18: Experimental $C^{\circ}_{p,\mathrm{m}}$ data for hematite at temperatures up to 1054.36 K (■: [1926PAR/KEL] (specular crystals only); △: [1959GRO/WES3]; ○: [1975GRO/SAM]; solid line: nine fitted functions for separate temperature ranges, as summarized in Table VII-10.

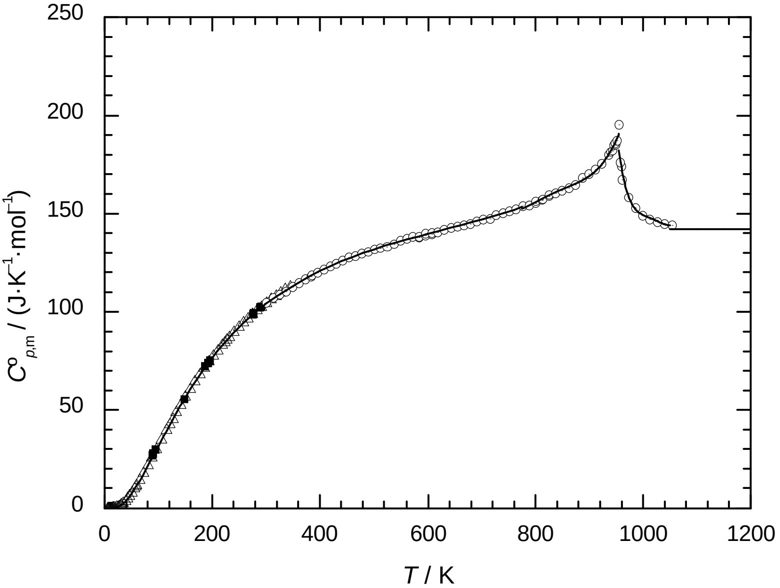


Table VII-10: Polynomial functions used to describe $C^{\circ}_{p,\mathrm{m}}$ (Fe_2O_3, α, T).

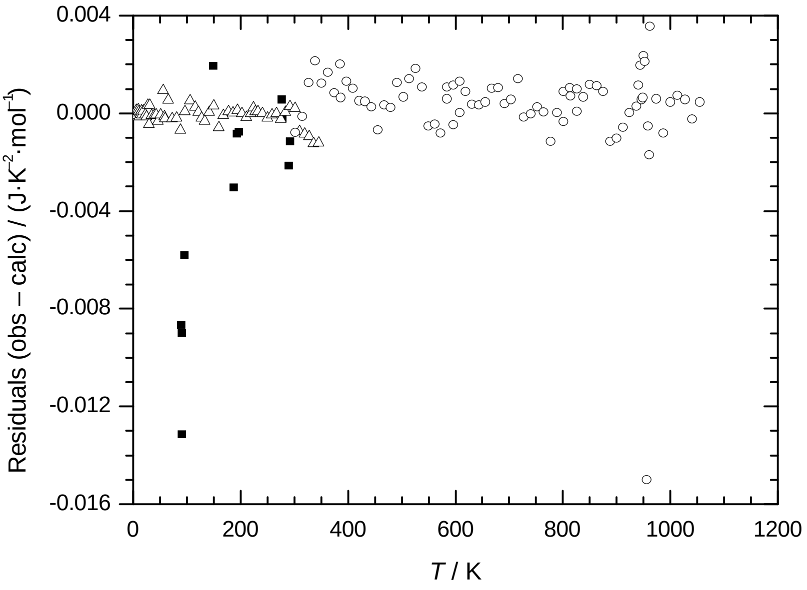
T range of application/K	T range of data used in fitting/K	$C^{\circ}_{p,\mathrm{m}}(T)$
0 - 6	18.97 - 42.76 (N = 9) (a)	$\mathrm{A}T^{\mathrm{B}}$
6 - 18	5.58 - 18.97 (N = 12) (a)	$\mathrm{A}T^{6} + \mathrm{B}T^{5} + \mathrm{C}T^{4} + \mathrm{D}T^{3} + \mathrm{E}T^{2} + \mathrm{F}T$
18 - 35	10.31 - 38.75 (N = 14) (a)	$\mathrm{A}T^{6} + \mathrm{B}T^{5} + \mathrm{C}T^{4} + \mathrm{D}T^{3} + \mathrm{E}T^{2} + \mathrm{F}T$
35 - 150	22.70 - 177.24 (N = 28) (a)	$\mathrm{A}T^{6} + \mathrm{B}T^{5} + \mathrm{C}T^{4} + \mathrm{D}T^{3} + \mathrm{E}T^{2} + \mathrm{F}T + \mathrm{G}$
150 - 298.15	121.39 - 345.42 (N = 29) (a)	$\mathrm{A}T^{6} + \mathrm{B}T^{5} + \mathrm{C}T^{4} + \mathrm{D}T^{3} + \mathrm{E}T^{2} + \mathrm{F}T + \mathrm{G}$
298.15 - 775	301.92 - 800.66 (N = 47) (b)	$\mathrm{A}T^{2} + \mathrm{B}T + \mathrm{C} + \mathrm{D}T^{-1} + \mathrm{E}T^{-2}$
775 - 955	751.72 - 955.51 (N = 12) (b)	$\mathrm{A}T^{2} + \mathrm{B}T + \mathrm{C} + \mathrm{D}T^{-1} + \mathrm{E}T^{-2}$
955 - 1050	958.54 - 1054.36 (N = 10) (b)	$\mathrm{A}T^{2} + \mathrm{B}T + \mathrm{C} + \mathrm{D}T^{-1} + \mathrm{E}T^{-2}$
1050 - 1100	1109.9 - 1588 (N = 18) (c)	constant

(a) Data from [1959GRO/WES3].

(b) Data from [1975GRO/SAM].

(c) Data from [1951COU/KIN].

Figure VII-19: Residuals (differences between observed and calculated values of $C^{\circ}_{p,\mathrm{m}}/T$), based on final, fitted and adjusted $C^{\circ}_{p,\mathrm{m}}(T)$ expressions (■: [1926PAR/KEL]; △: [1959GRO/WES3]; ○: [1975GRO/SAM]). Note the relatively large residuals for data from [1926PAR/KEL], the larger scatter (approximately three times higher standard deviation) in data from [1975GRO/SAM] compared to those from [1959GRO/WES3], and the difficulty in fitting the peak of the Néel transition at 955 K.



Instead of recommending either fragile fits or non-standard $C^{\circ}_{p,\mathrm{m}}(T)$ expressions, however, values of $C^{\circ}_{p,\mathrm{m}}(T)$, $[\Delta^{T}_{775\,\mathrm{K}}H^{\circ}_{\mathrm{m}}]$ H°_{m}, and $[\Delta^{T}_{775\,\mathrm{K}}S^{\circ}_{\mathrm{m}}]$ are listed in Table VII-11 for rounded temperatures between 775 and 1050 K. The tabulated values can be combined with the values $[\Delta^{775\,\mathrm{K}}_{298.15\,\mathrm{K}}H^{\circ}_{\mathrm{m}}]$ = (63.30 ± 0.40) $\mathrm{kJ \cdot mol^{-1}}$ and $S^{\circ}_{\mathrm{m}}(775\ \mathrm{K}) = (210.66 \pm 0.78)$ $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, based on the $C^{\circ}_{p,\mathrm{m}}(T)$ relationship recommended elsewhere in this section.

Previous tabulations of smoothed heat capacities include values for $C^{\circ}_{p,\mathrm{m}}$(Fe_2O_3, α, 298.15 K) of 103.93 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ [1975GRO/SAM], 103.76 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ [1959GRO/WES3], and 103.85 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ [1990HEM]. In the present assessment, when nine different polynomial functions were fitted using only the high-precision data for 249.68 to 345.42 K ($N = 12$) from [1959GRO/WES3], the resulting values for $C^{\circ}_{p,\mathrm{m}}$(Fe_2O_3, α, 298.15 K) were closely grouped between 103.79 and 103.81 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. When five measurements between 301.92 and 350.24 K from [1975GRO/SAM] were added to the data set, the resulting values ranged from 103.81 to 103.95 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. When four measurements between 275.9 and 291.9 K from [1926PAR/KEL] were added, results varied from 103.89 to 104.06 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$.

Table VII-11: Thermodynamic quantities for α-Fe_2O_3 at 775 to 1050 K.

T / K	$C^{\circ}_{p,\mathrm{m}}$ / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$[\Delta^{T}_{775\mathrm{K}}H^{\circ}_{\mathrm{m}}]$ / $\mathrm{kJ \cdot mol^{-1}}$	$[\Delta^{T}_{775\mathrm{K}}S^{\circ}_{\mathrm{m}}]$ / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$
775	152.6 *	0.00	0.00
800	155.7	3.85	4.89
825	159.3	7.79	9.74
850	162.5	11.81	14.54
875	165.4	15.91	19.29
900	169.2	20.09	24.00
925	175.8	24.40	28.72
950	187.6	28.93	33.55
955	190.8	29.87	34.54
960	173.2	30.76	35.47
965	166.3	31.61	36.35
970	161.1	32.42	37.20
975	157.3	33.22	38.02
1000	149.2	37.02	41.87
1025	146.3	40.72	45.52
1050	144.1 *	44.34	49.01

* Note the slight mis-matches with the values of $C^{\circ}_{p,\mathrm{m}}(775\,\mathrm{K})$ = 153.34 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ given by the recommended $C^{\circ}_{p,\mathrm{m}}(T)$ expression for 298.15 to 775 K (see the end of Section VII.2.2.2) and $C^{\circ}_{p,\mathrm{m}}(1050\,\mathrm{K})$ = 142.1 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, the constant value recommended for $T > 1050$ K.

The value:

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{Fe_2O_3}, \alpha, 298.15\ \mathrm{K}) = (103.93 \pm 0.17)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$$

is selected, *i.e.*, the value from [1975GRO/SAM] is retained with an uncertainty that encompasses all of the values listed above.

The initial fitted expression describing $C^{\circ}_{p,\mathrm{m}}(T)$ at 298.15 < T < 775 K, obtained from the data of [1975GRO/SAM], was adjusted by a constant value of 0.31 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. This corresponds to approximately half of the discrepancy between $[\Delta_{\mathrm{f}} H^{\circ}_{\mathrm{m}}]^{T}_{298.15\mathrm{K}}$ ($\mathrm{Fe_2O_3}$, α) values obtained by integration of the initial, fitted $C^{\circ}_{p,\mathrm{m}}$ expression and those obtained directly by Coughlin *et al.* [1951COU/KIN]. This adjustment thus amounts to giving equal weighting to the findings of [1975GRO/SAM] and [1951COU/KIN]. It also brings the fitted and recommended values of $C^{\circ}_{p,\mathrm{m}}$ ($\mathrm{Fe_2O_3}$, α, 298.15 K) into coincidence, and reduces the slight mismatch in the overlap region between the measurements of [1959GRO/WES3] and [1975GRO/SAM]. The resulting, adjusted $C^{\circ}_{p,\mathrm{m}}$ ($\mathrm{Fe_2O_3}$, α, T) expression for temperatures up to 775 K is as follows:

$$\begin{aligned}[C^{\circ}_{p,\mathrm{m}}]^{775\mathrm{K}}_{298.15\mathrm{K}}(\mathrm{Fe_2O_3}, \alpha, T)/\mathrm{J \cdot K^{-1} \cdot mol^{-1}} = {} & 2.834295 \times 10^{-4}\,(T/\mathrm{K})^{2} \\ & - 5.071968 \times 10^{-1}\,(T/\mathrm{K}) + 5.193440 \times 10^{2} \\ & - 1.263761 \times 10^{5}\,(T/\mathrm{K})^{-1} \\ & + 1.195435 \times 10^{7}\,(T/\mathrm{K})^{-2}\end{aligned}$$

VII.2.2.3 Entropy of hematite

Calculated entropies based on the present assessment (see above) agree with the smoothed, tabulated values of Grønvold and Westrum to within 0.03 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ up to 298.15 K [1959GRO/WES3]. Values deviate at higher temperatures from those tabulated by Grønvold and Samuelsen [1975GRO/SAM], because of the final adjustment to the fitted $C^{\circ}_{p,\mathrm{m}}(T)$ expressions, with a maximum discrepancy of 0.27 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ at 1050 K.

Grønvold and Westrum obtained S°_{m} ($\mathrm{Fe_2O_3}$, α, 298.15 K) = 87.40 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, which was reiterated by Grønvold and Samuelsen ([1959GRO/WES3], [1975GRO/SAM]). Integration of $C^{\circ}_{p,\mathrm{m}}/T$ from 0 to 298.15 K, based on the $C^{\circ}_{p,\mathrm{m}}(T)$ expressions obtained in this assessment, yields S°_{m} ($\mathrm{Fe_2O_3}$, α, 298.15 K) = 87.38 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, while numerical integration gives a value of 87.36 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. The following value is selected:

$$S^{\circ}_{\mathrm{m}}(\mathrm{Fe_2O_3}, \alpha, 298.15\ \mathrm{K}) = (87.40 \pm 0.16)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}.$$

That is, the value from [1959GRO/WES3] is retained with an uncertainty based on a standard deviation of 0.00026 $\mathrm{J \cdot K^{-2} \cdot mol^{-1}}$ in the values of $C^{\circ}_{p,\mathrm{m}}/T$, relative to the fitted $C^{\circ}_{p,\mathrm{m}}(T)$ expressions, between 0 and 300 K in Figure VII-19. This is slightly more optimistic than Hemingway's uncertainty of ± 0.21 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ [1990HEM].

Tabulated thermodynamic values for hematite given by Hemingway include an isothermal transition at 950 K with a $\Delta_{\mathrm{trs}}H_{\mathrm{m}}^{\circ}(\mathrm{Fe_2O_3}, \alpha)$ value of 1.848 $\mathrm{kJ\cdot mol^{-1}}$ [1990HEM]. This appears to be a fictive transition introduced to solve fitting difficulties, somewhat like the 670 $\mathrm{kJ\cdot mol^{-1}}$ term introduced at 950 K by Coughlin *et al.* to facilitate their data analysis for hematite [1951COU/KIN]. The five-term $C_{p,\mathrm{m}}^{\circ}(T)$ expression for hematite of Robie *et al.* [1979ROB/HEM], as cited by Diakonov *et al.* [1999DIA/SCH], is valid up to about 910 K.

Because the determination of $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}$ ($\mathrm{Fe_2O_3}$, α, 298.15 K) depends in large part on high-temperature magnetite-hematite equilibrium data, it is useful to estimate the uncertainty in S_{m}° ($\mathrm{Fe_2O_3}$, α, T) at temperatures of 1050 K and above.

The integral:

$$\int_{298.15}^{1050}\left(C_{p,\mathrm{m}}^{\circ}(T)/T\right)\mathrm{d}T\ ,$$

in accordance with the $C_{p,\mathrm{m}}^{\circ}(T)$ expressions discussed in Section VII.2.2.2, yields $[\Delta_{298.15\,\mathrm{K}}^{1050\,\mathrm{K}}S_{\mathrm{m}}^{\circ}](\mathrm{Fe_2O_3}, \alpha) = (172.27 \pm 1.28)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, the uncertainties being estimated from the fitting residuals in Figure VII-19. Combined with S_{m}° ($\mathrm{Fe_2O_3}$, α, 298.15 K) = $(87.40 \pm 0.16)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, this $[\Delta_{298.15\,\mathrm{K}}^{1050\,\mathrm{K}}S_{\mathrm{m}}^{\circ}]$ value yields S_{m}° ($\mathrm{Fe_2O_3}$, α, 1050 K) = $(259.67 \pm 1.29)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$. For $T > 1050$ K, we obtain:

$$S_{\mathrm{m}}^{\circ}(\mathrm{Fe_2O_3}, \alpha, T)/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = (259.67 \pm 1.29) + (142.1 \pm 0.4)\ln(T/1050).$$

This expression yields entropy values 0.29 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ greater than the tabulated value of [1975GRO/SAM] at 1050 K, and 0.33 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ less than that of [1990HEM] at 1100 K.

VII.2.2.4 Solubility of hematite

Most solubility studies on hematite are either comparative studies aimed at estimating the properties of metastable phases (*e.g.*, [1969BER], [1997TAY/OWE]; see Sections VII.2.9.1 and VII.2.4.2) or they are directed at determining the properties of dissolved species such as $\mathrm{Fe(OH)_4^-}$ (*e.g.*, [1999DIA/SCH]; see Section VII.1.4). These studies probably have no direct role in evaluating the thermodynamic properties of α-$\mathrm{Fe_2O_3}$, but may be helpful in evaluating the overall consistency of thermodynamic data for solid and aqueous Fe-O-H species. Vlek *et al.* attempted to obtain a solubility product value for hematite by an edta chelation method, but the oxide proved “too inert to yield reproducible solubilities” [1974VLE/BLO].

VII.2.3 Synthetic β-$\mathrm{Fe_2O_3}$

Except where otherwise indicated, the following information is taken from [1999ZBO/MAS], [2003ZBO/MAS], and references therein. This phase, the Fe end-member of the bixbyite solid solution, $\mathrm{(Mn,Fe)_2O_3}$, has been obtained by chemical-vapour-deposition and spray-pyrolysis procedures, as well as by thermal decomposition of $Fe_2(SO_4)_3$ and $NaFe(SO_4)_2$. The bixbyite structure, sometimes known as the C-type sesquioxide structure, is also adopted by the trivalent oxides of several rare-earth and main-group elements. It is derived from the fluorite (CaF_2) structure type by the ordered removal of one-quarter of the anions and relaxation of the remaining atomic positions to yield approximately octahedral coordination for the two crystallographically distinct M atoms (M = Mn or Fe). The structure is cubic, space group: *Ia*3, $Z = 16$, with $a_0 = 9.393$ Å for pure β-Fe_2O_3. Structure refinement has been reported for pure Mn_2O_3 and two $(Mn,Fe)_2O_3$ solid solutions [1971GEL2].[1]

There appear to be no published thermodynamic measurements for β-Fe_2O_3. It transforms to hematite above 770 K, and there is little doubt that it is metastable at lower temperatures. It is magnetically disordered at ambient temperature; Mössbauer spectra below the Néel temperature, which has reported values between 100 and 119 K, contain two magnetically split subspectra corresponding to the two crystallographically distinct Fe atomic positions.

VII.2.4 Maghemite, γ-Fe_2O_3

The existence of a ferromagnetic form of Fe_2O_3, produced by oxidation of magnetite or dehydration of lepidocrocite, was recognized in the mid-19th century but not fully demonstrated until the 1920s ([1925WEL/BAU], [1927TWE], [1934WEL/BAU], and references therein). The mineral name maghemite was coined by Wagner, who briefly described a natural occurrence in the Transvaal, South Africa [1927WAG]. The substance is now recognized as a fairly common soil mineral, while synthetic γ-Fe_2O_3 has great commercial importance in magnetic recording media [2001DRO].

The structural relationship between maghemite and magnetite remained unclear for some time, with early efforts focusing on excess-oxygen models [1925WEL/BAU], which are incompatible with the close-packed structure of magnetite. It is now understood that γ-Fe_2O_3 is a cation-deficient, fully oxidized variant of the magnetite structure: $Fe_{8/3}\square_{1/3}O_4$, where □ represents a cation vacancy ([1991WAY], [1995PEC/GON] and references therein). The unit cell is commonly described as cubic, with a slightly smaller cell dimension than that of magnetite; reported values of a_0 range from 8.33 to 8.36 Å, with higher values usually being associated with incomplete oxidation of magnetite [1987TAY], [1988EGG/SCH], [1988SCH/MCC], [1991WAY], [1997TAY/OWE][2]. According to Pecharromán *et al.* [1995PEC/GON], there are three

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[1] In pure Mn_2O_3, the symmetry is reduced to orthorhombic, space group: *Pcab*, with the cell dimensions $a = 9.4157$ Å, $b = 9.4233$ Å, $c = 9.4047$ Å, and five crystallographically distinct Mn atoms [1971GEL2].

[2] Note that magnetite-maghemite solid solutions are metastable with respect to magnetite + hematite at low temperatures.

possible idealized structures with different degrees of disorder: cubic, a_0 = 8.33 Å, space group *Fd*3*m* (totally random vacancy distribution) or $P4_132$ (partly ordered); tetragonal, a_0 = 8.33, c_0 = 24.99 Å, space group $P4_32_12$ (fully ordered vacancy distribution). Further subtle variations are possible [1991WAY].

VII.2.4.1 Heat capacity and entropy of maghemite

Only one low-temperature study of the heat capacity of maghemite has been reported, by Majzlan *et al.* [2003MAJ/LAN]. Their high-precision adiabatic measurements between 7.696 and 396.66 K, on a specimen of composition $Fe_2O_3 \cdot 0.042H_2O$, revealed no $C^{o}_{p,m}$ anomalies. Curve-fitting is therefore straightforward, and four equations were used in the final analysis: a simple power expression, $C^{o}_{p,m} = AT^{B}$, for 0 to 25 K, a sixth-order polynomial constrained to pass through the origin for 25 to 100 K, an unconstrained sixth-order polynomial for 100 to 225 K, and the following five-term expression for 225 to 396 K

$$\begin{aligned}[C^{o}_{p,m}]^{396\,K}_{225\,K}\,(Fe_2O_3, \gamma + 0.042H_2O, T)/J\cdot K^{-1}\cdot mol^{-1} = {} & 0.0002268474\,(T/K)^{2} \\ & - 0.2083585\,(T/K) + 254.6667 \\ & - 38175.75\,(T/K)^{-1} \\ & + 1941109\,(T/K)^{-2}.\end{aligned}$$

This approach left no obvious bias in the residuals, as shown in Figure VII-20 and Figure VII-21, and yielded the following thermodynamic quantities for the specimen of $Fe_2O_3 \cdot 0.042H_2O$

$$C^{o}_{p,m}\,(Fe_2O_3, \gamma, + 0.042H_2O, 298.15\ K) = (106.50 \pm 0.29)\ J\cdot K^{-1}\cdot mol^{-1},$$

$$S^{o}_{m}\,(Fe_2O_3, \gamma, + 0.042H_2O, 298.15\ K) = (94.85 \pm 0.34)\ J\cdot K^{-1}\cdot mol^{-1}.$$

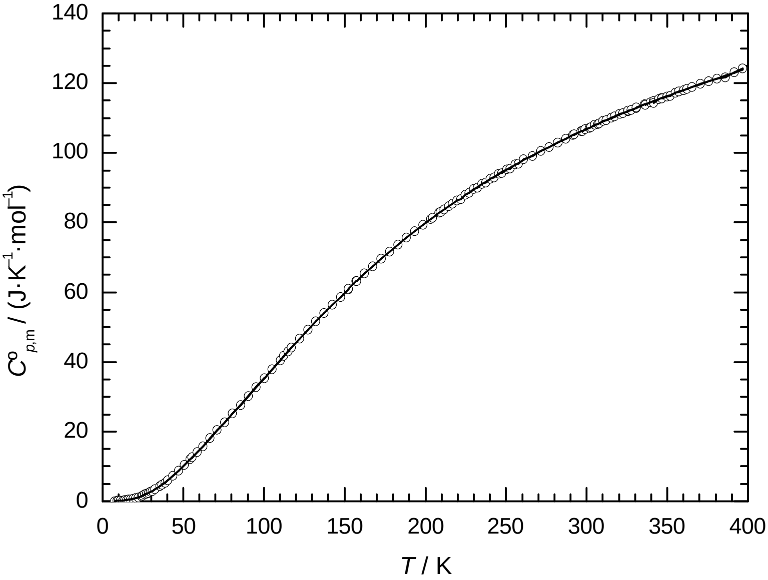
Correcting for the excess water content as hexagonal ice (see Section VII.2.1), we obtain the values $C^{o}_{p,m}(Fe_2O_3, \gamma, 298.15\ K) = (104.76 \pm 0.33)\ J\cdot K^{-1}\cdot mol^{-1}$ and $S^{o}_{m}(Fe_2O_3, \gamma, 298.15\ K) = (93.11 \pm 0.38)\ J\cdot K^{-1}\cdot mol^{-1}$, in close agreement with the values of 104.69 and $(93.04 \pm 0.22)\ J\cdot K^{-1}\cdot mol^{-1}$, respectively, derived by Majzlan *et al.* [2003MAJ/LAN]. We select the values from [2003MAJ/LAN] with slightly increased uncertainties to reflect points raised in Section VII.2.1

$$C^{o}_{p,m}\,(Fe_2O_3, \gamma, 298.15\ K) = (104.69 \pm 0.35)\ J\cdot K^{-1}\cdot mol^{-1},$$

$$S^{o}_{m}\,(Fe_2O_3, \gamma, 298.15\ K) = (93.04 \pm 0.40)\ J\cdot K^{-1}\cdot mol^{-1}.$$

Addressing the differences between ordered and disordered variants of maghemite, Majzlan *et al.* calculated an upper bound of 2.0 $J\cdot K^{-1}\cdot mol^{-1}$ for the entropy difference between ordered and disordered forms, based on the known site occupancies of cations and vacancies in the maghemite structure).[1] The data discussed here refer to ordered material, so the entropy for the variant with full cation/vacancy disorder would be about (95.0 ± 0.4) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$.

Figure VII-20: Measured $C^{\circ}_{p,\mathrm{m}}$ values [2003MAJ/LAN] (○) and fitted equations (solid line) from this assessment for a maghemite specimen of composition $\mathrm{Fe_2O_3\cdot 0.042H_2O}$.



High-temperature heat-capacity measurements for maghemite, as well as determination of the Néel temperature (estimated at about 950 K [2001DRO]), are hampered by the irreversible transformation to hematite, which may commence at temperatures as low as 450 K [1968GAL/FEI] and is normally rapid above ~ 800 K for pure specimens. Loss of excess water at elevated temperatures would also influence heat-capacity measurements. These factors may account for the rather erratic $C^{\circ}_{p,\mathrm{m}}$ measurements on maghemite, obtained by A.V. Korobeinikova (Ph.D. Thesis, Moscow State University, Russia, 1975, *fide* [1998DIA]; see Figure VII-22). Similarly, Majzlan *et al.* had difficulty obtaining reproducible $C^{\circ}_{p,\mathrm{m}}$ measurements on maghemite by DSC between about 400 and 700 K [2003MAJ/LAN]. However, they obtained "reasonable

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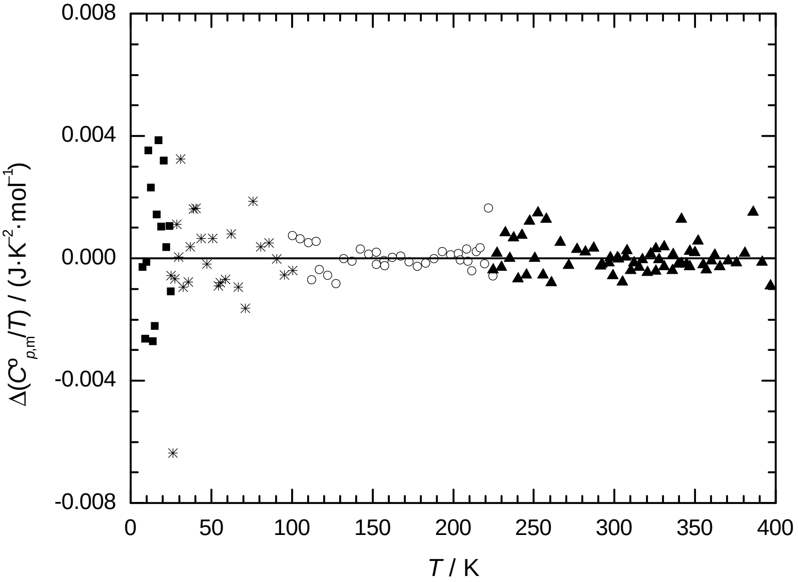
[1] Diakonov [1998DIA] obtained a value of 4.0 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, but the calculation by Majzlan *et al.* [2003MAJ/LAN] appears to reflect the crystallography more accurately.

data" between 700 and 800 K; surprisingly, no hematite was detected by XRD in the DSC specimens after scanning up to 800 K [2003MAJ/LAN]. The following Maier-Kelley equation, which bridges the two measurement ranges below 400 K and above 700 K, was proposed [2003MAJ/LAN].

$$[C^{\circ}_{p,\mathrm{m}}]^{760\,\mathrm{K}}_{273\,\mathrm{K}}\ (\mathrm{Fe_2O_3}, \gamma, T\,)/\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}} = 106.8 + 0.06509\ (T/\mathrm{K}) - 1886000\ (T/\mathrm{K})^{-2}.$$

Figure VII-21: Residual plot, expressed as $\Delta(C^{\circ}_{p,\mathrm{m}}/T)$, for experimental heat-capacity data for a maghemite specimen of composition $\mathrm{Fe_2O_3{\cdot}0.042H_2O}$ [2003MAJ/LAN], relative to four equations used for different temperature ranges in the present assessment.



This equation is also depicted in Figure VII-22, together with the slightly different tabulated values given by [2003MAJ/LAN].

Figure VII-23 illustrates the minor differences between experimental data (corrected for excess water as hexagonal ice, see Section VII.2.1), the Maier-Kelley expression of [2003MAJ/LAN] given above, and the smoothed, tabulated values of [2003MAJ/LAN]. All are shown relative to our fitted equation, given above, for maghemite, modified as follows using extrapolated estimates for the heat capacity of ice.

$$[C^{\circ}_{p,\mathrm{m}}]^{396.66\,\mathrm{K}}_{273.15\,\mathrm{K}}\ (\mathrm{H_2O, cr}, T)/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = 0.884885 + 0.136203\,(T/\mathrm{K});$$

$$\begin{aligned}[C^{\circ}_{p,\mathrm{m}}]^{396\,\mathrm{K}}_{225\,\mathrm{K}}\ (\mathrm{Fe_2O_3}, \gamma, T)/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = {} & 0.0002268474\,(T/\mathrm{K})^{2} - 0.2140790\,(T/\mathrm{K}) \\ & + 254.6295 - 38175.75\,(T/\mathrm{K})^{-1} \\ & + 1941109\,(T/\mathrm{K})^{-2}.\end{aligned}$$

This last expression is selected for $C^{\circ}_{p,\mathrm{m}}$ calculations between 273 and 400 K, with an uncertainty of about ± 0.5 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$. Because of the difficulty in measuring $C^{\circ}_{p,\mathrm{m}}$ for maghemite between 400 and 700 K, and the possibility of a contribution from hematite at higher temperatures, the Maier-Kelley bridging equation is considered a useful guide, but is not included in the recommended $C^{\circ}_{p,\mathrm{m}}$ expressions.

Figure VII-22: High-temperature $C^{\circ}_{p,\mathrm{m}}$ values for maghemite, γ-$\mathrm{Fe_2O_3}$, (■: uncorrected experimental measurements on $\mathrm{Fe_2O_3\cdot 0.042H_2O}$ [2003MAJ/LAN]; ○: corrected and smoothed values tabulated by [2003MAJ/LAN]; △: measurements on an ordered specimen (A. V. Korobeinikova, *fide* [1998DIA]); □: measurements on a disordered specimen (A. V. Korobeinikova, *fide* [1998DIA]); solid line: equation given by Majzlan *et al.* [2003MAJ/LAN]).

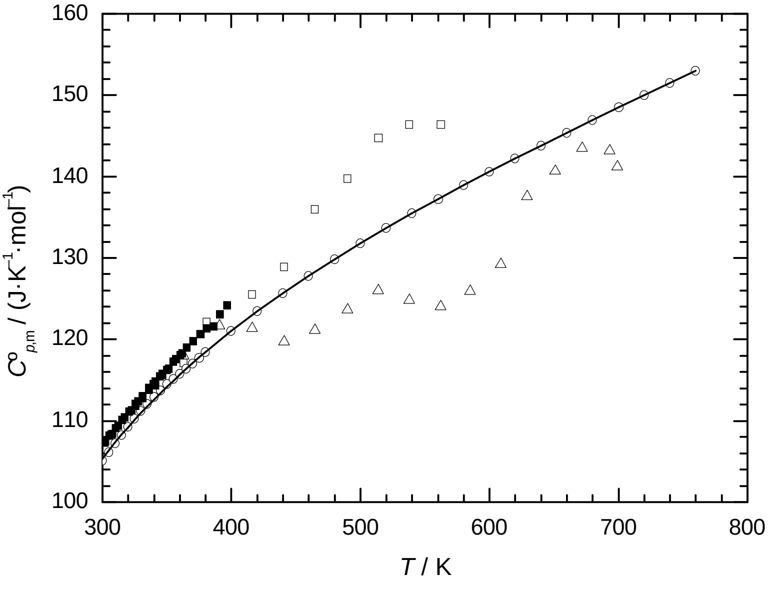
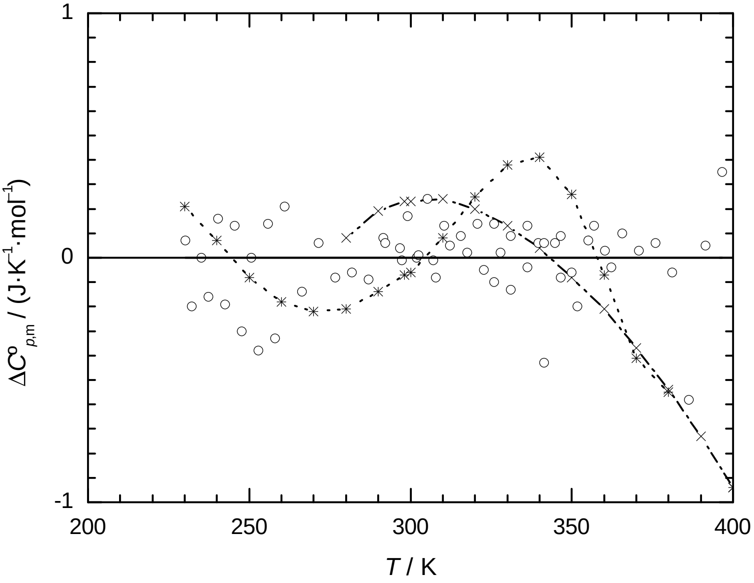


Figure VII-23: Comparison of experimental $C^{\circ}_{p,\mathrm{m}}$ measurements for maghemite, γ-Fe_2O_3 (from [2003MAJ/LAN], corrected for excess water by using a linear extrapolation for the $C^{\circ}_{p,\mathrm{m}}$ of ice (○)) with the Maier-Kelley equation (×) and smoothed, tabulated values from [2003MAJ/LAN] (✳). Values are shown relative to the polynomial expression, corrected for excess water, derived in the present assessment.



VII.2.4.2 Enthalpy of formation of maghemite

Most enthalpy values for maghemite are based either directly or indirectly on its transformation to hematite; in this section, we therefore assess the value of $\Delta_{\mathrm{trs}}H^{\circ}_{\mathrm{m}}$ (Fe_2O_3, $\gamma\rightarrow\alpha$, 298.15 K), then use the assessed transformation enthalpy to obtain $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ (Fe_2O_3, γ, 298.15 K).

Diakonov's review and recalculation of heats of dissolution of hematite and maghemite powders in aqueous HCl, measured by Fricke *et al.* at 343 K, yield $\Delta_{\mathrm{trs}}H^{\circ}_{\mathrm{m}}$ (Fe_2O_3, $\gamma\rightarrow\alpha$, 298.15 K) = $-(25 \pm 12)$ kJ·mol^{-1} [1934FRI/ACK], [1935FRI/KLE], [1937FRI/ZER], [1998DIA]. Trautmann [1966TRA] made some similar measurements at 298 K and obtained a transformation value of $-(20 \pm 9)$ kJ·mol^{-1}. Ferrier [1967FER] also compared the heats of dissolution at 343 K, and obtained a transformation enthalpy of $-(13.8 \pm 2.5)$ kJ·mol^{-1}; recalculation with improved corrections for impurities and surface area effects by Diakonov [1998DIA] yielded a value of $-(15.6 \pm 3.5)$ $\text{kJ}\cdot\text{mol}^{-1}$. Direct measurement of the heat of transformation by thermal analysis at temperatures near 800 K yields only approximate limits for $\Delta_{\text{trs}}H^{\circ}_{\text{m}}$ (Fe_2O_3, $\gamma\rightarrow\alpha$, 298.15 K) [1976DEM], [1975KOR/FAD], [1998DIA]. Contrary to a recent claim, Le Châtelier's 1895 study of the enthalpy difference between two different Fe_2O_3 specimens apparently did not involve maghemite, but rather two hematite specimens with different degrees of crystallinity [1895CHA], [2001DRO].

As noted in Appendix A, the results of [1998LAB/NAV], obtained by transposed temperature-drop (TTD) calorimetry and by high-temperature solution calorimetry in molten sodium molybdate, are considered to be preliminary, and are superseded by the acid dissolution data of Majzlan *et al.* [2003MAJ/GRE]. The latter authors were unable to obtain reliable TTD data for maghemite. Their acid dissolution calorimetric measurements in 5.0 M HCl at 340 K yield an enthalpy of transformation, $\Delta_{\text{trs}}H^{\circ}_{\text{m}}$ (Fe_2O_3, $\gamma\rightarrow\alpha$, 298.15 K) value of $-(18.30 \pm 1.49)$ $\text{kJ}\cdot\text{mol}^{-1}$, corrected for water content but not for the relatively small surface-area change of ~ 14 $\text{m}^2\cdot\text{g}^{-1}$, and adjusted for internal consistency with the current review. This value lies within the larger uncertainty limits for all of the earlier calorimetric determinations, and is recommended here as being representative of the best maghemite samples normally available, *i.e.*, chemically pure and crystallographically ordered, microcrystalline powders with a surface area of 10 to 20 $\text{m}^2\cdot\text{g}^{-1}$.

Combined with the value of $\Delta_{\text{f}}H^{\circ}_{\text{m}}$ (Fe_2O_3, α, 298.15 K) = $-(826.29 \pm 2.63)$ $\text{kJ}\cdot\text{mol}^{-1}$, this transformation enthalpy yields the selected value

$$\Delta_{\text{f}}H^{\circ}_{\text{m}}\ (\text{Fe}_2\text{O}_3,\ \gamma,\ 298.15\ \text{K}) = -(807.99 \pm 3.02)\ \text{kJ}\cdot\text{mol}^{-1},$$

almost identical to the value of $-(808.1 \pm 2.0)$ $\text{kJ}\cdot\text{mol}^{-1}$ derived by Majzlan *et al.* [2003MAJ/GRE]. The selected enthalpy and entropy values for the transformation yield $\Delta_{\text{f}}G^{\circ}_{\text{m}}$ (Fe_2O_3, $\gamma\rightarrow\alpha$, 298.15 K) = $-(16.6 \pm 1.5)$ $\text{kJ}\cdot\text{mol}^{-1}$, which corresponds to a pK_{s} value for maghemite (1.45 ± 0.13) higher than that of hematite.

$$\tfrac{1}{2}\ (\alpha\ \text{or}\ \gamma)\text{-Fe}_2\text{O}_3 + 1\tfrac{1}{2}\ \text{H}_2\text{O(l)} \rightleftharpoons \text{Fe}^{3+} + 3\ \text{OH}^-$$

Taylor and Owen [1997TAY/OWE] compared the solubilities of maghemite and hematite powders with similar morphology in aqueous HNO_3 at 298 K, and estimated pK_{s}(maghemite) – pK_{s}(hematite) = (1.16 ± 0.16). Recalculation in this review by the SIT procedure yielded pK_{s}(maghemite) – pK_{s}(hematite) = (1.25 ± 0.46). Sadiq and Lindsay [1988SAD/LIN] obtained pK_{s} = (40.36 ± 0.07) for the aqueous solubility equilibrium of a natural (soil) maghemite of somewhat uncertain composition, while Diakonov [1998DIA] obtained a value of (40.06 ± 0.16) from selected data of [1988SAD/LIN]. These values are comparable to a calculated pK_{s} value of (40.59 ± 0.29) for ordered maghemite (Section VII.2.16), obtained from data recommended in the current review. In both of these solubility studies, however, there is some question about the attainment of reversible equilibrium (metastable equilibrium in the case of maghemite). Thus, the experimental error may well exceed the statistical uncertainty of the solubility data.

VII.2.5 δ-Fe_2O_3

The δ-modification of FeOOH was apparently misidentified as a form of Fe_2O_3 when first discovered, and there is no valid δ-Fe_2O_3 ([1977CHU/ZVY] and references therein).

VII.2.6 Synthetic and biogenic ε-Fe_2O_3

This rare, metastable form of Fe_2O_3, first reported in 1934, can be prepared (sometimes admixed with other iron oxides) in various ways [1934FOR/GUI], [1965TRA/FOR], [1998TRO/CHA], [2002ZBO/MAS], [2003ZBO/MAS]. It is apparently unknown as a mineral, but natural ε-Fe_2O_3 has been detected as a constituent of phytoferritin, an iron storage substance in many plant species [2001MCC/SCH]. The crystal structure is orthorhombic, space group: $Pna2_1$, $Z = 8$, with unit cell dimensions $a_0 = 5.095$, $b_0 = 8.789$, $c_0 = 9.437$ Å [1998TRO/CHA]. It is isostructural with $GaFeO_3$, $AlFeO_3$, κ-Al_2O_3, and presumably ε-Ga_2O_3 [1998TRO/CHA]. The oxygen atoms have a double-hexagonal (*ABAC*) stacking sequence, while the iron atoms are divided between tetrahedral and octahedral sites in the ratio 1:3. As in hematite, all oxygen-layer “sandwiches” contain 0.67 Fe per O atom; as in maghemite, sandwiches containing only six-coordinated Fe alternate with those containing both six- and four-coordinated Fe [1998TRO/CHA]. A disordered variant with hexagonal symmetry and the dimensions $a_0 = 2.92$, $c_0 = 9.44$ Å has also been described [1998TRO/CHA]. Mössbauer spectroscopic studies showed that ε-Fe_2O_3 is a non-collinear antiferromagnet with a Morin transition above 80 K but below 293 K [1998TRO/CHA]. Details of the transition sequence between 80 and 150 K have recently been elucidated [2006GIC/FRO]. The Curie temperature is near 480 K [1965TRA/FOR].

The only thermodynamic measurement appears to be Trautmann’s heat-of-dissolution study using aqueous HCl at 298.15 K [1966TRA], which yielded a value of $\Delta_{\mathrm{trs}}H^{\circ}_{\mathrm{m}}(\mathrm{Fe_2O_3}, \varepsilon\rightarrow\alpha, 298.15\ \mathrm{K}) = -(28.2 \pm 6.5)\ \mathrm{kJ\cdot mol^{-1}}$. Combined with the value of $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{Fe_2O_3}, \alpha, 298.15\ \mathrm{K}) = -(826.29 \pm 2.63)\ \mathrm{kJ\cdot mol^{-1}}$, this transformation enthalpy yields

$$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{Fe_2O_3}, \varepsilon, 298.15\ \mathrm{K}) = -(798.0 \pm 7.0)\ \mathrm{kJ\cdot mol^{-1}},$$

essentially identical to the adjusted value of $-(798.0 \pm 6.6)\ \mathrm{kJ\cdot mol^{-1}}$ derived by Majzlan *et al.* [2004MAJ/NAV]. This value is uncorrected for the large surface area, but is probably representative of typical, finely divided synthetic ε-Fe_2O_3. Relative but not quantitative C_p measurements for an ε-Fe_2O_3/SiO_2 nanocomposite material show a broad anomaly at the Morin transition near 130 K [2006GIC/FRO]. It is therefore possible that the entropy of ε-Fe_2O_3 is slightly higher than that of γ-Fe_2O_3, which does not display any low-temperature C_p anomalies.

VII.2.7 Magnetite, Fe_3O_4(cr)

The magnetic properties of lodestone, which are due to magnetite and/or maghemite, were known in ancient Greece and first used in ancient China. Magnetite itself was apparently first described in 1845 [1845HAI]; it is now recognized as a widespread mineral and corrosion product. The crystal structure of magnetite and other spinels was deduced by W.H. Bragg in 1915 with numerous subsequent refinements [1915BRA], [1994NEI/DOL]. The distinction between "normal" and "inverse" spinels was clarified by Verwey and co-workers [1936VER/BOE], [1941VER/HAA], [1947VER/HEI]. In a normal spinel, AB_2O_4, A^{2+} cations occupy one-eighth of the tetrahedral sites, and B^{3+} cations occupy one-half of the octahedral sites, in a cubic close-packed O^{2-} sublattice. In an inverse spinel, the tetrahedral cation sites are occupied by B^{3+}, while the octahedral sites are shared equally by A^{2+} and B^{3+} cations. Magnetite and most other iron spinels have inverse structures, $ZnFe_2O_4$ and $CdFe_2O_4$ being exceptions [1947VER/HEI]. The crystal structure is cubic, space group: $Fd3m$, $Z = 4$. A cell dimension $a_0 = 8.3970$ Å is recommended by O'Neill and Dollase for pure Fe_3O_4; they attribute slightly lower values, which are commonly obtained, to minor quantities of maghemite in solid solution [1994NEI/DOL].

Rapid electron exchange (dynamic disorder) between Fe^{2+} and Fe^{3+} ions in the octahedral sites of magnetite results in high electrical conductivity [1947VER/HAA]. Below about 124 K, ordering of these ions causes a drop in electrical conductivity and other property changes, as well as a reduction in crystallographic symmetry from cubic to orthorhombic [2000GAS/TAN]. This phenomenon, the Verwey transition, was detected in early $C^{\circ}_{p,\mathrm{m}}$ measurements [1926PAR/KEL], [1929MIL]. The position and profile of the C_p anomaly are sensitive to minor dopants and variation in O:M stoichiometry (*e.g.*, [1972EVA/WES], [1985SHE/KOE], [1991SHE/KOE], [1994TAK/AKI], and references therein), as discussed in Section VII.2.7.1.1.

Magnetite is ferrimagnetic; the Curie transition is characterized by a major λ-type anomaly in the heat capacity with a peak between 845.1 and 848.5 K [1974GRO/SVE], [1990HEM]. An additional, gradual transition, leading to complete randomization of Fe^{2+} and Fe^{3+} among the tetrahedral and octahedral sites, is predicted to be about half complete at 1000 K and complete at about 1500 K [1967NAV/KLE], [1974GRO/SVE], [1981WU/MAS].

Pure magnetite at equilibrium is essentially stoichiometric Fe_3O_4 up to about 1000 K, and shows a substantial compositional range, primarily on the iron-deficient side, from there to the liquidus above 1800 K ([1993GRO/STO] and references therein; see Figure VII-16). Low-temperature oxidation, however, leads to metastable $Fe_{3-x}O_4$ and γ-Fe_2O_3 [1968GAL/FEI]. Magnetite powders, in particular, are sensitive to oxidation and often have a higher Fe^{3+}:Fe^{2+} ratio than 2:1. This is a frequent source of uncertainty in studies of magnetite (*e.g.*, [1988NEI], [1990HEM], appendix of [1993GRO/STO]; see Section VII.1.2). Non-stoichiometric magnetite compositions can also be quenched from high temperatures (*e.g.*, [1991SHE/KOE] and references therein).

VII.2.7.1 Heat capacity and entropy of magnetite

VII.2.7.1.1 Heat-capacity measurements

This assessment is based mainly on nine studies of the heat capacity or high-temperature enthalpy of magnetite as a function of temperature, all of which are summarized in Appendix A [1926PAR/KEL], [1929MIL], [1951COU/KIN], [1969WES/GRO], [1974GRO/SVE], [1976BAR/WES], [1976BAR/WES2], [1990HEM], [1994TAK/AKI]. A number of investigations have focused on the Verwey transition, including the effects of dopant elements, changes in the O:Fe ratio, defects, and residual strain (*e.g.*, [1991SHE/KOE], [1976BAR/WES2], [1994TAK/AKI], and references therein). Given the abundance of high-precision, tabulated $C^{\circ}_{p,\mathrm{m}}$ measurements in most of the studies cited above, publications that include only graphical representations of heat capacity are not reviewed here.

The combined data from [1969WES/GRO] and [1994TAK/AKI] are fitted adequately up to about 35 K by an expression of the type $C^{\circ}_{p,\mathrm{m}} = \mathrm{A}T^{\mathrm{B}}$, and this was used for entropy calculations from 0 to 30 K. Low-temperature heat-capacity measurements on magnetite were reported by Dixon *et al.* [1965DIX/HOA] and Koenitzer *et al.* [1989KOE/KEE]. They described their measurements with fitted equations of the type:

$$C_p \text{ or } C_v = \alpha T^{3/2} + \beta T^{3}$$

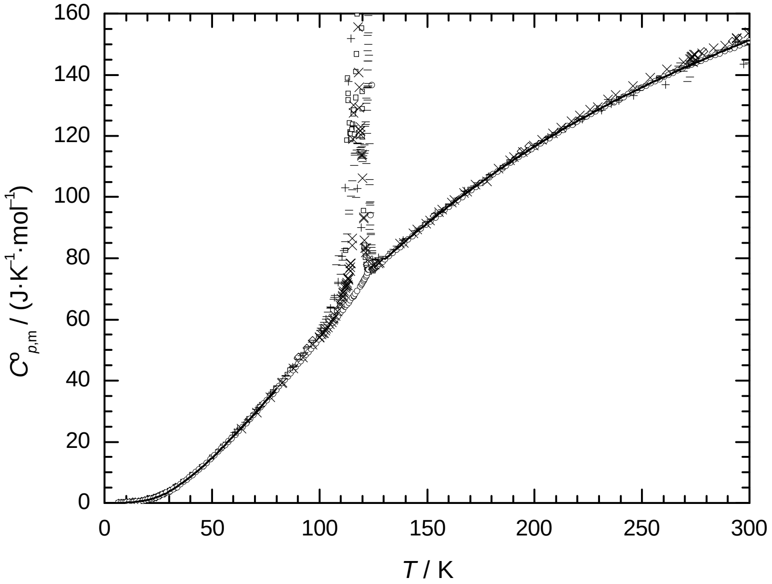
for the temperature ranges 1.2 to 4.2 K and 0.3 to ~ 8.3 K, respectively. The corresponding entropy contributions over these temperature ranges differ from those given by our expression (fitted for 0 to 35 K, above) by $< 0.005\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ for the equations obtained by [1965DIX/HOA] and by only $0.0005\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ for the equation obtained by [1989KOE/KEE] for stoichiometric Fe_3O_4. Therefore, no further refinement was attempted.

Figure VII-24 shows very good agreement among 6 sources of $C^{\circ}_{p,\mathrm{m}}$ data up to 300 K, with the exception of the Verwey transition region (~ 100 to 130 K) and a few data points near ambient temperature.

Close examination of the discrepancies between the six sub-ambient $C^{\circ}_{p,\mathrm{m}}$ data sets and preliminary fitted polynomial functions, excluding data between 80 and 130 K, showed systematic deviations between natural and synthetic specimens at $T > 200$ K, probably linked to impurities. Measurements from [1926PAR/KEL] and

[1976BAR/WES2] were almost 3% higher near ambient temperature than those for synthetic specimens. The data of [1929MIL] showed deviations of as much as – 7%, perhaps indicating an over-correction for impurities and thermal artifacts.

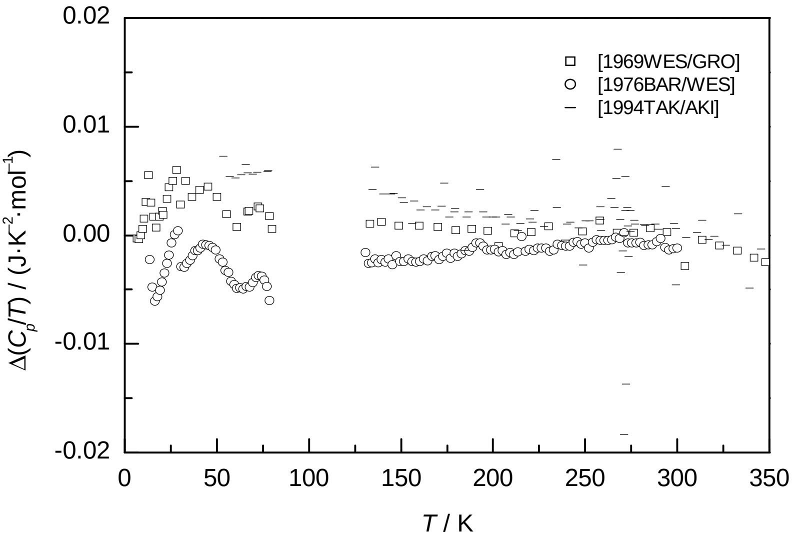
Figure VII-24: Experimental heat-capacity measurements for magnetite up to 300 K (◇: [1926PAR/KEL]; +: [1929MIL]; □: [1969WES/GRO]; −: [1976BAR/WES]; ×: [1976BAR/WES2]; and ○: [1994TAK/AKI]; solid line: fitted curves for temperatures from 0 to 80 K and from 130 to 300 K).



When expressed as $C^{\circ}_{p,\mathrm{m}}/T$, all but two measurements from the three remaining, large data sets from [1969WES/GRO], [1976BAR/WES], and [1994TAK/AKI] agree within ± 0.01 J·K^{-2}·mol^{-1}, as shown in Figure VII-25. Nevertheless, slight biases are apparent; values from [1994TAK/AKI] are generally the lowest, and those from [1976BAR/WES] are generally on the high side. These biases correspond to entropy contributions (sum of the deviations in $[\Delta_{0\,\mathrm{K}}^{80\,\mathrm{K}} S^{\circ}_{\mathrm{m}}]$ and $[\Delta_{130\,\mathrm{K}}^{298.15\,\mathrm{K}} S^{\circ}_{\mathrm{m}}]$ relative to the overall fit), estimated by numerical integration, of – 0.43 J·K^{-1}·mol^{-1} for [1994TAK/AKI], + 0.28 J·K^{-1}·mol^{-1} for [1969WES/GRO], and + 0.49 J·K^{-1}·mol^{-1} for [1976BAR/WES]. The numerical order of these values is the reverse of the order for calculations of $[\Delta_{80\,\mathrm{K}}^{130\,\mathrm{K}} S^{\circ}_{\mathrm{m}}]$, which are 33.57 J·K^{-1}·mol^{-1} for [1994TAK/AKI], 33.33 J·K^{-1}·mol^{-1} for [1969WES/GRO], and 33.11 J·K^{-1}·mol^{-1} for

[1976BAR/WES].[1, 2] This suggests that pre- and post-transition tails can contribute to measured $C^{\circ}_{p,\mathrm{m}}$ values below 80 K and above 130 K. This is consistent with the findings of Takai *et al.* [1994TAK/AKI], who detected a tail region extending between about 80 and 220 K, even though their observed transition was exceedingly sharp. It should be noted that the unusually high transition temperature of 123.82 K observed by Takai *et al.* suggests that their magnetite specimen may have been slightly iron-rich, $\mathrm{Fe}_{3+x}\mathrm{O}_4$ (see [1991SHE/KOE], [1996STO/GLO] and references therein).

Figure VII-25: Residual plots for experimental heat-capacity measurements for magnetite up to 350 K (excluding data between 80 and 130 K) from [1969WES/GRO], [1976BAR/WES], and [1994TAK/AKI], relative to preliminary fitted curves for the pooled data.



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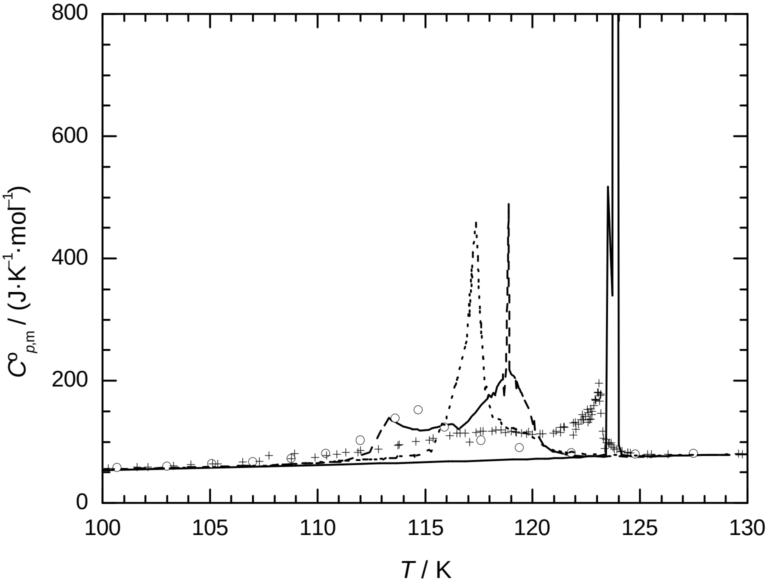
[1] These values for $[\Delta_{80\mathrm{K}}^{130\mathrm{K}} S^{\circ}_{\mathrm{m}}]$ were obtained by numerical integration. In the case of Takai *et al.*, they include a contribution of 6.16 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ for the isothermal portion of the transition that they observed at 123.83 K [1994TAK/AKI]. In all cases, curve-fitted interpolations were used to estimate C_p at 80 and 130 K.

[2] Corresponding values for $[\Delta_{80\mathrm{K}}^{130\mathrm{K}} S^{\circ}_{\mathrm{m}}]$ obtained from the data of [1929MIL] and [1976BAR/WES2] were 32.72 and 32.82 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, respectively.

VII.2.7.1.2 Calculation of standard entropy

The previous section suggests that S°_{m} (Fe_3O_4, cr, 298.15 K) is best assessed by individual treatment of the $C^{\circ}_{p,\mathrm{m}}$ data sets; this is supported by the wide variation in observed profiles for the Verwey transition, as shown in Figure VII-26. Values for $[\Delta_{0\,\mathrm{K}}^{298.15\,\mathrm{K}} S^{\circ}_{\mathrm{m}}]$($Fe_3O_4$, cr) obtained in this way are 145.65 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ for [1994TAK/AKI], 146.20 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ for [1969WES/GRO], and 146.19 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ for [1976BAR/WES]. The first of these values accords well with the values of 145.67 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ tabulated by [1994TAK/AKI] and 145.72 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ obtained by numerical integration. The second and third values agree closely with the tabulated value of 146.15 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ given by [1969WES/GRO], retained by [1993GRO/STO], and changed only marginally to 146.14 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ by [1990HEM]. Earlier estimates for S°_{m} (Fe_3O_4, cr, 298.15 K) of 146.9 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ [1926PAR/KEL] and 145.14 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ [1929MIL] also show good agreement, as do the values of (145.52 ± 0.21) to (146.23 ± 0.21) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ for Zn- and Cd-doped magnetites [1976BAR/WES2].

Figure VII-26: Experimental heat-capacity measurements for magnetite between 100 and 130 K showing variation of the Verwey transition profile (○: [1929MIL]; dash line: [1969WES/GRO]; +: [1976BAR/WES]; dotted line: [1976BAR/WES2]; solid line: [1994TAK/AKI]). The peak apparent $C^{\circ}_{p,\mathrm{m}}$ value for [1994TAK/AKI] is over 3×10^4 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$.



The uncertainty in the portion of $[\Delta_{0\,\mathrm{K}}^{298.15\,\mathrm{K}} S_{\mathrm{m}}^{\circ}](\mathrm{Fe_3O_4}, \mathrm{cr})$ derived from fitted curves, based on the standard deviations given above for the residual plot, is ± 0.19 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. The uncertainty from the isothermal portion of the Verwey transition can not be assessed from [1994TAK/AKI]. Shepherd *et al.* obtained an average value of (5.91 ± 0.12) $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, plus about 0.25 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ for the immediate pre- and post-transition region [1991SHE/KOE], the sum of which is in excellent agreement with the value of 6.16 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ from [1994TAK/AKI]. By combining these uncertainties, we obtain $[\Delta_{0\,\mathrm{K}}^{298.15\,\mathrm{K}} S_{\mathrm{m}}^{\circ}](\mathrm{Fe_3O_4}, \mathrm{cr}) = (145.65 \pm 0.22)$ $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ for [1994TAK/AKI] and, by a similar procedure, we estimate uncertainty limits of (146.20 ± 0.35) $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ for data from [1969WES/GRO], which are slightly more pessimistic than the uncertainty of ± 0.21 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ given by Bartel and Westrum [1976BAR/WES2]. It is difficult to obtain a fully independent entropy value from the data of [1976BAR/WES], because they do not extend below 53.37 K, but the uncertainty is likely very similar to that derived for [1969WES/GRO], *i.e.*, $[\Delta_{0\,\mathrm{K}}^{298.15\,\mathrm{K}} S_{\mathrm{m}}^{\circ}](\mathrm{Fe_3O_4}, \mathrm{cr}) = (146.19 \pm 0.35)$ $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. The mean of these three values is:

$$[\Delta_{0\,\mathrm{K}}^{298.15\,\mathrm{K}} S_{\mathrm{m}}^{\circ}](\mathrm{Fe_3O_4}, \mathrm{cr}) = (145.89 \pm 0.16)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}},$$

and the recommended value, allowing for some slight, unquantifiable residual bias in the individual values, is:

$$[\Delta_{0\,\mathrm{K}}^{298.15\,\mathrm{K}} S_{\mathrm{m}}^{\circ}](\mathrm{Fe_3O_4}, \mathrm{cr}) = (145.89 \pm 0.30)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}.$$

VII.2.7.1.3 The question of zero-point entropy

Anderson suggested a possible zero-point entropy in magnetite, stating that the octahedral sites in a spinel structure may achieve perfect short-range order (alternation of $\mathrm{Fe^{2+}}$ and $\mathrm{Fe^{3+}}$ in the case of magnetite), while maintaining a finite entropy [1956AND]. Following correspondence with L. Onsager, he estimated a zero-point entropy of $[(0.404R \cdot \mathrm{mol^{-1}}\ \mathrm{Fe_3O_4}) + (10\text{–}20\%)]$, *i.e.*, $S_{\mathrm{m}}^{\circ}(\mathrm{Fe_3O_4}, \mathrm{cr}, 0\ \mathrm{K}) = (3.9 \pm 0.2)$ $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$.

Several researchers have sought experimental evidence for this zero-point entropy from high-temperature equilibrium thermodynamic data involving magnetite, as discussed in Appendix A [1969WES/GRO], [1972RAU], [1974GRO/SVE], [1987NEI2]. In general, recent publications either explicitly disfavour a finite zero-point entropy (*e.g.*, [1987NEI2], [1992HAA/HEM]) or ignore the possibility (*e.g.*, [1991SHE/KOE], [1993GRO/STO]). Treatment of the first-order Verwey transition of stoichiometric $\mathrm{Fe_3O_4}$ by Shepherd *et al.* appears to preclude a finite zero-point entropy, at least in near-stoichiometric $\mathrm{Fe_3O_4}$ [1991SHE/KOE]. Therefore we select:

$$S_{\mathrm{m}}^{\circ}(\mathrm{Fe_3O_4}, \mathrm{cr}, 298.15\ \mathrm{K}) = [\Delta_{0\,\mathrm{K}}^{298.15\,\mathrm{K}} S_{\mathrm{m}}^{\circ}](\mathrm{Fe_3O_4}, \mathrm{cr}) = (145.89 \pm 0.30)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}.$$

VII.2.7.1.4 The heat capacity at 298.15 K

The value of $C^{\circ}_{p,\mathrm{m}}$ (Fe_3O_4, cr, 298.15 K) was evaluated by fitting various polynomial functions to the combined $C^{\circ}_{p,\mathrm{m}}$ data from 250 to 350 K from five different sources [1969WES/GRO], [1974GRO/SVE], [1976BAR/WES], [1990HEM], and [1994TAK/AKI]. The standard deviation was estimated from residuals for the 36 data for temperatures between 275 and 325 K. The resulting selected value is:

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{Fe_3O_4, cr, 298.15\ K}) = (150.78 \pm 1.25)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

This compares well with previous tabulated values of 150.41 to 151.17 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ [1969WES/GRO], [1976BAR/WES], [1990HEM], [1992HAA/HEM], [1993GRO/STO], [1994TAK/AKI].

VII.2.7.1.5 Heat capacity and entropy above 298.15 K

The situation with the high-temperature heat capacity of magnetite is similar to that with hematite (Section VII.2.2.2), *i.e.*, it is difficult to obtain reliable high-temperature $C^{\circ}_{p,\mathrm{m}}(T)$ functions for the large λ-type anomaly at the Curie transition, T_C. As with hematite, polynomial functions were obtained with extremely large coefficients that require as many as 10 significant figures for accurate calculation of $C^{\circ}_{p,\mathrm{m}}$ and derived thermodynamic properties. Others have evidently encountered similar difficulties (*e.g.*, [1990HEM], see Appendix A).

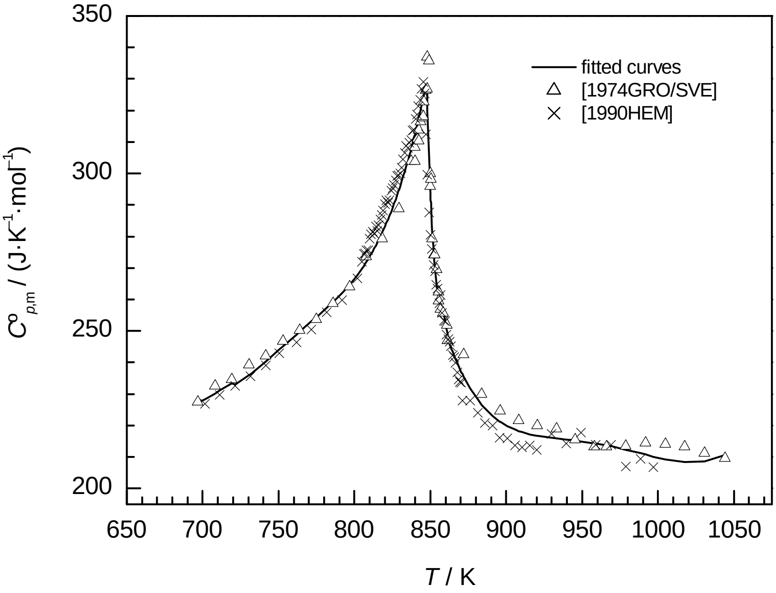
The difficulty of fitting the $C^{\circ}_{p,\mathrm{m}}$ data in the Curie transition region is compounded by the significantly different results of [1974GRO/SVE] and [1990HEM], the latter being consistently higher than the former near 830 K (just below T_C) and lower near 890 K (just above T_C), as shown in Figure VII-27, whereas integrated properties at 1000 K are quite similar.

In the current assessment, pooled $C^{\circ}_{p,\mathrm{m}}$ data from [1974GRO/SVE] and [1990HEM] below 700 K were fitted by two expressions covering the arbitrary temperature ranges 298.15 to 516.66 K and 516.66 to 713.66 K; this gave a slightly better fit than a single polynomial over the entire range from 250 to 800 K. The value of 516.66 K was chosen simply because it is the crossover point for the two selected $C^{\circ}_{p,\mathrm{m}}$ expressions. The expression for 298.15 to 516.66 K was adjusted to give exact agreement with the selected value of $C^{\circ}_{p,\mathrm{m}}$ (298.15 K).

$$\begin{aligned}[C^{\circ}_{p,\mathrm{m}}]^{516.66}_{298.15}(\mathrm{Fe_3O_4}, \alpha, T)/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = {} & 1.05758 \times 10^{-3}\,(T/\mathrm{K})^{2} - 1.66142\,(T/\mathrm{K}) \\ & + 1.24795 \times 10^{3} - 2.99131 \times 10^{5}(T/\mathrm{K})^{-1} \\ & + 2.73311 \times 10^{7}\,(T/\mathrm{K})^{-2}\end{aligned}$$

$$\begin{aligned}[C^{\circ}_{p,\mathrm{m}}]^{713.66}_{516.66}(\mathrm{Fe_3O_4}, \alpha, T)/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = {} & 8.50170 \times 10^{-3}\,(T/\mathrm{K})^{2} - 1.97310 \times 10^{1}\,(T/\mathrm{K}) \\ & + 1.75512 \times 10^{4} - 6.78706 \times 10^{6}\,(T/\mathrm{K})^{-1} \\ & + 9.89090 \times 10^{8}\,(T/\mathrm{K})^{-2}\end{aligned}$$

Figure VII-27: Experimental heat-capacity measurements for magnetite between 700 and 1050 K from [1974GRO/SVE] and [1990HEM], and final fitted curves.



Above 700 K, the data sets were each fitted by three separate five-term polynomial expressions spanning the transition region and the average values of the coefficients were taken, yielding expressions for the temperature ranges 713.66 to 847.57 K, 847.57 to 861.97 K, and 861.97 to 1044 K. This amounts to giving equal weight to each of the two data sets as a whole, which is equivalent to weights of about 1.0 and 0.56 to the individual measurements of [1974GRO/SVE] and [1990HEM], respectively. Grønvold *et al.* [1993GRO/STO] used a more complex weighting scheme to evaluate $C^{\circ}_{p,\mathrm{m}}(T)$ for magnetite, with relatively low weights applied to Hemingway's data, in part because of disagreement over the hematite content of the material used in both studies [1974GRO/SVE], [1990HEM].

The $C^{\circ}_{p,\mathrm{m}}(T)$ equations for $T > 700$ K are not recommended because of the high precision they demand; instead, smoothed $C^{\circ}_{p,\mathrm{m}}$ values and incremental thermodynamic properties for temperatures from 700 to 1040 K are listed in Table VII-12. The tabulated values can be combined with the values $H^{\circ}_{\mathrm{m}}(700\ \mathrm{K}) - H^{\circ}_{\mathrm{m}}(298.15\ \mathrm{K}) = (76.98 \pm 0.38)\ \mathrm{kJ \cdot mol^{-1}}$ and $S^{\circ}_{\mathrm{m}}(700\ \mathrm{K}) = (305.15 \pm 0.81)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, based on the $C^{\circ}_{p,\mathrm{m}}(T)$ relationship recommended elsewhere in this section. Overall fits and residuals for all fitted equations and all temperatures except between 80 and 130 K are shown in Figure VII-28 and Figure VII-29.

Table VII-12: Thermodynamic quantities for Fe_3O_4(cr) between 700 and 1040 K.

T / K	$C^{o}_{p,m}$ / J·K^{-1}·mol^{-1}	$[\Delta^{T}_{700\,K}H^{o}_{m}]$ / kJ·mol^{-1}	$[\Delta^{T}_{700\,K}S^{o}_{m}]$ / J·K^{-1}·mol^{-1}
700	228.06	0.00	0.00
713.66 *	231.76	3.14	4.44
720	232.75	4.61	6.50
740	239.68	9.33	12.96
760	248.16	14.21	19.46
780	256.49	19.25	26.02
800	266.58	24.48	32.63
820	283.12	29.96	39.40
840	312.90	35.89	46.54
847.57 *	329.27	38.32	49.42
860	252.75	41.73	53.42
861.97 *	246.83	42.23	53.99
880	229.04	46.50	58.90
900	220.02	50.97	63.93
920	216.76	55.34	68.72
940	215.52	59.66	73.37
960	214.23	63.96	77.89
980	212.19	68.22	82.29
1000	209.78	72.44	86.55
1020	208.31	76.62	90.69
1040	209.77	80.79	94.74

* The temperatures of 713.66, 847.57, and 861.97 K are crossover points for the different fitted functions used. Note the slight mis-match at 1040 K with the constant $C^{o}_{p,m}$ value of (204 ± 5) J·K^{-1}·mol^{-1} recommended for $T > 1040$ K.

Figure VII-28: Experimental heat-capacity measurements for magnetite (from the 9 sources discussed in the text: ◇: [1926PAR/KEL]; +: [1929MIL]; □: [1969WES/GRO]; △: [1974GRO/SVE]; –: [1976BAR/WES]; |: [1976BAR/WES2]; ×: [1990HEM]; ✳: [1990HEM] table 5; ○: [1994TAK/AKI]) and final fitted curves; the curves include a baseline for the Verwey transition region according to data from [1994TAK/AKI]. The horizontal line at $T > 1050$ K represents the constant $C^{\circ}_{p,\mathrm{m}}$ value between 1050 and ~ 1500 K, derived from [1951COU/KIN].

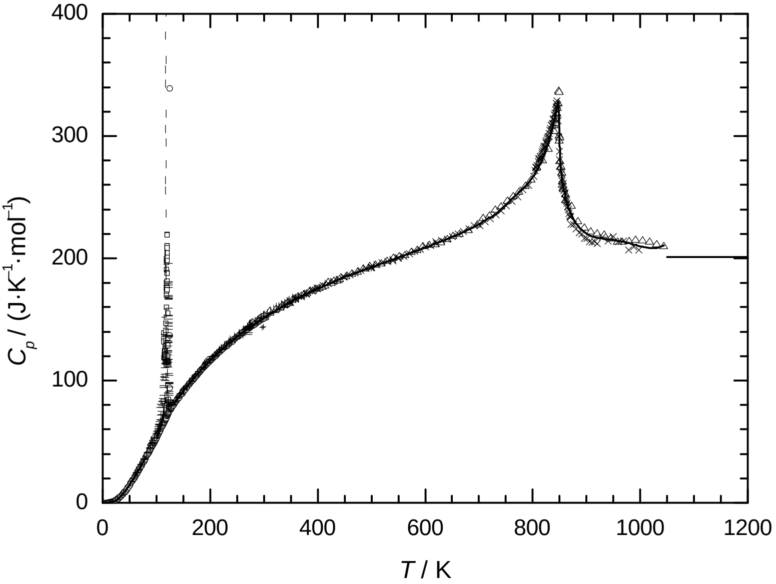
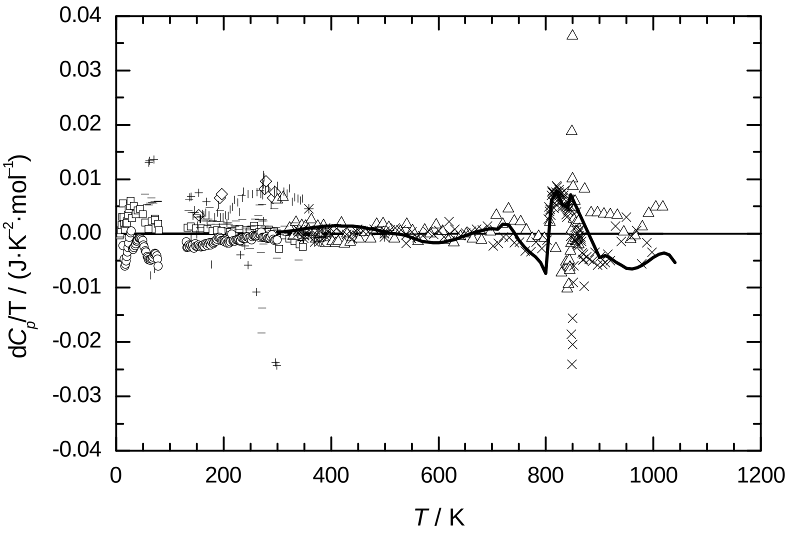
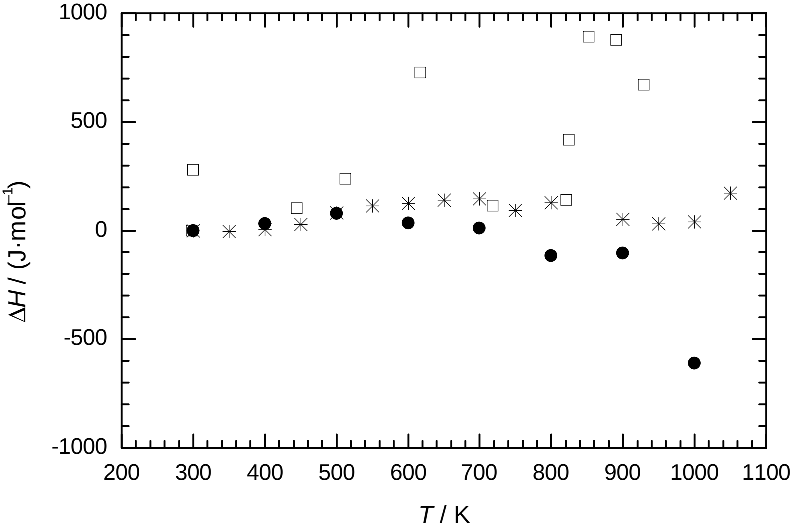


Figure VII-29: Residual plots for experimental heat-capacity measurements for magnetite from the 9 sources discussed in the text, relative to the final fitted curves, excluding data between 80 and 130 K (◇: [1926PAR/KEL]; +: [1929MIL]; □: [1969WES/GRO]; △: [1974GRO/SVE]; −: [1976BAR/WES]; |: [1976BAR/WES2]; ×; [1990HEM]; ✳: Table 5 of [1990HEM]; ○: [1994TAK/AKI]). The bold, solid line represents the expressions recommended by Hemingway from 290 to 800 K, 800 to 845 K, and 900 to 1800 K.



Enthalpy differences, $\Delta_{0\,\mathrm{K}}^{T}H_{\mathrm{m}}^{\mathrm{o}}$ (Fe_3O_4, cr), obtained by integration of the heat-capacity expressions derived here, are compared with smoothed, tabulated values from [1990HEM] and [1993GRO/STO] and with experimental, drop-calorimetric values from [1951COU/KIN] in Figure VII-30. Agreement with the first two sources is excellent (within 0.15 $\mathrm{kJ\cdot mol^{-1}}$ up to 900 K), and the small discrepancies are consistent with the differences in data selection and weighting. As noted by Grønvold *et al.* [1993GRO/STO] and others, the drop-calorimetric measurements diverge markedly from those obtained by adiabatic calorimetry measurements above about 800 K. Grønvold *et al.* [1993GRO/STO] suggested that this may be due to a quenching effect in the drop-calorimetric measurements, perhaps an incomplete reversal of the high-temperature disorder of Fe^{2+} and Fe^{3+} between octahedral and tetrahedral sites [1981WU/MAS]. This explanation seems plausible, therefore no further adjustment is made to the $C_{p,\mathrm{m}}^{\mathrm{o}}$ expressions to improve agreement with the data of [1951COU/KIN].

Figure VII-30: Discrepancies between enthalpy-difference values, $[\Delta_{0\,\mathrm{K}}^{T} H_{\mathrm{m}}^{\mathrm{o}}]$ (Fe_3O_4, cr), derived by integration of the equations described in Table VII-12, and the smoothed values tabulated by [1990HEM] (●) and [1993GRO/STO] (✳) on the basis of heat-capacity measurements, and experimental measurements by drop calorimetry from [1951COU/KIN] (□).



Data from Coughlin *et al.* [1951COU/KIN] remain the sole source of heat-capacity estimates for magnetite above 1050 K. Linear regression of their data between 1044.8 and 1766 K yields a constant value of $C_{p,\mathrm{m}}^{\mathrm{o}}$ (Fe_3O_4, cr) = (200.2 ± 0.6) $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ (they obtained 200.8 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ for the temperature range 900 to 1800 K). Their final data point is at 1825 K, a temperature close to the magnetite solidus; it deviates markedly from the regression line, and may have been influenced by partial melting. Note that this constant value is about 4% lower than might be expected from extrapolation of the C_p data of [1990HEM] and [1993GRO/STO]. This could represent (a) a systematic bias between the direct $C_{p,\mathrm{m}}^{\mathrm{o}}$ measurements and the enthalpy-based values, (b) a tail of the Néel anomaly extending to $T > 1044$ K, or (c) a minor $C_{p,\mathrm{m}}^{\mathrm{o}}$ anomaly near 1000 K. Given this uncertainty, a conservative approach is taken and the following value is selected:

$$[C_{p,\mathrm{m}}^{\mathrm{o}}]_{1050\,\mathrm{K}}^{1800\,\mathrm{K}}(\mathrm{Fe_3O_4, cr}, T) = (204 \pm 5)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}.$$

VII.2.7.2 Enthalpy of formation of magnetite

VII.2.7.2.1 Calorimetric determinations

Early values for $\Delta_f H_m^\circ$ (Fe_3O_4, cr), discussed briefly in Appendix A, were based on heats of acid dissolution [1881BER], combustion of iron [1912RUF/GER], [1913RUF/GER], [1913MIX], [1929ROT], and fusion with sodium peroxide [1913MIX]. The uncertainties in these values are all too large for them to be included in the current assessment. A heat-of-dissolution study by Roth and Wienert [1934ROT/WIE], performed because of difficulties with direct bomb-calorimetry measurements [1929ROT], yielded the most reliable calorimetric measurement of $\Delta_f H_m^\circ$ (Fe_3O_4, cr). Recalculation from the acid-dissolution data of [1934ROT/WIE] gives $\Delta_f H_m^\circ$ (Fe_3O_4, cr, 298.15 K) = $-(1116.35 \pm 2.14)$ $kJ \cdot mol^{-1}$, very close to the reported value of $\Delta_f H_m^\circ$ (Fe_3O_4, cr, 293.85 K) = $-(1116.12 \pm 0.92)$ $kJ \cdot mol^{-1}$ [1934ROT/WIE] but with a larger uncertainty estimate.

VII.2.7.2.2 Third-law determinations from Fe(cr)-Fe_3O_4(cr) equilibrium

Many experimental values for $\Delta_f H_m^\circ$ (Fe_3O_4, cr, 298.15 K) are based on high-temperature measurements of iron oxide equilibria, notably in the Fe-O, Fe-H-O, Fe-C-O, and Fe-Si-O systems. More recent, high-precision, solid-state electrochemical measurements are based mainly on the Fe-O, Fe-Ni-O, and Fe-Cu-O systems, *i.e.*, cell-potential measurements on iron oxide couples *vs.* Fe-wüstite, Ni-NiO, or Cu-Cu_2O couples.

As noted by O’Neill [1988NEI], iron metal-oxide equilibria have been technically important for at least 3000 years. Qualitative thermochemical studies date back to Priestley [1796PRI], Berthollet [1803BER], and their contemporaries at the dawn of modern chemistry. Reactions in gas mixtures, both H_2-H_2O and CO-CO_2, were investigated as early as the 1850s [1857DEB], and the first equilibrium measurements in H_2-H_2O gas mixtures were attempted (with heroic efforts at temperature control) by Deville [1870DEV]. While Deville’s approach was adapted by many researchers over more than 60 years (*e.g.*, [1921CHA], [1923WOH/GUN], [1924EAS/EVA], [1933EMM/SHU]), results were often inaccurate and a reasonable understanding of the iron-wüstite-magnetite system did not emerge until the 1920s. Particularly important contributions demonstrated the existence of the Fe-wüstite-magnetite eutectoid near 840 K [1921CHA] and the variable, non-stoichiometric composition of wüstite [1927SCH/DIN]. A 1922 review revealed poor agreement among various equilibrium studies in H_2O-H_2 and CO-CO_2 gas mixtures [1922EAS]. Emmett and Shultz identified thermal diffusion effects within the apparatus (in particular, the partial separation of H_2 and H_2O) as an important source of error in such studies [1933EMM/SHU]. This problem was evaluated further by Darken and Gurry [1945DAR/GUR].

Relatively few researchers have investigated the Fe-magnetite equilibrium directly, presumably because reaction kinetics limit both electrochemical and gas-solid equilibrium measurements to a small experimental window below the Fe-wüstite-magnetite eutectoid, between about 700 and 840 K.

The more reliable measurements on Fe-Fe_3O_4 equilibrium in H_2-H_2O atmospheres:

$$3\ \mathrm{Fe(cr)} + 4\ \mathrm{H_2O(g)} \rightleftharpoons \mathrm{Fe_3O_4(cr)} + 4\ \mathrm{H_2(g)}.$$

yield values for $\Delta_f H_m^\circ$ (Fe_3O_4, cr, 298.15 K) of $-(1113.65 \pm 1.68)$ kJ·mol^{-1} [1921CHA], $-(1117.46 \pm 0.19)$ kJ·mol^{-1} [1933EMM/SHU], and $-(1114.95 \pm 0.40)$ kJ·mol^{-1} [1972RAU], excluding for now the relatively large uncertainties in the thermal data used in the third-law analysis (see Appendix A). Data from Fricke *et al.* [1941FRI/WAL] are excluded because of uncertainties arising from the reactive powders they used.

Many researchers have studied the Fe-wüstite and wüstite-Fe_3O_4 equilibria in CO-CO_2 mixtures, but few have measured the Fe-Fe_3O_4 equilibrium in such mixtures [1922EAS].

$$3\ \mathrm{Fe(cr)} + 4\ \mathrm{CO_2(g)} \rightleftharpoons \mathrm{Fe_3O_4(cr)} + 4\ \mathrm{CO(g)}$$

Data are excluded from the current assessment, because of slow reaction kinetics and because this equilibrium is metastable with respect to carbon deposition, as are the wüstite-Fe_3O_4 equilibrium below about 923 K and the Fe-wüstite equilibrium below about 993 K (*e.g.*, [1921CHA], [1922EAS], [1928GAR]). Iron carbide solid-solution formation, which would affect iron activity, is also possible at higher temperatures; for example, Darken and Gurry estimated an equilibrium concentration of 0.03 weight-% C in Fe(cr) for their Fe-wüstite experiments at 1273 K [1945DAR/GUR].

Gas-solid equilibrium studies have been largely supplanted by solid-state electrochemistry, following the development of solid ZrO_2- and ThO_2-based oxygen-conducting electrolytes that permit accurate cell-potential measurements on oxide systems over a wide range of T and p_{O_2} [1957KIU/WAG]. The Fe-wüstite couple is frequently used as a reference electrode in such studies. O’Neill and co-workers at the Australian National University went to great lengths to calibrate this couple (as well as Ni-NiO and Cu-Cu_2O) against an air electrode, and to investigate other important iron oxide equilibria [1986HOL/NEI], [1987NEI], [1988NEI].

Relatively few such cell-potential measurements have been performed at temperatures below about 900 K, because of technical problems including physical leakage of oxygen [1966BIR] and limits on the performance of Pt electrodes for gaseous (usually air) reference measurements [1988NEI]. O’Neill used a Y-doped ThO_2 electrode for the air reference to measure Fe-Fe_3O_4 equilibrium potentials down to 750 K [1988NEI], while Birks reported measurements using a high-density electrolyte down to ~ 700 K [1966BIR]. O’Neill’s meticulous experimental approach gives confidence that all sources of experimental uncertainty and systematic error were minimized; he obtained the following relationship for the chemical potential of oxygen for the Fe-Fe_3O_4 couple between 750 and 833 K.

$$1½\ \mathrm{Fe(cr)} + \mathrm{O_2(g)} \rightleftharpoons ½\ \mathrm{Fe_3O_4(cr)}$$

$$\mu_{\mathrm{O_2}}\ /\ \mathrm{J\cdot mol^{-1}} = (-\ 607673 + 1060.994\ (T/\mathrm{K}) - 132.3909\ (T/\mathrm{K})\ \ln\ (T/\mathrm{K}) + 0.0665(T/\mathrm{K})^2) \pm 214\ (2\sigma).$$

The Gibbs energy of formation of Fe_3O_4(cr) is equal to twice this oxygen chemical potential.

Based on these measurements and selected calorimetric data for Fe(cr) and Fe_3O_4(cr) in a third-law analysis, O'Neill obtained $\Delta_f H_m^o$ (Fe_3O_4, cr, 298.15 K) = $-$ (1115.39 ± 0.38) kJ·mol^{-1}. Using calorimetric data assessed in the current review, we obtain a value of $-$ (1115.04 ± 0.42) kJ·mol^{-1}. Unlike O'Neill's calculation (see Fig. 6 of [1988NEI]), the present calculation yields a perceptible residual temperature dependence of about $-$ 5 (J·mol^{-1})·K^{-1} in the calculated enthalpy of formation. This probably reflects a systematic error in $\Delta C_{p,m}^o$ for the formation reaction; note that the experimental conditions coincide with the steeply rising portion of the C_p curve for Fe_3O_4 between 750 and 850 K, leading up to the Curie transition, where there is significant divergence between the $C_{p,m}^o$ measurements of [1974GRO/SVE] and [1990HEM], and fitting difficulties were encountered (see Section VII.2.7.1.5).

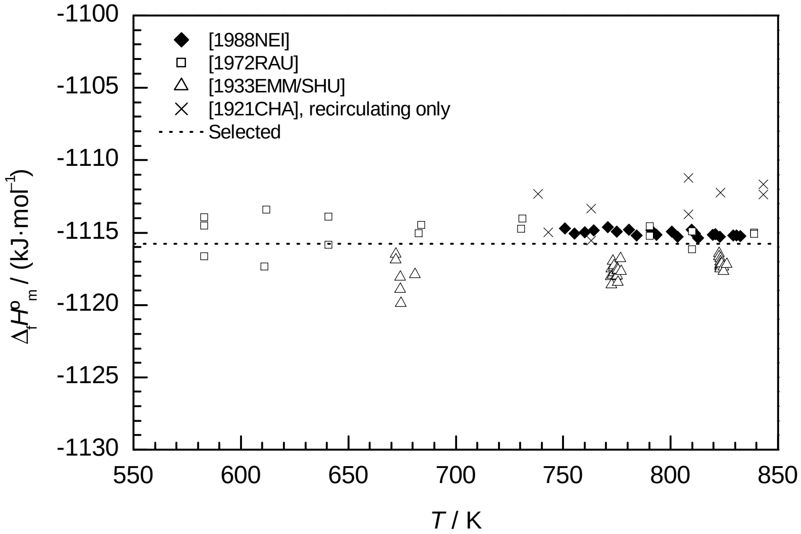
Data measured from Fig. 1 of Birks [1966BIR] yield values for $\Delta_f G_m^o$ (Fe_3O_4, cr, T), and hence $\Delta_f H_m^o$ (Fe_3O_4, cr, 298.15 K), averaging 3.8 kJ·mol^{-1} more negative than those obtained by O'Neill (see above). Potential relationships from Sugimoto *et al.* [1980SUG/KUW] for the Fe-Pb-O system yield values about 5.3 kJ·mol^{-1} less negative than O'Neill's values. Data from both these sources appear to be substantially less accurate than those of [1988NEI]. Data compiled by Haas [1992HAA/HEM] from four other sources show wide variations in $\Delta_f H_m^o$ (Fe_3O_4, cr, 298.15 K), with values ranging from about $-$ 1110 to $-$ 1131 kJ·mol^{-1} and a highly variable temperature dependence. Because of the unusually meticulous measurements, the value of $\Delta_f H_m^o$ (Fe_3O_4, cr, 298.15 K) = $-$ (1115.04 ± 0.42) kJ·mol^{-1}, derived here from O'Neill's data, is retained. As noted above, this value does not include the uncertainty in thermal data used in the third-law calculation. Using the uncertainty estimates for $S_m^o(T)$ and $C_{p,m}^o(T)$ of Fe(cr) and Fe_3O_4(cr) up to 800 K in the current assessment, we obtain a value of $\Delta_f H_m^o$ (Fe_3O_4, cr, 298.15 K) = $-$ (1115.04 ± 2.42) kJ·mol^{-1}, in good agreement with the value of $-$ (1116.35 ± 2.14) kJ·mol^{-1} obtained from the calorimetric data of [1934ROT/WIE] (see Section VII.2.7.2.1). Combination of these last two values yields a final selected value of:

$$\Delta_f H_m^o\ (\mathrm{Fe_3O_4},\ \mathrm{cr},\ 298.15\ \mathrm{K}) = -\ (1115.78 \pm 1.60)\ \mathrm{kJ\cdot mol^{-1}},$$

which is almost identical to Hemingway's assessment of $-$ 1115.73 kJ·mol^{-1} (no uncertainty given; [1990HEM]) and close to the value of $-$ (1116.64 ± 2.25) kJ·mol^{-1} in Haas's exhaustive, unpublished assessment [1992HAA/HEM].

To clarify the relative precision and apparent biases of some of the studies described above, Figure VII-31 shows the results of some of the third-law enthalpy calculations on data from [1988NEI], [1972RAU], [1933EMM/SHU], and the recirculating experiments of [1921CHA].

Figure VII-31: Values of $\Delta_f H^{\circ}_m$ (Fe_3O_4, cr, 298.15 K) calculated by the third-law method from Fe(cr)-Fe_3O_4(cr) equilibrium measurements by several authors.



VII.2.7.2.3 Third-law determinations from other equilibria

High-temperature thermodynamic information on magnetite can also be obtained from the much-studied iron–wüstite–magnetite and iron-quartz-fayalite-magnetite systems. The former system is complicated by the variable stoichiometry of wüstite, and involves three reactions at any temperature.

$$3\ \text{Fe(cr)} + {}^{3x}/_{2}\ \text{O}_2\text{(g)} \rightleftharpoons 3\ \text{FeO}_x\text{(cr)}$$

$$3\ \text{FeO}_x\text{(cr)} + {}^{3(y-x)}/_{2}\ \text{O}_2\text{(g)} \rightleftharpoons 3\ \text{FeO}_y\text{(cr)}$$

$$3\ \text{FeO}_y\text{(cr)} + {}^{(4-3y)}/_{2}\ \text{O}_2\text{(g)} \rightleftharpoons \text{Fe}_3\text{O}_4\text{(cr)}$$

These reactions can be evaluated from the bounding T- p_{O_2} relationships, the limiting compositions FeO_x and FeO_y, and the composition- p_{O_2} relationship within the wüstite phase field. As with the Fe-Fe_3O_4 equilibrium, early studies on solid-gas equilibria in

H_2O-H_2 and CO_2-CO atmospheres have been superseded by more recent solid-state cell-potential measurements.

Because of the high temperatures of these equilibrium measurements (~ 1000 K), the contribution to the uncertainty in $\Delta_f H_m^o$ (Fe_3O_4, cr, 298.15 K) from $\Delta_r S_m^o$ and $\Delta_r C_{p,m}^o$ values is somewhat higher than for the Fe-Fe_3O_4 equilibrium, around ± 3 kJ·mol^{-1}. Inclusion of such data is unlikely to improve the assessment of $\Delta_f H_m^o$ (Fe_3O_4, cr, 298.15 K). These systems are therefore reviewed briefly to establish their consistency with direct Fe-Fe_3O_4 equilibrium measurements, but a full evaluation is beyond the scope of the current review, and very high-temperature studies such as [1940CHI/MAR] are excluded.

Because wüstite is stable only above ~ 840 K, early attempts to measure limiting compositions (FeO_x and FeO_y, corresponding to the Fe-wüstite and wüstite-Fe_3O_4 phase boundaries) were mostly unreliable. The first reliable measurements came with the painstaking study of Darken and Gurry [1945DAR/GUR]. More recent publications include [1962HOC/IYE], [1964VAL/CAR], [1965GER/DOD], [1969RIZ/GOR], [1970PIC/DOD], [1970CAM/BOU], [1970CIR/BUR], [1974GID/GOR], [1981BAR/BLE], and several reviews [1973GID/GOR], [1978SPE/KUB], [1983KNA], and [1991SUN]. An uncritical compilation from these sources yielded the following approximate empirical relationships, valid between 1050 and 1300 K with mean deviations of 0.005 in x and 0.008 in y:

$$x = 1.0624 - 0.000009206\,(T/\text{K}) \qquad \text{and} \qquad y = 0.9846 + 0.00011882\,(T/\text{K}).$$

There is greater variation among experimental values of x and y at temperatures outside this range.

Numerous studies indicate a linear or near-linear relationship between oxygen potential and O:Fe ratio within the wüstite phase field (*e.g.*, [1945DAR/GUR], [1964BAR2], [1968RIZ/SMI], [1973GID/GOR], [1974GID/GOR], and references therein). Departures from linearity, observed by some researchers, have been interpreted in terms of subphases within the wüstite field (*e.g.*, [1964VAL/RAC], [1969FEN/RIL], [1984HAZ/JEA], [1986VAL/CAR], and references therein). If real, the subphase transitions are incompletely understood and the associated calorimetric effects are evidently small [1993GRO/STO]. There is no doubt that at least some of the observed deviations are due to experimental error [1973GID/GOR], [1974GID/GOR]; a linear relationship between T and $\log_{10}(p_{O_2})$ is assumed here. The calculation of $\Delta_f G_m^o$ (Fe_3O_4, cr, T) from the Fe-wüstite-Fe_3O_4 reaction sequence then reduces to the following expression.

$$\Delta_f G_m^o\,(Fe_3O_4, \text{cr}, T)/\text{kJ}\cdot\text{mol}^{-1} = 1\tfrac{1}{2}[\mu_1\, x + \tfrac{1}{2}(y - x)\,(\mu_2 - \mu_1) + \mu_2\,({}^{4}/_{3} - y)]$$

where $\mu_1(T)$ and $\mu_2(T)$ are the oxygen chemical potentials of the limiting wüstite compositions FeO_x and FeO_y at temperature T.

Substitution of the $\mu_1(T)$ and $\mu_2(T)$ relationships from O'Neill [1988NEI] and the $x(T)$ and $y(T)$ expressions given above, followed by a third-law calculation, yields values of $\Delta_f H_m^\circ$ (Fe$_3$O$_4$, cr, 298.15 K) ranging from − 1115.22 kJ·mol^{-1} for equilibrium at 1000 K to − 1114.21 kJ·mol^{-1} for 1300 K. These values are in excellent agreement with those from the Fe-Fe$_3$O$_4$ equilibrium, illustrating the good internal consistency of O'Neill's data and available compositional information. The slight drift of these values with temperature may reflect residual bias in the C_p expressions used. Figure VII-32 and Figure VII-33 compare Fe-wüstite and wüstite-Fe$_3$O$_4$ data (high-temperature Gibbs energies of reaction) from several selected sources with the expressions for the chemical potential of oxygen from O'Neill [1988NEI]. Some discrepancies persist among contemporary, cell-potential measurements; see, for example, the synopses of Mallika *et al.* [1986MAL/PAN] and Sjödén *et al.* [1986SJO/SEE].

Figure VII-32: Comparison of values at 1050 to 1350 K from O'Neill's expression [1988NEI] for the oxygen chemical potential of the Fe-wüstite couple with selected values from the CO-CO$_2$ equilibrium [1903BAU/GLA], [1921CHA], [1921MAT], [1945DAR/GUR], [1965VAL/RAC], H$_2$-H$_2$O equilibrium [1921CHA], [1930EMM/SHU], [1933EMM/SHU], [1972RAU], and cell-potential measurements [1957KIU/WAG], [1968CHA/FLE], [1969MOR/SAT], [1969RIZ/GOR], [1972DAV/SME], [1974SAI], [1978BON/PER], [1979MYE/GUN], [1981JAC/ROS], [1981SCH/KUS].

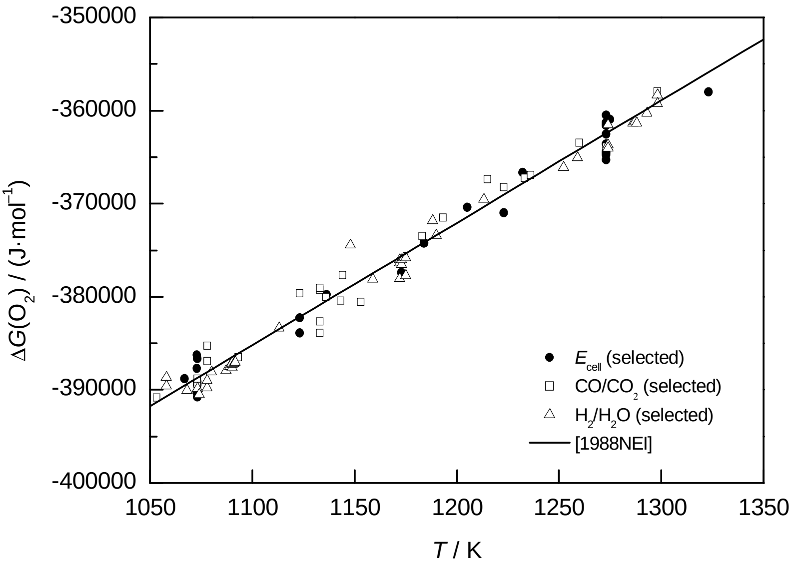
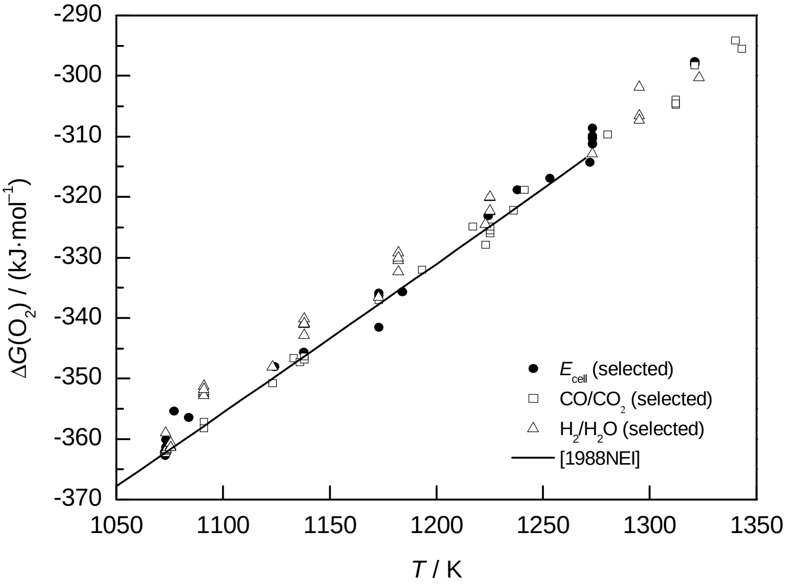


Figure VII-33: Comparison of values at 1050 to 1350 K from O'Neill's expression [1988NEI] for the oxygen chemical potential of the wüstite-Fe_3O_4 couple with selected data from the CO-CO_2 equilibrium [1903BAU/GLA], [1921CHA], [1921MAT], [1924EAS/EVA], [1945DAR/GUR], [1965VAL/RAC], H_2-H_2O equilibrium [1921CHA], [1930EMM/SHU], [1933EMM/SHU], [1972RAU], and solid-state cell-potential measurements [1957KIU/WAG], [1966BIR], [1968CHA/FLE], [1968RIZ/SMI], [1969MOR/SAT], [1969RIZ/GOR], [1978BON/PER], [1981SCH/KUS].



The Fe-Si-O system and, in principle, other ternary oxide systems offer the advantage that the complexity of wüstite is avoided, and $\Delta_f G^\circ_m$ (Fe_3O_4, cr, T) can be determined at temperatures above the Fe-wüstite-Fe_3O_4 eutectoid as a linear combination of $\Delta_r G^\circ_m$ values for two reactions. Specifically, for the Fe-Si-O system, the quartz-fayalite-Fe (QFI) and quartz-fayalite-Fe_3O_4 (QFM) equilibria have been employed.

$$Fe_2SiO_4(cr)\ (fayalite) \rightleftharpoons 2\ Fe(cr) + O_2(g) + SiO_2(cr)\ (quartz) \qquad (VII.28)$$

$$3\ Fe_2SiO_4(cr) + O_2(g) \rightleftharpoons 2\ Fe_3O_4(cr) + 3\ SiO_2(cr) \qquad (VII.29)$$

$$3\ Fe(cr) + 2\ O_2(g) \rightleftharpoons Fe_3O_4(cr) \qquad (\tfrac{1}{2} \times (VII.29)) - (1\tfrac{1}{2} \times (VII.28))$$

Sluggish reaction kinetics have made these equilibria difficult to measure, but O'Neill obtained data yielding a value of $\Delta_f H^\circ_m$ (Fe_3O_4, cr, 298.15 K) = − (1115.43 ± 0.60 [2σ])

$kJ\cdot mol^{-1}$, essentially identical to his value of − (1115.39 ± 0.38 [2σ]) $kJ\cdot mol^{-1}$ from Fe-Fe_3O_4 equilibrium measurements [1987NEI2], [1988NEI], again showing excellent internal consistency. Calculations using the enthalpy and heat-capacity values derived in the current assessment yielded values ranging from − 1114.78 $kJ\cdot mol^{-1}$ for equilibrium at 1000 K to − 1113.87 $kJ\cdot mol^{-1}$ for 1300 K, again apparently reflecting a slight residual error in the C_p expressions. The thermodynamic properties of fayalite are discussed in Section X.2.1.1.

VII.2.7.3 Solubility of magnetite

Several detailed solubility studies on magnetite have been reported (*e.g.*, [1970SWE/BAE], [1980TRE/LEB], [1995ZIE/JON]), and their interpretation was aimed mainly at elucidating the properties of hydrolysed aqueous iron species. These studies are therefore discussed in Section VII.1.2.

VII.2.8 Wüstite, $Fe_{1-x}O$(cr)

The name wüstite (after German geologist Ewald Wüst) was coined by Schenck and Dingmann [1927SCH/DIN]. Though mainly known by its metallurgical occurrence, wüstite occurs rarely in natural settings, *e.g.*, in the fusion crusts of iron meteorites and in natural coke [1997GAI/SKI]. The related phase magnesiowüstite, (Mg,Fe)O, is thought to be an important component of the earth's lower mantle ([1984HAZ/JEA] and references therein).

Early research on wüstite was impeded by its misidentification as "FeO". In fact, pure iron(II) oxide does not exist, except perhaps at pressures greater than 10 GPa, and iron-deficient wüstite, $Fe_{1-x}O$,[1] is unstable with respect to Fe + Fe_3O_4 below about 840 K. These facts were not established until the 1920s [1921CHA], [1927SCH/DIN], [1933JET/FOO], [1933JET/FOO2]. By 1945 the composition and temperature limits for wüstite were fairly well determined [1945DAR/GUR], though substantial uncertainties persist between the eutectoid and about 1100 K [1991SUN], [1992HAA/HEM], [1993GRO/STO]; see Figure VII-16.

Compositions near the eutectoid can be quenched and studied at low temperatures; for example, heat capacities have been measured for selected compositions up to about 450 K [1993GRO/STO]. A metastable, near-stoichiometric

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[1] While the formulation $Fe_{1-x}O$ is crystallographically correct, it is sometimes useful to describe the composition as FeO_{1+y} or Fe_zO_{1-z} and convert molar thermodynamic quantities appropriately. To convert thermodynamic quantities for $Fe_{1-x}O$ to corresponding quantities for FeO_{1+y} or Fe_zO_{1-z}, multiply by $1/(1-x)$ or $1/(2-x)$, respectively. Variants of the FeO_{1+y} formulation are used to discuss iron-wüstite-magnetite equilibria in Sections VII.2.7.2.3 and VII.2.8.3; for example, the eutectoid composition and the iron-wüstite and wüstite-magnetite limiting compositions are simplified in specific contexts to FeO_w, FeO_x, and FeO_y.

composition (~ $Fe_{0.99}O$) can be obtained, along with Fe_3O_4 and traces of Fe, by controlled, partial disproportionation of quenched wüstite near the eutectoid composition [1996STO/GLO]. Based on a detailed thermodynamic study and literature review, Grønvold *et al.* estimated the ambient-pressure eutectoid composition, $Fe_{0.932\pm0.004}O$, and temperature, (847 ± 7) K [1993GRO/STO]. Details of the wüstite phase field and boundaries, relevant to assessing $\Delta_f H^o_m$ (Fe_3O_4, cr, 298.15 K), are discussed in Section VII.2.7.2.3. This section is largely restricted to the eutectoid composition, because high-temperature, solid-solution behaviour is beyond the nominal scope.

Wüstite has a cation-deficient, charge-compensated NaCl-type crystal structure, $Fe^{2+}_{1-3x}Fe^{3+}_{2x}\square_xO$, where □ represents a cation vacancy [1933JET/FOO], [1984HAZ/JEA]. Near and above ambient temperature it is cubic, space group *Fm*3*m*; measured ambient-temperature cell dimensions a_0 vary from 4.285 Å for $Fe_{0.894}O$ to 4.326 Å for $Fe_{0.99}O$ [1933JET/FOO], [1993GRO/STO], [1996STO/GLO]. Various superstructure-type cells have been proposed, based on displacement of iron to tetrahedrally coordinated sites and clustering of adjoining octahedral vacancies, but the associated thermal effects are small ([1973GID/GOR], [1978SPE/KUB], [1993GRO/STO], and references therein). These structural modifications are not considered in the current review. Wüstite is paramagnetic at ambient temperature and undergoes antiferromagnetic ordering (Néel transition) below about 190 K with a reduction in symmetry (see Section VII.2.8.1). The low-temperature form of $Fe_{0.99}O$, for example, is monoclinic, space group *C*2/*m*, with the cell dimensions at 10 K: $a = 5.2615$, $b = 3.0334$, $c = 3.0602$ Å, $\beta = 124.649$ [2002FJE/HAU].

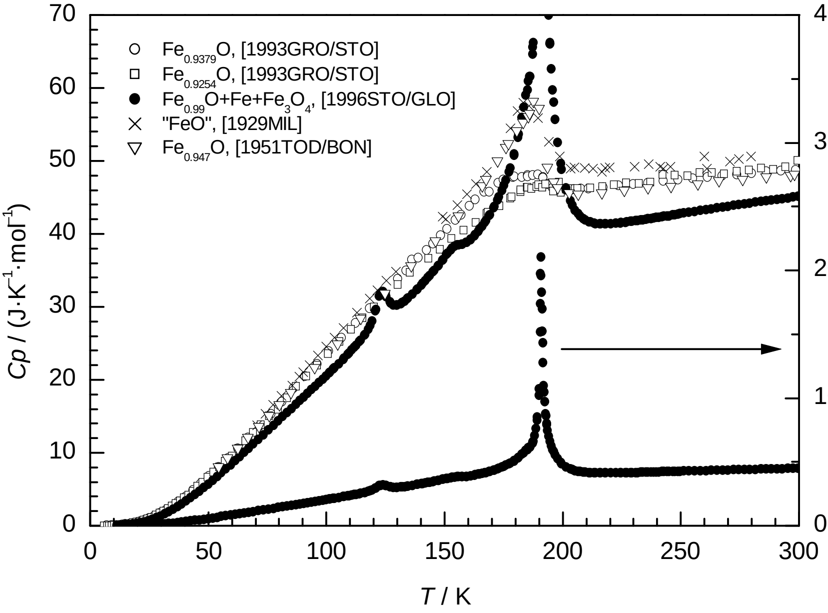
VII.2.8.1 Heat capacity of wüstite

The most detailed and reliable $C^o_{p,m}$ measurements on wüstite were carried out by Grønvold *et al.*, who studied two near-eutectoid compositions, $Fe_{0.9254}O$ and $Fe_{0.9379}O$, and also reported data for $Fe_{0.9427}O$ [1993GRO/STO]. These authors considered the $C^o_{p,m}$ measurements of Todd and Bonnickson [1951TOD/BON] and enthalpy-increment measurements of Coughlin *et al.* [1951COU/KIN] to be the best previous studies, effectively superseding those of Millar [1929MIL] and White [1933WHI]. They dismissed most of the enthalpy-increment measurements by Vladimirov and Ponomarev [1959VLA/PON] as “too high to be credible”. Also of interest are the $C^o_{p,m}$ measurements by Stølen *et al.* [1996STO/GLO] on a partly decomposed specimen with overall composition $Fe_{0.9374}O$, from which the authors extracted thermodynamic quantities for a near-stoichiometric wüstite, $Fe_{0.99}O$.

The shape and position of the $C^o_{p,m}$ anomaly at the Néel transition are strongly dependent on composition [1968MAI/BOU], being sharpest for $Fe_{0.99}O$ and little more than a shoulder for compositions farthest from stoichiometry [1996STO/GLO], [1951TOD/BON], [1993GRO/STO], as shown in Figure VII-34. Note that the data from

[1996STO/GLO] were obtained from a mixture of $\mathrm{Fe_{0.99}O}$, $\mathrm{Fe_3O_4}$ and Fe; the anomaly near 124 K represents the Verwey transition of magnetite (see Sections VII.2.7, VII.2.7.1.1, and VII.2.7.1.2), while the small feature near 150 K was tentatively ascribed to wüstite [1996STO/GLO].

Figure VII-34: Heat-capacity data for wüstite specimens of different compositions [symbols from top to bottom in legend]: $\mathrm{Fe_{0.9379}O}$ from [1993GRO/STO]; $\mathrm{Fe_{0.9254}O}$ from [1993GRO/STO]; mixture of $\mathrm{Fe_{0.99}O + Fe + Fe_3O_4}$ with overall composition $\mathrm{Fe_{0.9374}O}$ from [1996STO/GLO]; "FeO" from [1929MIL]; $\mathrm{Fe_{0.947}O}$ from [1951TOD/BON].



The following values of $C^{\mathrm{o}}_{p,\mathrm{m}}$ ($\mathrm{Fe_{1-\mathit{x}}O}$, cr, 298.15 K) were reported in the above-cited studies: 47.43 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ for $\mathrm{Fe_{0.99}O}$ [1996STO/GLO], 48.1 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ for $\mathrm{Fe_{0.947}O}$ [1951TOD/BON], 48.81 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ for $\mathrm{Fe_{0.9379}O}$ [1993GRO/STO], and 49.19 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ for $\mathrm{Fe_{0.9254}O}$ [1993GRO/STO]; note that the values increase with decreasing Fe/O ratio.[1] In the present review, a linear fit of $C^{\mathrm{o}}_{p,\mathrm{m}}$ data between 250 and 350 K yielded values of $C^{\mathrm{o}}_{p,\mathrm{m}}$ ($\mathrm{Fe_{0.9254}O}$, cr, 298.15 K) and $C^{\mathrm{o}}_{p,\mathrm{m}}$ ($\mathrm{Fe_{0.9379}O}$, cr, 298.15

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[1] Often the $C^{\mathrm{o}}_{p,\mathrm{m}}$ data are reported per mole of [Fe + O], *i.e.*, for the molar quantity $^{1}/_{(2-x)}\mathrm{Fe_{1-\mathit{x}}O}$.

K) identical to those published by Grønvold *et al.* [1993GRO/STO]. A linear interpolation yields the following estimate for $Fe_{0.932}O$, the eutectoid composition as assessed in [1993GRO/STO]:

$$C^{o}_{p,\mathrm{m}}\,(\mathrm{Fe_{0.932}O, cr, 298.15\ K}) = (66/125)\,(48.77 \pm 0.22) + (59/125)\,(49.19 \pm 0.56) = (48.97 \pm 0.29)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}.$$

All heat-capacity measurements on wüstite outside its equilibrium field depend on the kinetic stability of quenched material; thus, measurements are only possible below about 400 K, above about 840 K for the eutectoid composition, and above the phase boundary (even higher than 840 K) for other compositions.[1] At intermediate temperatures, the heat of decomposition interferes with heat-capacity measurements; Grønvold *et al.* [1993GRO/STO] therefore devised the following equations to bridge the gaps in their $C^{o}_{p,\mathrm{m}}$ data between 454.02 and 903.61 K for $Fe_{0.9379}O$ and between 346.71 and 957.08 K for $Fe_{0.9254}O$.

$$[C^{o}_{p,\mathrm{m}}]^{\sim 1000\,\mathrm{K}}_{298.15\,\mathrm{K}}\,(\mathrm{Fe_{0.9379}O, cr}, T)/\mathrm{J \cdot K^{-1} \cdot mol^{-1}} = 51.129 + 0.00485282\,(T/\mathrm{K}) - 334908.9\,(T/\mathrm{K})^{-2} - 40.433488 \times 10^{-12}\,(T/\mathrm{K})^{3}$$

$$[C^{o}_{p,\mathrm{m}}]^{\sim 1000\,\mathrm{K}}_{298.15\,\mathrm{K}}\,(\mathrm{Fe_{0.9254}O, cr}, T)/\mathrm{J \cdot K^{-1} \cdot mol^{-1}} = 50.804 + 0.00416562\,(T/\mathrm{K}) - 248170.7\,(T/\mathrm{K})^{-2} - 451.70487 \times 10^{-12}\,(T/\mathrm{K})^{3}.$$

These functions are only valid if there are no $C^{o}_{p,\mathrm{m}}$ anomalies in the bridged temperature ranges, which is a reasonable assumption given the low value of the Néel temperature. A linear interpolation of these equations yields the following expression for $Fe_{0.932}O$, modified slightly to be consistent with the value derived above for $C^{o}_{p,\mathrm{m}}$ ($Fe_{0.932}O$, cr, 298.15 K):

$$[C^{o}_{p,\mathrm{m}}]^{\sim 1000\,\mathrm{K}}_{298.15\,\mathrm{K}}\,(\mathrm{Fe_{0.932}O, cr}, T)/\mathrm{J \cdot K^{-1} \cdot mol^{-1}} = 50.9417 + 0.00452846\,(T/\mathrm{K}) - 293968.5\,(T/\mathrm{K})^{-2} + 191.85582 \times 10^{-12}\,(T/\mathrm{K})^{3}.$$

This expression is plotted from 200 to 1000 K in Figure VII-35, together with the measured $C^{o}_{p,\mathrm{m}}$ data for $Fe_{0.9379}O$ and $Fe_{0.9254}O$ from [1993GRO/STO]; it appears to be valid down to about 260 K, near the upper tail of the Néel transition, and is selected here to describe the heat capacity of $Fe_{0.932}O$(cr).

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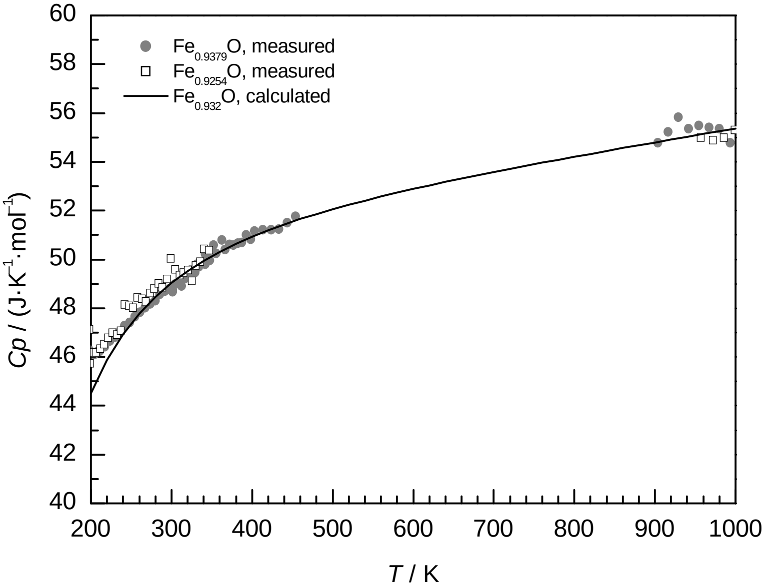
[1] Note that oxygen-rich compositions are particularly difficult to quench without at least partial precipitation of magnetite. When quenched material is re-heated to temperatures where wüstite is stable, some time may be necssary to regain homogeneity.

Figure VII-35: Measured heat-capacity values for $Fe_{0.9379}O$ and $Fe_{0.9254}O$ from [1993GRO/STO], and fitted bridging expression for $C^{\mathrm{o}}_{p,\mathrm{m}}$ from 298.15 to 1000 K..



VII.2.8.2 Entropy of wüstite

Todd and Bonnickson obtained $S^{\mathrm{o}}_{\mathrm{m}}$ ($Fe_{0.947}O$, cr, 298.15 K)[1] = (59.2 ± 0.8) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ ([1951TOD/BON]; see Appendix A); earlier entropy estimates for wüstite were much less precise. More recent values of $[\Delta_{0\,\mathrm{K}}^{298.15\,\mathrm{K}} S^{\mathrm{o}}_{\mathrm{m}}]$($Fe_{1-x}O$, cr) are 57.09 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ for $Fe_{0.9379}O$ [1993GRO/STO], 56.24 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ for $Fe_{0.9254}O$ [1993GRO/STO], and 60.45 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ for $Fe_{0.99}O$ [1996STO/GLO]. Based on an extensive literature review, Grønvold *et al.* suggested the following values for rounded compositions: $[\Delta_{0\,\mathrm{K}}^{298.15\,\mathrm{K}} S^{\mathrm{o}}_{\mathrm{m}}]$ = (61 ± 1) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ for hypothetical FeO and $[\Delta_{0\,\mathrm{K}}^{298.15\,\mathrm{K}} S^{\mathrm{o}}_{\mathrm{m}}]$ = (55 ± 1) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ for $Fe_{0.9}O$ [1993GRO/STO].

In the present review, entropy values for $Fe_{0.9379}O$ and $Fe_{0.9254}O$ were recalculated from the $C^{\mathrm{o}}_{p,\mathrm{m}}$ data of [1993GRO/STO] by numerical integration and by curve-fitting procedures similar to those described for hematite and magnetite. Fitted $C^{\mathrm{o}}_{p,\mathrm{m}}$ curves are depicted together with the experimental data in Figure VII-36. All calculated values for $[\Delta_{0\,\mathrm{K}}^{298.15\,\mathrm{K}} S^{\mathrm{o}}_{\mathrm{m}}]$ agreed with those of Grønvold *et al.* [1993GRO/STO] within 0.04 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$. Plots of the residuals for the fitting equations

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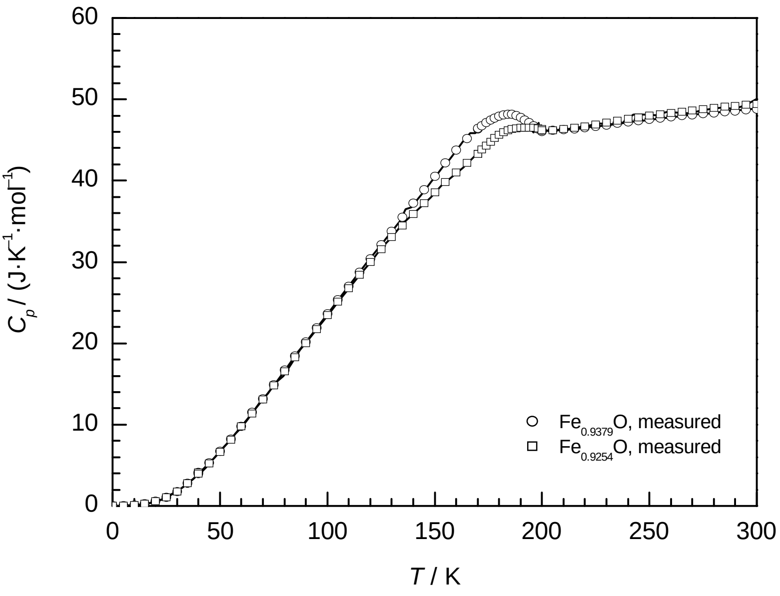
[1] 298.16 K in the original paper.

showed no significant anomalies; the largest discrepancies in $C^{\circ}_{p,\mathrm{m}}/T$ for individual data points were 0.0046 $\mathrm{J\cdot K^{-2}\cdot mol^{-1}}$ for $\mathrm{Fe_{0.9379}O}$ and 0.0039 $\mathrm{J\cdot K^{-2}\cdot mol^{-1}}$ for $\mathrm{Fe_{0.9254}O}$. Interpolation of the values from [1993GRO/STO], with standard deviations calculated from the residuals of our empirical fits, yields the following entropy value for the eutectoid composition of wüstite.

$$[\Delta_{0\,\mathrm{K}}^{298.15\,\mathrm{K}} S^{\circ}_{\mathrm{m}}]\,(\mathrm{Fe_{0.932}O, cr}) = (56.69 \pm 0.49)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

This entropy value explicitly does not include any zero-point configurational contribution, the calculated maximum value of which is 2.07 $\mathrm{J\cdot K^{-1}\ mol^{-1}}$ for complete disorder of vacancies in the composition $\mathrm{Fe_{0.932}O}$ (excluding any contribution from tetrahedral site occupancy by $\mathrm{Fe^{3+}}$). This value is consistent with the contribution of 0.41 $\mathrm{cal\cdot K^{-1}\cdot mol^{-1}}$ (1.72 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$) calculated for the composition $\mathrm{Fe_{0.947}O}$ by Todd and Bonnickson [1951TOD/BON]. However, the existence of short-range order (vacancy clusters) in wüstite, even at high temperatures ([1984HAZ/JEA], [1996COR/SCH], and references therein), suggests that the zero-point entropy will be much lower than these maximum values.

Figure VII-36: Measured $C^{\circ}_{p,\mathrm{m}}$ values for $\mathrm{Fe_{0.9379}O}$ and $\mathrm{Fe_{0.9254}O}$ from [1993GRO/STO]; bold lines represent the fitting expressions used in the entropy calculation.



VII.2.8.3 Enthalpy of formation of wüstite

Early, direct calorimetric measurements of $\Delta_f H_m^o$ for wüstite, described at the time as "FeO" (*e.g.*, [1895CHA], [1913RUF/GER], [1934ROT/WIE]), are unreliable because of difficulties obtaining complete conversion with pure material of known composition.

Some early research suggested the solubility of oxygen in Fe(cr) ("oxoferrite") at the Fe-wüstite boundary amounts to several weight-%; *e.g.*, [1924EAS/EVA], [1927SCH/DIN], but more recent data indicate very low solubility: a mole fraction of 2.1×10^{-7} at the wüstite eutectoid point, gradually increasing to 2.8×10^{-4} at the liquidus near 1800 K [1967SWI/TUR], [1991SUN]. Therefore, for present purposes, O-saturated Fe can be treated as pure Fe (*i.e.*, unit activity).

In this section, the formula FeO_x denotes any wüstite composition, FeO_w the eutectoid composition, and T_C the eutectoid temperature. Because wüstite is unstable with respect to Fe(cr) + Fe_3O_4(cr) at $T < T_C$, the enthalpy of formation at 298.15 K is of limited use, especially for the low-temperature applications envisaged for thermodynamic values recommended in the current review. Any estimate of $\Delta_f H_m^o$ (FeO_x, cr, 298.15 K) necessitates a third-law calculation from equilibrium data obtained at $T \geq T_C$, and the uncertainties in the associated $C_{p,m}^o(T)$ functions greatly exceed the experimental uncertainty in high-quality oxygen chemical-potential measurements ([1988NEI] and several references therein). Here, we estimate only $\Delta_f H_m^o$ (FeO_w, cr, 298.15 K). Much more detailed treatments of the high-temperature thermodynamic properties of wüstite are available in several reviews and assessments, *e.g.*, [1978SPE/KUB], [1991SUN], [1992HAA/HEM], [1993GRO/STO] and the many references they cite.

Values for $\Delta_f H_m^o$ (FeO_w, cr, 298.15 K) can be derived from knowledge of the eutectoid by at least three, partly independent calculations based on $C_{p,m}^o(T)$ functions for FeO_w(cr), Fe(cr), Fe_3O_4(cr), and O_2(g), as required by the different reactions considered. These include the estimated bridging function for $C_{p,m}^o$ (FeO_w, cr, T), described in Section VII.2.8.1. It is difficult to estimate the uncertainty in the enthalpy values so obtained, because the accuracy of this bridging function and its composition dependence are unknown, but it is perhaps as large as $\pm$ 2 $kJ \cdot mol^{-1}$. First, it is necessary to evaluate T_C and the stoichiometric ratio w.

Grønvold *et al.* [1993GRO/STO] noted that most reported values of T_C lie between 833 and 853 K; their own detailed calorimetric studies led to a value of (847 ± 7) K. Values far outside this range indicate either poor self-consistency, as discussed by O'Neill [1988NEI], or overly long extrapolations of fitted expressions, *e.g.*, the value of T_C = 884 K from [1965VAL/RAC]. The proximity of T_C to the Curie point of Fe_3O_4 (~ 848 K, see Section VII.2.7.1) may be a complicating factor in some measurements and estimates. Estimated values of T_C from gas-solid equilibrium measurements include 843 K [1921CHA], 832 K [1933EMM/SHU], and 843 K [1972RAU]. Solid-state potential-difference measurements have yielded values of 842 and 850 K [1964BAR], 838 K [1966BIR], and three values between 826 and 836 K [1988NEI]. Credible estimates thus range from 826 to 854 K, and we use T_C = (840 ± 14) K for the current calculations.

Recently assessed values for the eutectoid composition, FeO_w, vary significantly: $FeO_{1.073 \pm 0.004}$ [1993GRO/STO], $FeO_{1.056}$ [1991SUN], and $FeO_{1.091}$ [1992HAA/HEM]. Experimental measurements at temperatures just above T_C have yielded estimates of $FeO_{1.065}$ [1964BAR2], [1969FEN/RIL], and $FeO_{1.0585}$ [1973GID/GOR]. For the current calculations we use the composition from [1993GRO/STO], but with a larger uncertainty: $FeO_{1.073 \pm 0.018}$ (or $Fe_{0.932 \pm 0.017}O$).

For the eutectoid composition, by definition, $\Delta_r G^\circ_m$ (VII.30) = 0 at T_C for the disproportionation reaction:

$$(4/w)\ FeO_w(cr) \rightleftharpoons Fe_3O_4(cr) + [(4 - 3w)/w]\ Fe(cr) \qquad \text{(VII.30)}$$

A third-law calculation based on $\Delta_r G^\circ_m$ (VII.30) = 0 at 840 K for w = 1.073 yields $\Delta_f H^\circ_m$ ($FeO_{1.073}$, cr, 298.15 K) = − 285.2 kJ·mol^{-1}.

Grønvold *et al.* [1993GRO/STO] measured $\Delta_r H^\circ_m$ (VII.30) = − (9.7 ± 0.3) kJ·mol^{-1} at (847 ± 7) K, which yields $\Delta_f H^\circ_m$ ($FeO_{1.073}$, cr, 298.15 K) = − 287.1 kJ·mol^{-1}.

A third approach, using a third-law calculation that does not involve magnetite, is based on the oxygen chemical potential at the eutectoid. Three potential-temperature expressions in [1988NEI] for the Fe-Fe_3O_4, Fe-wüstite, and wüstite-Fe_3O_4 equilibria are probably the most accurate available (see Section VII.2.7.2.3). The average of the three intersection points for these expressions is 832 K at an oxygen chemical potential of − 419.62 kJ·mol^{-1}, which corresponds to $\Delta_f G^\circ_m$ (FeO_w, cr, 832 K) = − (419.62w/2) kJ·mol^{-1}. Using w = 1.073 (see above) to perform a third-law calculation on the formation reaction:

$$Fe + (w/2)\ O_2 \rightleftharpoons FeO_w$$

we obtain $\Delta_f H^\circ_m$ ($FeO_{1.073}$, cr, 298.15 K) = − 284.3 kJ·mol^{-1}.

The first of these three estimates is selected:

$$\Delta_f H^\circ_m (FeO_{1.073}, \text{cr}, 298.15\ \text{K}) = -(285.2 \pm 2.0)\ \text{kJ·mol}^{-1}\ \text{or}$$

$$\Delta_f H^\circ_m (Fe_{0.932}O, \text{cr}, 298.15\ \text{K}) = -(265.8 \pm 1.9)\ \text{kJ·mol}^{-1}.$$

Comparison with other assessments is difficult, because they deal with slightly different compositions, *e.g.*, $\Delta_f H^\circ_m$ ($FeO_{1.058}$, cr, 298.15 K) = − 278.3 kJ·mol^{-1} [1978SPE/KUB], $\Delta_f H^\circ_m$ ($FeO_{1.056}$, cr, 298.15 K) = − 281.4 kJ·mol^{-1} [1986HOL/NEI], $\Delta_f H^\circ_m$ ($FeO_{1.056}$, cr, 298.15 K) = − 280.0 kJ·mol^{-1} [1991SUN]. Using the observation that the enthalpy of formation per mole O in wüstite is approximately constant over the composition range [1945DAR/GUR], we can convert these values to estimates for

$\Delta_f H_m^o$ ($FeO_{1.073}$, cr, 298.15 K) of − 282.2, − 285.9, and − 284.5 kJ·mol^{-1}, respectively. The latter two, more recent values agree closely with the above selected value.

VII.2.8.4 Solubility of wüstite

There appear to be no published solubility studies, and it is unlikely that such studies would provide any useful thermodynamic information, since alteration products such as Fe_3O_4 would likely control solubility.

VII.2.9 Goethite, α-FeOOH

Goethite is an abundant mineral, though macroscopic crystals are rare. Goethite and lepidocrocite (γ-FeOOH) were often confused in the early literature; indeed the 1806 type specimen for goethite was later shown to be lepidocrocite [1944PAL/BER]. Goethite is commonly found in iron(III) "hydroxide" precipitates; the preferred synthesis is by aging freshly precipitated ferrihydrite in silica-free alkaline solution at 343 K [2000SCH/COR].

Goethite is isostructural with diaspore (α-AlOOH), orthorhombic, space group: *Pbnm*, $Z = 4$. The crystal structure was first studied by Böhm [1928BOH] and most recently refined in a single-crystal study by Yang *et al.* [2006YAN/LU], who obtained the cell dimensions $a_0 = 4.5979(2)$, $b_0 = 9.9510(5)$, $c_0 = 3.0178(1)$ Å. Slightly different values have been obtained by powder Rietveld refinements [2003MAJ/LAN], [2005MAZ/NAV] and in T- and p-dependent studies [1999GUA/VEN], [2003NAG/KAG]. The anions are hexagonal close-packed, with ordered occupation of one-half of the octahedral sites by Fe. Each O and OH is coordinated to three Fe atoms, and double chains of edge-sharing $FeO_3(OH)_3$ octahedra are linked through vertex sharing and hydrogen bonding into a three-dimensional network.

Goethite is antiferromagnetic and the Néel point varies between 330 and 403 K, probably reflecting variations in particle size and purity ([2003MAJ/LAN], and references therein). Rapid dehydration to hematite above ~ 400 K [1999GUA/VEN] precludes high-temperature property measurements. Some specimens, known as A-goethite, reportedly have two internal magnetic fields with separate critical points of ~ 340 and ~ 370 K ([1966SZY/BUR] and references therein). A small heat-capacity anomaly near 1 K is attributed to magnetic ordering in defects and interfaces and is therefore not an innate property of α-FeOOH [2003MAJ/LAN], [2003MAJ/NAV2].

VII.2.9.1 Enthalpy of formation of goethite

Most published values for $\Delta_f H_m^o$ (FeOOH, α) are based on comparative measurements on goethite and hematite that yield either the enthalpy, $\Delta_r H_m^o$ ((VII.31), T) or the Gibbs energy, $\Delta_r G_m^o$ ((VII.31), T) of Reaction (VII.31).

$$\tfrac{1}{2}\alpha\text{-}Fe_2O_3 + \tfrac{1}{2} H_2O(l) \rightleftharpoons \alpha\text{-}FeOOH \qquad \text{(VII.31)}$$

$$\Delta_r H_m^o \text{(VII.31)} = \Delta_f H_m^o \text{(FeOOH, } \alpha) - ½\{\Delta_f H_m^o (\text{Fe}_2\text{O}_3, \alpha) + \Delta_f H_m^o (\text{H}_2\text{O, l})\}$$

Like most iron oxides and oxyhydroxides, goethite can persist for long periods of time as an extremely fine-grained powder, even in strongly acidic or basic solutions. Enthalpy measurements are therefore modified by particle-size effects that can be as large as 20 - 30 $\text{kJ}\cdot\text{mol}^{-1}$ for nanometer-scale powders. These effects, known since the 1930s, include a surface-enthalpy term and a correction for loosely bound water [2005MAZ/NAV]. Harder to define are the excess enthalpies associated with imperfect crystallization (stacking faults and other defects, partly amorphous material, and intermediate phases such as protohematite) and the different energetics of specific crystallographic surfaces. These effects may be particularly important for measurements of non-aqueous solid decomposition:

$$\alpha\text{-FeOOH} \rightleftharpoons ½\ \alpha\text{-Fe}_2\text{O}_3 + ½\ \text{H}_2\text{O(g)},$$

such as those cited by Ferrier [1964FER] and Diakonov *et al.* [1994DIA/KHO].

Fricke and co-workers [1934FRI/ACK], [1935FRI/KLE] measured heats of solution for goethite and hematite powders with different grain sizes in aqueous HF at 304 - 307 K. Evaluating this work, Diakonov *et al.* [1994DIA/KHO] obtained $\Delta_r H_m^o$ ((VII.31), 298.15 K) = − (6.05 ± 3.15) $\text{kJ}\cdot\text{mol}^{-1}$, corrected to zero surface area, but with large uncertainties in surface-area estimates.

Ferrier measured heats of solution for numerous hematite and goethite powders, with measured particle sizes, near 344 K in aqueous HCl [1964FER], [1965FER], [1966FER], [1968FER]. He reported $\Delta_r H_m^o$ ((VII.31), 344.15 K) = − (2.5 ± 0.6) $\text{kJ}\cdot\text{mol}^{-1}$ for the most crystalline hematite and goethite powders at his disposal [1964FER], whence $\Delta_r H_m^o$ ((VII.31), 298.15 K) = − (1.9 ± 0.6) $\text{kJ}\cdot\text{mol}^{-1}$. Later surface-area-dependent studies yielded: $\Delta_r H_m^o$ ((VII.31), 344.15 K) = − 6.4 $\text{kJ}\cdot\text{mol}^{-1}$ [1965FER] and − 7.2 $\text{kJ}\cdot\text{mol}^{-1}$ [1966FER], [1968FER], which correspond to $\Delta_r H_m^o$ ((VII.31), 298.15 K) values of − 5.8 and − 6.6 $\text{kJ}\cdot\text{mol}^{-1}$, respectively. Re-evaluation by Diakonov *et al.* yielded $\Delta_r H_m^o$ ((VII.31), 298.15 K) = − (6.55 ± 1.2) $\text{kJ}\cdot\text{mol}^{-1}$, which they considered the best surface-area-corrected value then available [1994DIA/KHO].

The surface enthalpy for goethite from Ferrier's studies (1.25 $\text{J}\cdot\text{m}^{-2}$ according to [1966FER]; 1.55 $\text{J}\cdot\text{m}^{-2}$ as re-evaluated in [1994DIA/KHO]) is much higher than the value of 0.6 $\text{J}\cdot\text{m}^{-2}$ (see below) obtained more recently by Mazeina and Navrotsky [2005MAZ/NAV]. This difference probably reflects a non-surface enthalpy contribution due to crystalline imperfections (see above) arising from the low-temperature, solid-state decomposition routes used by Ferrier to convert "hydrated ferric oxide" gel to goethite and hematite. Thus, Ferrier's assumption that surface enthalpy is the principal cause of the observed variations in heats of dissolution in his experiments is probably not valid.

Barany measured the heats of solution of a natural goethite specimen and a reagent-grade hematite powder in 20.1 weight-% aqueous HF at 344.85 K [1965BAR]. Results were corrected for impurities, but details were not provided; a value of $\Delta_r H^o_m$ ((VII.31), 298.15 K) = − (3.8 ± 0.4) $kJ\cdot mol^{-1}$ was obtained. While the specimen was relatively coarsely ground, the crystallite dimensions were likely small [1994DIA/KHO].

Berner compared the solubilities of reagent-grade hematite powder and an aged goethite precipitate in 0.12 M aqueous HCl at 358 K [1969BER]. The observed solubility ratio (goethite:hematite) of 2.32 yields $\Delta_r G^o_m$ ((VII.31), 358 K) = 2.5 $kJ\cdot mol^{-1}$ and hence $\Delta_r H^o_m$ ((VII.31), 298.15 K) = − (4.4 ± 0.4) $kJ\cdot mol^{-1}$, uncorrected for surface-area effects. This study is discussed further in Section VII.1.4.

A series of three, increasingly precise and detailed calorimetric studies by Navrotsky and co-workers furnished the most recent thermodynamic measurements on goethite [1998LAB/NAV], [2003MAJ/GRE], [2005MAZ/NAV]. Some inconsistencies in the tabulated data of [1998LAB/NAV], however, prevent its inclusion in the current assessment.

Majzlan *et al.* compared hematite and goethite by high-temperature transposed temperature-drop and acid-solution calorimetry methods [2003MAJ/GRE]. Both specimens were relatively coarse powders ([2003MAJ/LAN], [2003MAJ/GRE]; see Appendix A). Our recalculated value of $\Delta_r H^o_m$ ((VII.31), 298.15 K) = − (4.5 ± 0.7) $kJ\cdot mol^{-1}$, based on the acid-dissolution data, differs only slightly from the published value of − (4.7 ± 0.7) $kJ\cdot mol^{-1}$ [2003MAJ/GRE]. Published and recalculated values for the transposed temperature-drop method are identical: $\Delta_r H^o_m$ ((VII.31), 298.15 K) = − (3.5 ± 0.8) $kJ\cdot mol^{-1}$ [2003MAJ/GRE].

Mazeina and Navrotsky [2005MAZ/NAV] studied carefully characterized goethite specimens of varying surface area by both acid-solution and high-temperature oxide-melt calorimetry. They obtained a value of 0.6 $J\cdot m^{-2}$ for the surface enthalpy of goethite, corrected for loosely bound H_2O (treated as bulk liquid[1]). The aqueous synthetic routes give more confidence in this result than the values from Ferrier (see above); nevertheless, some uncertainty remains about the exact nature of the surface enthalpy (*e.g.*, degree of surface hydration; properties of crystallographically different surfaces). The oxide-melt method yielded more reproducible data, while acid-dissolution calorimetry necessitated the use of lepidocrocite (γ-FeOOH) as a secondary standard, because of incomplete dissolution with hematite and coarse-grained goethite

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[1] Note that there appears to be an inconsistency here, in that enthalpy measurements were corrected for surplus water on the basis of liquid-like properties, whereas $C^o_{p,m}$ measurements (and subsequent entropy calculations) on goethite and other iron oxyhydroxides were corrected on the basis of ice-like properties [2003MAJ/LAN].

[2005MAZ/NAV]. While good agreement was obtained between the two techniques, only the oxide-melt measurements are considered here.

Close correlation was observed between the BET surface areas and surplus water contents of these goethite specimens, consistent with the water being weakly surface-bound; sequential linear regressions of the surplus-water and surface-area effects yielded a zero-surface-area value of $\Delta_r H^o_m$ ((VII.31), 298.15 K) = − 5.5 kJ·mol^{-1} [2005MAZ/NAV]. In the current assessment, separate linear regressions with respect to water content and surface area yielded a mean value of $\Delta_r H^o_m$ ((VII.31), 298.15 K) = − (4.4 ± 1.5) kJ·mol^{-1}, including a small surface-area correction for hematite[1], which was apparently not included by [2005MAZ/NAV]. Data for the coarsest-grained goethite specimen, with no surface-area correction, gave $\Delta_r H^o_m$ ((VII.31), 298.15 K) = − 3.8 kJ·mol^{-1}, well within the uncertainty limits of the zero-surface-area value.

The surface-area-corrected values for $\Delta_r H^o_m$ ((VII.31), 298.15 K) discussed above range from − 4.4 to − 6.6 kJ·mol^{-1}, while values based on relatively well-crystallized hematite and goethite, without surface-area corrections, range from − 1.9 to − 4.7 kJ·mol^{-1}. Of the latter, all but Ferrier's preliminary value [1964FER] lie between − 3.8 and − 4.7 kJ·mol^{-1}. The value of $\Delta_r H^o_m$ ((VII.31), 298.15 K) = − (4.4 ± 1.5) kJ·mol^{-1} is therefore adopted. Combined with the NEA selected values of $\Delta_f H^o_m$ (H_2O, l, 298.15 K) = − (285.83 ± 0.04) kJ·mol^{-1} and $\Delta_f H^o_m$ (Fe_2O_3, α, 298.15 K) = − (826.29 ± 2.63) kJ·mol^{-1}, this yields the selected value:

$$\Delta_f H^o_m \text{ (FeOOH, α, 298.15 K)} = -\,(560.46 \pm 1.99)\ \text{kJ·mol}^{-1}.$$

VII.2.9.2 Heat capacity and entropy of goethite

Heat-capacity measurements on natural goethite at 53.07 to 295.98 K by King and Weller [1970KIN/WEL] yielded the values $C^o_{p,m}$ (FeOOH, α, 298.15 K) = 74.48 J·K^{-1}·mol^{-1} and S^o_m (FeOOH, α, 298.15 K) = (60.38 ± 0.63) J·K^{-1}·mol^{-1}. Diakonov *et al.* [1994DIA/KHO] tabulated eight previously unpublished $C^o_{p,m}$ measurements on synthetic goethite at 309 to 490 K by A. V. Korobeinikova (Ph.D. Thesis, Moscow State University, Russia, 1975, *fide* [1998DIA]). A more detailed study on synthetic goethite of composition FeOOH·0.083H_2O yielded 250 $C^o_{p,m}$ measurements from 0.7 to 396.15 K [2003MAJ/LAN], [2003MAJ/NAV2]. In the present assessment, data from this study were fitted satisfactorily by a series of four equations. Measurements between 2 and 20 K fit an expression of the form $C^o_{p,m}$ = AT^B. The large number of measurements below 2 K were excluded, because the weak $C^o_{p,m}$ anomaly perturbed this fit. The entropy contribution from the anomaly is very small, ~ 0.1 mJ·K^{-1}·mol^{-1},

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[1] Based on a surface enthalpy for hematite of 0.87 J·m^{-2}, the average of three published values tabulated in [2005MAZ/NAV].

and was ignored. Measurements between 10 and 220 K were fitted by an unconstrained sixth-order polynomial function. Remaining data were fitted by the following two functions, which permit heat-capacity and entropy calculations up to 396 K.

$$[C^{\circ}_{p,\mathrm{m}}]^{372.6\,\mathrm{K}}_{200\,\mathrm{K}}(\mathrm{FeOOH},\ \alpha + 0.083\mathrm{H_2O},\ T)/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = 0.0003768913\,(T/\mathrm{K})^{2} - 0.07625551\,(T/\mathrm{K}) + 80.43469 - 2014.245\,(T/\mathrm{K})^{-1} - 594081.2\,(T/\mathrm{K})^{-2}$$

(based on data for $181.21 < T/\mathrm{K} < 375.33$)

$$[C^{\circ}_{p,\mathrm{m}}]^{396\,\mathrm{K}}_{372.6\,\mathrm{K}}(\mathrm{FeOOH},\ \alpha + 0.083\mathrm{H_2O},\ T)/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = 1.01228346\,(T/\mathrm{K})^{2} - 1455.04034\,(T/\mathrm{K}) + 779756.914 - 184428534.4\,(T/\mathrm{K})^{-1} + 16233060709\,(T/\mathrm{K})^{-2}$$

(based on data for $375.04 < T/\mathrm{K} < 396.15$)

The first of these expressions yields $C^{\circ}_{p,\mathrm{m}}$(FeOOH, α + $0.083\mathrm{H_2O}$, 298.15 K) = (77.76 ± 0.24) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, the uncertainty being estimated from residuals between 250 and 350 K. The two functions intersect at 372.6 K, slightly below the peak temperature of the Néel transition. Integration of $C^{\circ}_{p,\mathrm{m}}/T$, using the fitted expressions, yields the value S°_{m}(FeOOH, α + $0.083\mathrm{H_2O}$, 298.15 K) = (63.11 ± 0.37) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$. Correcting for the excess water content as hexagonal ice (see Section VII.2.1), we obtain $C^{\circ}_{p,\mathrm{m}}$(FeOOH, α, 298.15 K) = (74.32 ± 0.42) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ and S°_{m}(FeOOH, α, 298.15 K) = (59.67 ± 0.50) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, in good agreement with the values of $C^{\circ}_{p,\mathrm{m}}$(FeOOH, α, 298.15 K) = 74.36 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ and S°_{m}(FeOOH, α, 298.15 K) = (59.70 ± 0.16) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ given by Majzlan *et al.* [2003MAJ/LAN]. There is also good agreement with the values of King and Weller [1970KIN/WEL], cited above (see also Figure VII-37). The values of [2003MAJ/LAN] are selected with slightly increased uncertainties (see Section VII.2.1).

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{FeOOH},\ \alpha,\ 298.15\ \mathrm{K}) = (74.36 \pm 0.42)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

$$S^{\circ}_{\mathrm{m}}(\mathrm{FeOOH},\ \alpha,\ 298.15\ \mathrm{K}) = (59.70 \pm 0.50)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

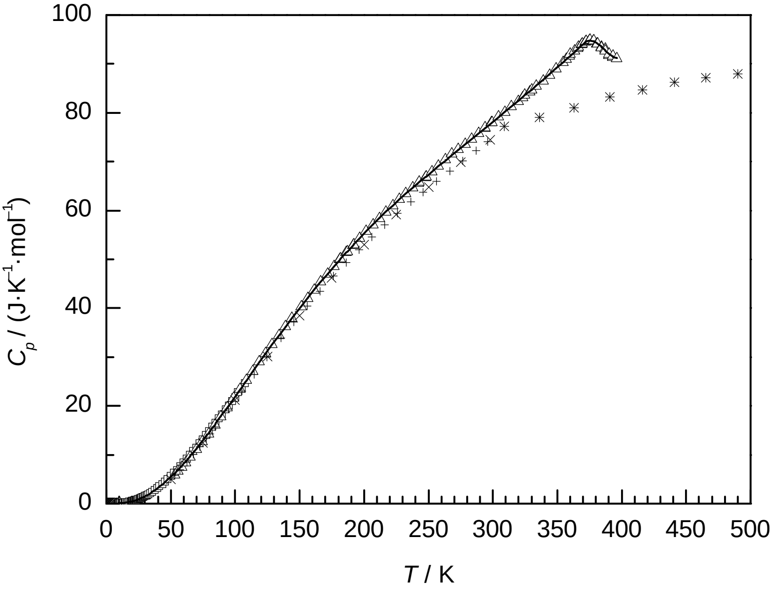
The relatively pessimistic uncertainty limits arise partly from the differences between C_p data sets obtained with two different techniques at 50 to 110 K [2003MAJ/LAN], as well as the 10% uncertainty applied to the correction for excess water. The following selected polynomial expressions reproduce within 0.15 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ the smoothed, tabulated $C^{\circ}_{p,\mathrm{m}}$ values of [2003MAJ/LAN] up to 396 K, again corrected for excess water as ice. The mismatch with the selected 298.15 K heat-capacity value is only 0.04 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$.

$$\begin{aligned}[C^{\mathrm{o}}_{p,\mathrm{m}}]^{372.6\,\mathrm{K}}_{200\,\mathrm{K}}(\mathrm{FeOOH}, \alpha, T)/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} &= 0.0003768913\,(T/\mathrm{K})^{2} - 0.08756035\,(T/\mathrm{K}) \\ &\quad + 80.36125 - 2014.245\,(T/\mathrm{K})^{-1} \\ &\quad - 594081.2\,(T/\mathrm{K})^{-2}\end{aligned}$$

$$\begin{aligned}[C^{\mathrm{o}}_{p,\mathrm{m}}]^{396\,\mathrm{K}}_{372.6\,\mathrm{K}}(\mathrm{FeOOH}, \alpha, T)/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} &= 1.01228346\,(T/\mathrm{K})^{2} - 1455.051643\,(T/\mathrm{K}) \\ &\quad + 779756.841 - 184428534.4\,(T/\mathrm{K})^{-1} \\ &\quad + 16233060709\,(T/\mathrm{K})^{-2}.\end{aligned}$$

No recommendation is made for calculating $C^{\mathrm{o}}_{p,\mathrm{m}}$ at $T > 396$ K. While the data of Korobeinikova (*fide* [1998DIA]) may represent goethite behaviour up to ~ 500 K (see Figure VII-37), they do not show the expected anomaly near the Néel transition; it is possible that the specimen was partly converted to hematite by the prior heat treatment at 470 K. In any case, goethite is not normally expected to persist for more than a few hours at ambient pressure and $T > 400$ K.

Figure VII-37: Values for the heat capacity of goethite: uncorrected experimental data from [2003MAJ/LAN] for $\mathrm{FeOOH\cdot 0.083H_2O}$ by semi-adiabatic pulse (55 measurements between 0.70 and 10.62 K), isothermal (◇), and adiabatic calorimetry (△); corrected measurements (+) and smoothed values (×) from [1970KIN/WEL]; elevated-temperature data from Korobeinikova (*fide* [1998DIA]) as cited by [1994DIA/KHO] (*). The solid line represents the polynomial equations obtained in this assessment to fit the uncorrected data from [2003MAJ/LAN].



VII.2.10 Akaganéite, “β-FeOOH”

This mineral is named for the Akagané mine in Japan, where it was reported by Nambu in 1961, as described by Mackay [1962MAC], who previously reviewed literature on synthetic “β-FeOOH” dating back to 1935 [1960MAC]. Most syntheses are based on oxidation of $FeCl_2$ or hydrolysis of $FeCl_3$ in aqueous solutions. Akaganéite is now recognized as a soil mineral and corrosion product, sometimes associated with geothermal brines. Though often referred to as β-FeOOH, it typically contains several weight-% of chloride (and sometimes fluoride), in both natural and synthetic specimens, unless subjected to prolonged dialysis.[1]

The hollandite-like structure of β-FeOOH was deduced by Bernal *et al.* [1959BER/DAS] and confirmed by Mackay [1960MAC]. Structure refinement of an akaganéite with composition $Fe_{7.6}Ni_{0.4}O_{6.35}(OH)_{9.65}Cl_{1.25}$ by Post and Buchwald [1991POS/BUC] confirmed that Cl^- or other univalent anions are not impurities, but an inherent structural component. The structure proved to be monoclinic, space group: *I*2/*m* (not tetragonal, *I*4/*m*, as first reported), with $Z = 8$ for the idealized FeOOH formula. The cell dimensions of this specimen were a_0 = 10.600, b_0 = 3.0339, c_0 = 10.513 Å, β = 90.24° (*cf.* a_0 = 10.48, c_0 = 3.023 Å for the tetragonal cell of [1960MAC]).[2] There are indications, not yet fully documented, that macrocrystalline akaganéite is tetragonal, but becomes distorted to monoclinic symmetry as the particle size decreases [2005DEO/MAZ].

As in goethite, $Fe(O,OH)_6$ octahedra in akaganéite are linked by a combination of edge- and vertex-sharing into a three-dimensional network. The structure is relatively open, however, with tunnels (parallel to the *b* axis), that contain Cl^- or other anions and varying amounts of H_2O; as a result, the volume per “FeOOH” unit is much higher than in goethite (42.3 Å^3 *vs.* 34.6 Å^3). The structure can be derived from hexagonal close packing by removing one-ninth of the anions and displacing the packing planes from hexagonal to near-tetragonal symmetry, which allows the tunnels to dilate to a more symmetrical configuration, capable of accommodating small ions or molecules.[3] The O:OH ratio in the mineral composition (see above) deviates from 1.0 to achieve charge compensation for the additional anions and for partial substitution of Ni^{2+} for Fe^{3+}. There are two anion sites per unit cell, but the short inter-site spacing of 3.03 Å permits

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[1] Nambu’s type material, however, appears to have been Cl-free, having been formed from iron(III) sulfate solutions as an alteration product of pyrrhotite. While his analytical data do not include any measurement of Cl, >99.3% of the mass is accounted for.

[2] Slightly different values are given by Post *et al*. [2003POS/HEA].

[3] Theoretical values for perfect hexagonal symmetry: $c/a = 0.8272$ (actual, 0.9918); $\beta = 82.69°$ (actual, 90.24°). As stated by Mackay [1960MAC], the structure can also be described in terms of distorted, anion-deficient body-centred cubic packing.

only about 2/3 occupancy by Cl^- ions [1991POS/BUC].[1] Various authors have described partial removal of chloride from "β-FeOOH" by repeated washing [1960MAC], [2001CAI/LIU], while prolonged dialysis can reduce it to negligible levels [2006MAZ/DEO].

Akaganéite displays complex magnetic behaviour at temperatures below the Néel point of about 295 K [1979MUR]. The low-temperature Mössbauer spectra have attracted much attention; for example, Murad [1979MUR] cited 18 studies between 1964 and 1979. A more recent study concluded that "the magnetic structure behaves as a system which consists of two asperimagnetic-like structures antiferromagnetically coupled, and not as a collinear antiferromagnet as usually assumed" [2006BAR/GAR].

VII.2.10.1 Thermodynamic properties of akaganéite

There appear to be just two reported determinations of the enthalpy of formation of β-FeOOH [1998LAB/NAV], [2006MAZ/DEO]. The surface-area dependent study by Mazeina *et al.* superseded the calorimetric measurements of [1998LAB/NAV], and yielded a value for hypothetical, anhydrous, zero-surface-area material of $\Delta_f H_m^o$ (FeOOH, β, 298.15 K) = − (554.7 ± 1.9) $kJ\cdot mol^{-1}$. Surface enthalpies were evaluated as (0.44 ± 0.04) $J\cdot m^{-2}$ for H_2O-free surfaces and (0.34 ± 0.04) $J\cdot m^{-2}$ for hydrated surfaces. Based on discussion in Appendix A, the following values are suggested for relatively coarse-grained (~ 40 - 50 $m^2\cdot g^{-1}$) synthetic akaganéite: $\Delta_f H_m^o$ (FeOOH, β, 298.15 K) = − (551.5 ± 2.2) $kJ\cdot mol^{-1}$ for material with water-free external surfaces and − (555.1 ± 2.2) $kJ\cdot mol^{-1}$ for material with chemisorbed water. The enthalpy of tunnel water is apparently indistinguishable from that of liquid water [2006MAZ/DEO].

Based on heat-capacity measurements by Lang [2005LAN], adjusted as described in Appendix A, the following values are representative of akaganéite, and are therefore suggested for use in calculations.

$$C_{p,m}^o(\beta\text{-FeOOH}\cdot 0.551H_2O\cdot 0.0096HCl,\ cr,\ 298.15\ K) = (91.50 \pm 0.20)\ J\cdot K^{-1}\cdot mol^{-1}$$

$$\Delta_0^{298.15K} S_m^o(\beta\text{-FeOOH}\cdot 0.551H_2O\cdot 0.0096HCl,\ cr) = (79.9 \pm 1.0)\ J\cdot K^{-1}\cdot mol^{-1}$$

Additional, recent heat-capacity measurements on akaganéite [2011SNO/SMI] will be assessed in detail in TDB-Iron Part 2.

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[1] Mackay suggests a maximum occupancy of 84% in fresh synthetic material, and notes that full occupancy of the tunnel sites by water molecules in Cl-free material would yield the composition $Fe_2O_3\cdot 1.5H_2O$ [1960MAC].

VII.2.11 Lepidocrocite, γ-FeOOH

First described in the early 19th century [1944PAL/BER], lepidocrocite is a common sedimentary mineral and corrosion product ([1998DIA2] and references therein). Macroscopic natural crystals are rare, while synthetic material is limited to fine powders. Lepidocrocite is frequently found in iron oxyhydroxide precipitates; the preferred synthesis is by controlled air-oxidation of $FeCl_2$ solutions [1984TAY2], [2000SCH/COR].

The crystal structure, determined by Ewing [1935EWI] and refined by Oleś *et al.* [1970OLE/SZY], is orthorhombic, space group: *Cmcm*, $Z = 4$, isostructural with boehmite (γ-AlOOH). Cell dimensions vary slightly [1970OLE/SZY], [2007MAJ/MAZ]; the following values represent pure, relatively well-crystallized synthetic material: $a_0 = 3.068$, $b_0 = 12.527$, $c_0 = 3.870$ Å [2003MAJ/LAN]. The topology of interlinked $Fe(O,OH)_6$ octahedra differs from goethite and akaganéite, with each O^{2-} tetrahedrally coordinated to four Fe^{3+} and each OH^- linked to only two Fe^{3+} ions: $FeO_{4/4}(OH)_{2/2}$ rather than $FeO_{3/3}(OH)_{3/3}$. The resulting two-dimensional sheets, linked by hydrogen bonding, account for the dominant {010} growth and cleavage planes. The anion sublattice is modified from cubic close-packing by a $c/2$ shear displacement (corresponding to the *C*-centring) of successive sheets. The crystallographic volume is higher than that of goethite (37.2 $Å^3$ *vs.* 34.6 $Å^3$ per FeOOH unit).

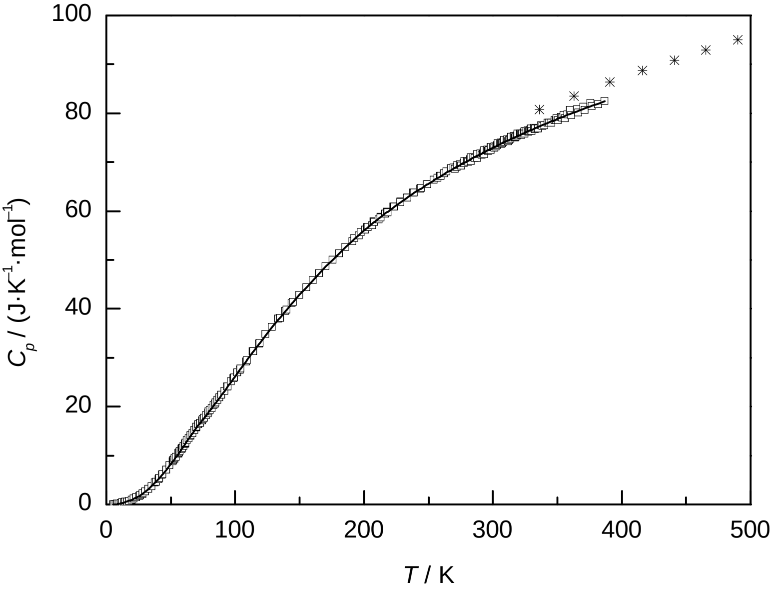
Lepidocrocite is antiferromagnetic at low temperatures; reported values for the Néel temperature vary from about 50 to 77 K ([1984MUR/SCH], [2002HIR/LAN], and references therein). As with goethite, decomposition to Fe_2O_3 prevents thermodynamic measurements on lepidocrocite above about 400 K.

VII.2.11.1 Heat capacity and entropy of lepidocrocite

This discussion is based on 237 adiabatic $C^{\circ}_{p,\mathrm{m}}$ measurements between 5.707 and 387.01 K on a synthetic lepidocrocite of composition $FeOOH \cdot 0.087H_2O$ ([2003MAJ/LAN]; data provided by J. Majzlan), shown in Figure VII-38. The seven measurements at 336 to 490 K by Korobeinikova (reproduced in [1998DIA2]) are depicted but were not included in the assessment.

Data treatment was similar to that for goethite. An equation of the type $C^{\circ}_{p,\mathrm{m}} = \mathrm{A}T^{\mathrm{B}}$ proved satisfactory from 0 to 15 K, while two unconstrained sixth-order polynomial functions described $C^{\circ}_{p,\mathrm{m}}$ from 15 to 70 K and 70 to 200 K. The division at 70 K is near the peak of the Néel transition, which appears as only a minor heat-capacity anomaly, while the arbitrary division at 200 K reduced residual bias in the final fit. The following function was obtained by fitting with data for 70.13 to 387.01 K.

Figure VII-38: Experimental $C^{\circ}_{p,\mathrm{m}}$ measurements for lepidocrocite with the composition FeOOH·0.087H$_2$O [2003MAJ/LAN] and line representing the fitted equations obtained in the current assessment. The asterisks represent seven elevated-temperature measurements by Korobeinikova, on a specimen of lepidocrocite pre-dried at 443 K, as reproduced in [1998DIA2].



$$[C^{\circ}_{p,\mathrm{m}}]^{387\,\mathrm{K}}_{200\,\mathrm{K}}(\mathrm{FeOOH}, \gamma + 0.087\mathrm{H_2O}, T)/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = -\,0.00002981829\,(T/\mathrm{K})^{2} + 0.05574878\,(T/\mathrm{K}) + 91.00766 - 10922.627\,(T/\mathrm{K})^{-1} + 386789.9\,(T/\mathrm{K})^{-2}$$

This treatment yielded the following thermodynamic values for the specimen, including excess water:

$$C^{\circ}_{p,\mathrm{m}}\,(\mathrm{FeOOH}, \gamma + 0.087\ \mathrm{H_2O}, 298.15\ \mathrm{K}) = (72.70 \pm 0.43)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}},$$

$$S^{\circ}_{\mathrm{m}}\,(\mathrm{FeOOH}, \gamma + 0.087\ \mathrm{H_2O}, 298.15\ \mathrm{K}) = (68.66 \pm 0.29)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

A relatively large degree of scatter was noted in the $C^{\circ}_{p,\mathrm{m}}$ measurements above about 260 K.

Correcting for the excess water content as hexagonal ice (see Section VII.2.1), we obtain the values $C^{\circ}_{p,\mathrm{m}}$ (FeOOH, γ, 298.15 K) = (69.09 ± 0.56) J·K^{-1}·mol^{-1} and S°_{m} (FeOOH, γ, 298.15 K) = (65.06 ± 0.46) J·K^{-1}·mol^{-1}, in close agreement with the published values, 69.14 and (65.08 ± 0.16) J·K^{-1}·mol^{-1} [2003MAJ/LAN]. In keeping with the discussion in Section VII.2.1 and the data treatment for maghemite and goethite (Sections VII.2.4.1 and VII.2.9.2), the following, slightly adjusted relationships are selected.

$$[C^{\circ}_{p,\mathrm{m}}]^{387\,\mathrm{K}}_{200\,\mathrm{K}}(\mathrm{FeOOH}, \gamma, T)/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = -\,0.00002981829\,(T/\mathrm{K})^{2} + 0.04389913\,(T/\mathrm{K}) + 90.98067 - 10922.627\,(T/\mathrm{K})^{-1} + 386789.9\,(T/\mathrm{K})^{-2}$$

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{FeOOH}, \gamma, 298.15\ \mathrm{K}) = (69.14 \pm 0.56)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

$$S^{\circ}_{\mathrm{m}}(\mathrm{FeOOH}, \gamma, 298.15\ \mathrm{K}) = (65.08 \pm 0.46)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

Additional, recent heat-capacity measurements on lepidocrocite [2011SNO/SMI] will be assessed in detail in TDB-Iron Part 2.

VII.2.11.2 Enthalpy of formation of lepidocrocite

Early attempts to measure the enthalpy of formation of lepidocrocite were hampered by large uncertainties in specific surface areas ([1937FRI/ZER], [1975KOR/FAD], as reviewed by Diakonov [1998DIA2]). Diakonov derived a value of $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ (FeOOH, γ, 298.15 K) = − (556.4 ± 2.0) $\mathrm{kJ\cdot mol^{-1}}$ from a single heat-of-solution measurement for natural lepidocrocite [1937FRI/ZER], but the estimated uncertainty seems over-optimistic. Indeed, Majzlan *et al.* [2003MAJ/GRE] dismiss the results of [1937FRI/ZER] as "perhaps only of historical interest" because of large differences (> 20 $\mathrm{kJ\cdot mol^{-1}}$) between heats of solution for natural and synthetic lepidocrocite.

Majzlan *et al.* [2003MAJ/GRE] obtained $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ (FeOOH, γ, 298.15 K) = − (549.4 ± 1.4) $\mathrm{kJ\cdot mol^{-1}}$ from the heat of dissolution of a well-characterized lepidocrocite with composition $\mathrm{FeOOH\cdot(0.087 \pm 0.005)\,H_2O}$ and a specific surface area of 23 $\mathrm{m^2\cdot g^{-1}}$. This is adjusted for consistency with the current evaluation of hematite (α-$\mathrm{Fe_2O_3}$) and goethite (α-FeOOH) to the following selected value:

$$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{FeOOH, cr}, \gamma, 298.15\ \mathrm{K}) = -\,(549.2 \pm 2.0)\ \mathrm{kJ\cdot mol^{-1}}.$$

The value of $\Delta_{\mathrm{r}}H^{\circ}_{\mathrm{m}}$ (FeOOH, $\gamma \rightarrow \alpha$, 298.15 K) = − (11.3 ± 0.8) $\mathrm{kJ\cdot mol^{-1}}$ based on data from [2003MAJ/GRE] agrees well with an earlier value of − (11.1 ± 1.4) $\mathrm{kJ\cdot mol^{-1}}$ obtained from Laberty and Navrotsky [1998LAB/NAV]. Their $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ values are about 5 $\mathrm{kJ\cdot mol^{-1}}$ more negative than those from [2003MAJ/GRE], however, because of the rather large and uncertain corrections then available for surface area and excess water [1998LAB/NAV].

Recent surface-area-dependent heats of dissolution for lepidocrocite yielded $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ (FeOOH, γ, 298.15 K) = − (552.0 ± 1.6) $\mathrm{kJ\cdot mol^{-1}}$ for hypothetical, stoichiometric material with zero surface area [2007MAJ/MAZ]. The effective surface enthalpy was evaluated as (0.62 ± 0.14) $\mathrm{J\cdot m^{-2}}$ for $\mathrm{H_2O}$-free surfaces, relaxing to (0.40 ± 0.16) $\mathrm{J\cdot m^{-2}}$ for a hydrated surface. These values should be used for thermodynamic calculations on γ-FeOOH of specified surface area and moisture content. The value of $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ (FeOOH,

γ) = − (549.2 ± 2.0) $\text{kJ}\cdot\text{mol}^{-1}$, selected above, is recommended for more generic calculations on reasonably well-crystallized lepidocrocite.

Evaluation of various solubility and equilibrium potential studies is hampered by uncertainties with sample characterization (both phase identity and surface area estimates), aqueous speciation, and activity corrections [1968DOY], [1973HAS/MIS], [1972MOH/BAR], [1974VLE/BLO], as reviewed by [1998DIA2]. These difficulties exist for all iron oxides and hydroxides, as discussed in Section VII.1.4 and the introduction to Section VII.2.

VII.2.12 Feroxyhyte, δ- or δ′-FeOOH

First synthesized in 1939, this substance was described as a mineral (sometimes spelled feroxyhite) in 1976 ([1977CHU/ZVY], [1993DRI/SAK], and references therein). Some researchers distinguish between magnetically ordered δ-FeOOH and slightly ordered δ′-FeOOH, likely with varying degrees of crystallinity. Ferrimagnetic ordering exists at 77 K for ~ 200-Å particles, and persists well above 298 K for ~ 1000-Å particles [1977CHU/ZVY]. Though generally rare, feroxyhyte occurs abundantly with vernadite (δ-MnO_2) in ferromanganese nodules on the deep ocean floor [1977CHU/ZVY]. Synthesis is usually by the reaction of Fe^{2+} solutions with strong oxidants or by air oxidation of $Fe(OH)_2$(s) [1959BER/DAS], [1994LUT/MOL].

Always poorly crystalline, feroxyhyte has a brucite-like hexagonal unit cell with the approximate dimensions a_0 = 2.95, c_0 = 4.53 Å, Z = 1 [1959BER/DAS], [1977CHU/ZVY]. A larger cell with a_0 = 5.08, c_0 = 4.6 Å, Z = 3, has been reported for some specimens [1977CHU/ZVY]. The structure can be described as a derivative of $Fe(OH)_2$(s) (see Section VII.2.18) in which all Fe^{2+} cations are oxidized to Fe^{3+} and one-half of the OH^- anions are replaced by O^{2-}[1959BER/DAS], [1994LUT/MOL], or as a disordered variant of hematite with one-quarter of the Fe^{3+} removed and one-half of the O^{2-} replaced by OH^-. Examination of δ-FeOOH by XRD and EXAFS has yielded a partial understanding of the disorder [1993DRI/SAK], [1993MAN/DRI].

The observed partial transformation of synthetic δ-FeOOH to hematite within 10 days in near-neutral solutions, plus the apparent spontaneous transformation of natural feroxyhyte to goethite, leaves little doubt that all variants are metastable [1976CHU/ZVY]. This qualitative conclusion is borne out by recent enthalpy determinations and an entropy estimate for a series of synthetic feroxyhyte samples [2008MAJ/BEN], which indicated that feroxyhyte is comparable in stability to maghemite and lepidocrocite; this paper will be assessed in detail in TDB-Iron Part 2.

VII.2.13 Bernalite, $Fe(OH)_3$

This rare, dark green, crystalline mineral was discovered at Broken Hill, Australia, where specimens were collected by R.T. Slee in the early 1920s but not identified until about 70 years later [1993BIR/PRI], [1995MCC/PRI]. The unit cell is orthorhombic, space group: *Immm* [1993BIR/PRI] or *Pmmn* [2005WEL/CRI], $Z = 8$, with dimensions $a_0 = 7.544$, $b_0 = 7.560$, $c_0 = 7.558$ Å [1993BIR/PRI]. The idealised structure is a network of vertex-sharing octahedra, $Fe(OH)_{6/2}$, resembling a perovskite (ABO_3) with the eight-coordinate B cation sites vacant except for minor impurities. The unit cell corresponds to a doubling of all three axes in the ideal, cubic perovskite structure with slight orthorhombic distortion. Microprobe analysis yielded the following structural formula, assuming that all impurities are in solid solution, not adsorbed or occluded [1995MCC/PRI]:

$$[(H_2O)_{0.04}(CO_2)_{0.03}Pb_{0.01}]\ (Fe_{0.93}Si_{0.06}Zn_{0.01})(OH)_{2.95}O_{0.04}.$$

There appear to be no published thermodynamic measurements; given the extreme rarity of this mineral and the apparent lack of a synthetic procedure, thermodynamic data will be difficult to obtain.

VII.2.14 Synthetic $Fe(OH)_3(s)$

The literature abounds with references to "$Fe(OH)_3$", usually as an amorphous species. The only substance that approaches $Fe(OH)_3$ as a crystallographic composition is bernalite (see above). Claimed syntheses of at least two forms of microcrystalline $Fe(OH)_3$ [1984AUY/DEN], [1985AUY/EAT], using a novel approach with inorganic oxidants, appear to be erroneous, since the major XRD peaks correspond to lepidocrocite and goethite. It is likely that adsorbed water led to misleading compositions.

Given the frequent isostructural relationships and intersubstitution in iron and aluminium oxides and oxyhydroxides, it is surprising that iron analogues of the $Al(OH)_3$ polymorphs (gibbsite, bayerite, nordstrandite, and doyleite [1985CHA/BAK]) have never been identified, though ferrihydrite (see below) does have structural elements related to gibbsite. It appears that interlayer condensation and cross-linking are too strongly favoured in the iron system for gibbsite-like $Fe(OH)_3$ sheets to crystallize.

Because the composition of ferrihydrite is indeterminate, although the iron is usually all Fe(III), the ideal formulae FeOOH or $Fe(OH)_3$ are often used as an aid to comparing solubilities or simply as convenient labels in a stability diagram. All thermodynamic measurements for "$Fe(OH)_3$" are treated here as referring to ferrihydrite (see below), unless there is evidence that another phase was involved.

VII.2.15 Ferrihydrite, $Fe_2O_3.xH_2O(s)$

The substance once known as amorphous or colloidal "$Fe(OH)_3$" was demonstrated by Towe and Bradley [1967TOW/BRA] to have a diagnostic X-ray diffraction pattern, albeit with extremely broad peaks; it is therefore nanocrystalline rather than amorphous. The mineral ferrihydrite was described by Chukhrov *et al.* [1974CHU/ZVY] on the basis of specimens from Kazakhstan, and shown to be widespread in springs, mines, soils, sediments, and corrosion products. Its importance in both natural systems and industrial applications is now well recognized ([1998JAM/DUT], [2007MIC/EHM], and references therein). Jambor and Dutrizac reviewed ferrihydrite chemistry and mineralogy at length, but with only passing reference to solubility measurements and none to thermodynamic properties [1998JAM/DUT].

Because of the low degree of crystallinity, the large amount of loosely associated water, and the absence of well-known structural analogues, the composition and structure of ferrihydrite have long defied accurate description. Jambor and Dutrizac [1998JAM/DUT] considered the formula $Fe_2O_3\cdot 1.8H_2O$ proposed by Towe and Bradley [1967TOW/BRA] to be “excessively hydrous”, since much of the water can be displaced by various adsorbates.

Ferrihydrite specimens are usually classified by the number of XRD features with d spacings between 1.48 and 2.6 Å, most commonly “2-line” and “6-line” types with coherent scattering domains of about 20 to 30 Å and 40 to 60 Å, respectively ([1998JAM/DUT] and references therein). Specific surface areas typically exceed 200 $m^2\cdot g^{-1}$. The 6-line ferrihydrite pattern can be assigned to a trigonal or hexagonal unit cell with the dimensions a_0 = 5.08, c_0 = 9.4 Å [1967TOW/BRA], though other variants have been reported ([1998JAM/DUT] and references therein). The anion stacking sequence is double-hexagonal (ABAC).

Numerous structural models have been proposed for ferrihydrite [1998JAM/DUT]. It has even been suggested, on the basis of electron nanodiffraction, that there is not a single structure for ferrihydrite ([2001JAN/COW] and references therein), implying that it is not a phase in the true thermodynamic sense. These studies also indicated that 6-line ferrihydrite could not be considered as simply “better crystallized” than 2-line material [2000JAN/COW]; [2001JAN/COW]. Recent interpretation of X-ray scattering data, however, points to a single structure for all ferrihydrite specimens, related to the rare mineral akdalaite ($Al_{10}O_{14}(OH)_2$) [2007MIC/EHM]. The cell dimensions are markedly different from those originally assigned by Towe and Bradley: a_0 ~ 5.95, c_0 ~ 9.06 Å. The ideal structure of $Fe_{10}O_{14}(OH)_2$ [= $Fe_2O_3\cdot 0.2H_2O$ or $FeO_{1.4}(OH)_{0.2}$] would comprise 20% tetrahedral and 80% octahedral Fe, with each tetrahedral Fe being linked through oxygen bridges to twelve octahedral Fe. The electron nanodiffraction studies, cited above, appear to have been confounded by partial alteration of specimens in the electron beam, which is not uncommon with hydrous and/or redox-sensitive materials. More recent developments towards understanding the structure of ferrihydrite will be discussed in TDB-Iron Part 2.

Ferrihydrite is paramagnetic at ambient temperature [1967TOW/BRA]. At low temperatures 6-line ferrihydrite is antiferromagnetic, with a parasitic ferromagnetic moment; the poorly defined Néel temperature is about 120 K [2000ZER/HIR].

VII.2.15.1 Thermodynamic properties of ferrihydrite

Majzlan *et al.* [2004MAJ/NAV] studied five ferrihydrite specimens (including 2-line and 6-line types) by acid-solution calorimetry at 298.15 K, using lepidocrocite (γ-FeOOH) as a reference material. The resulting values of $\Delta_f H_m^\circ$ (“FeOOH·xH$_2$O”, s, 298.15 K) varied between − 654 and − 772 kJ·mol^{-1}, reflecting the variation in x between 0.395 and 0.801 [2004MAJ/NAV]. When expressed by a hypothetical fixed composition, such as Fe(OH)$_3$[1], the span of enthalpy values between the least crystalline 2-line and the most crystalline 6-line specimens is reduced to just 3.1 kJ·mol^{-1}. Values for $\Delta_r H_m^\circ$ (Fe(OH)$_3$(s) → γ-FeOOH + H$_2$O(l), 298.15 K) range from − (8.3 ± 0.5) to − (5.1 ± 0.4) kJ·mol^{-1}, corresponding to the following enthalpy values, adjusted for internal consistency:

$$\Delta_f H_m^\circ \text{ (Fe(OH)}_3\text{, s, nominal, 2-line. 298.15 K)} = -(826.7 \pm 2.1) \text{ kJ}\cdot\text{mol}^{-1};$$

$$\Delta_f H_m^\circ \text{ (Fe(OH)}_3\text{, s, nominal, 6-line. 298.15 K)} = -(829.9 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}.$$

For ferrihydrite compositions expressed in the general form (FeOOH·xH$_2$O), values of $\Delta_f H_m^\circ$ (FeOOH·xH$_2$O, 298.15 K) can be obtained by adding 285.83(x − 1) to the nominal Fe(OH)$_3$ values. The value of x is − 0.4 for the ideal akdalaite-analogue formulation, FeO$_{1.4}$(OH)$_{0.2}$, discussed in Section VII.2.15. Note that these are suggested values to facilitate calculations, and not selected NEA values in the normal sense.

The only heat-capacity data for ferrihydrite appear to be some early measurements by Hüttig and Garside [1929HUT/GAR], which yield $C_{p,m}^\circ$ (Fe(OH)$_3$, 298 K) ≈ (152 ± 5) J·K^{-1}·mol^{-1}. Accurate heat-capacity measurements on ferrihydrite have proved very difficult to obtain, because of strong absorption of He at low temperatures and extremely long equilibration times (J. Majzlan, personal observation in peer review). Majzlan *et al.* [2004MAJ/NAV] argue that S_m° (Fe(OH)$_3$, nominal, 6-line, 298 K) lies between 122 J·K^{-1}·mol^{-1} (estimated for hypothetical, crystalline, gibbsite-like Fe(OH)$_3$) and 135 J·K^{-1}·mol^{-1} (for γ-FeOOH + H$_2$O(l)). It is unlikely that the transformation entropy from 2-line to 6-line ferrihydrite is more than a few J·K^{-1}·mol^{-1} (presumably negative to reflect increased crystallinity), therefore:

$$\Delta_r G_m^\circ \text{ (Fe(OH)}_3\text{), nominal, 2-line} \rightarrow \text{6-line, 298.15 K)} \approx -(2.5 \pm 1.0) \text{ kJ}\cdot\text{mol}^{-1}.$$

VII.2.15.2 Solubility measurements on Fe(OH)$_3$ and ferrihydrite

Much of the literature on “ferric hydroxide” and ferrihydrite solubility is reviewed in the context of Fe^{3+} hydrolysis in Section VII.1.4. For information on the age-dependent solubility of ferrihydrite, refer to the synopses of [1957BIE/SCH], [1961LEN/BUS], [1961LEN/BUS2], and [1963SCH/MIC]. Although these studies predate the proper characterization of ferrihydrite, it is likely that the authors’ “active” and “inactive”

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[1] By adding (1 – x)H$_2$O(l) to the composition and adjusting the thermodynamic quantities accordingly.

precipitated iron(III) hydroxide correspond to 2-line and 6-line ferrihydrite, respectively. These studies indicate a Gibbs energy of transformation between these two forms of ~ 2-3 $\text{kJ}\cdot\text{mol}^{-1}$. This value is comparable to the difference estimated from thermodynamic measurements [2004MAJ/NAV], adjusted to constant composition, as discussed in Section VII.2.15.1.

VII.2.16 Calculated solubilities of Fe(III) oxyhydroxides

The thermodynamic values assessed in this review allow us to recalculate the solubility products, as defined by Eq. (VII.18), for most of the Fe(III) oxyhydroxides. The resulting values (Table VII-13) span about three orders of magnitude, bounded at the lower end by hematite and at the upper end by ferrihydrite.

Table VII-13: Calculated solubility products, $K_{s,0} = a_{\text{Fe}^{3+}}(a_{\text{OH}^-})^3$, for Fe(III) oxyhydroxides at 298.15 K.$^{(1)}$

Phase	$\log_{10} K_{s,0}$ (± 2σ)
Hematite, α-Fe_2O_3	– 42.05 ± 0.26
Maghemite, γ-Fe_2O_3	– 40.59 ± 0.29 $^{(2)}$
Goethite, α-FeOOH	– 41.83 ± 0.37
Lepidocrocite, γ-FeOOH	– 40.13 ± 0.37
Ferrihydrite, exact composition uncertain	– 38.97 ± 0.64 $^{(3)}$

[1] Values refer to the most crystalline material that is normally available, rather than ideal values for well-crystallized material with minimal surface area.

[2] This value refers to ordered maghemite; the $\log_{10} K_{s,0}$ value for disordered material of otherwise comparable crystallinity is less negative by about 0.1.

[3] Six-line ferrihydrite, based on an estimated entropy of (130 ± 10) $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for the idealized composition $Fe(OH)_3$ (see Section VII.2.15.1). The $\log_{10} K_{s,0}$ value for 2-line ferrihydrite is expected to be less negative by about 0.4.

VII.2.17 "Ferrosic hydroxides", $Fe_3(OH)_8$ and $Fe_4(OH)_{10}$

The existence of these phases, suggested in a solubility study by Arden [1950ARD] and favoured by some soil chemists, seems doubtful in the light of recent work on hydroxycarbonate green rust [2005GEN/AIS], which is discussed in Section X.1.2.2.2.

VII.2.18 Synthetic $Fe(OH)_2$(s) ("white rust")

Iron(II) hydroxide is an air-sensitive material, obtained as a gelatinous precipitate by mixing solutions of $FeCl_2$ or $FeSO_4$ with alkaline hydroxides. White when pure, it rapidly darkens on contact with traces of oxygen ([1931HUT/MOL], [1934WEL/BAU] and references therein). The brucite-type ($Mg(OH)_2$) structure reported by Natta and

Cassaza [1927NAT/CAS] and confirmed by others [1959BER/DAS] has been refined for partly deuterated material, $Fe(OH_{0.86}D_{0.14})_2$ [2000PAR/MAR]. The structure is trigonal, space group: $P\bar{3}m1$; $Z = 1$, with $a_0 = 3.265$ Å and $c_0 = 4.601$ Å. In a hexagonal close-packed array of OH, alternating layers of octahedral sites are occupied by Fe. The $Fe(OH)_{6/3}$ octahedra form a sheet structure by edge sharing. Iron(II) hydroxide is antiferromagnetic at low temperatures, with a doubled *c* axis and lowered symmetry [2000PAR/MAR]. The Néel transition temperature is about 34 K ([1999REF/BON] and references therein).

VII.2.18.1 Thermodynamics of $Fe(OH)_2$(s)

Several solubility and equilibrium-potential measurements have led to estimates for $\Delta_f G^\circ_m$ ($Fe(OH)_2$, s, 298.15 K), and one temperature-dependent solubility study yielded enthalpy and entropy values. Solid characterization in these studies is limited at best, though some authors (notably [1953LEU/KOL]) have specified procedures and analyses to assure minimal incorporation of anionic impurities in the $Fe(OH)_2$(s) precipitate. The limited stability of $Fe(OH)_2$(s) appears to preclude hydrothermal recrystallization and to hinder separation and characterization, though small specimens have been isolated for crystallographic and spectroscopic analyses [1994LUT/MOL], [2000PAR/MAR]. Ziemniak *et al.* [1995ZIE/JON] inferred that a surface film of $Fe(OH)_2$(s) was the saturating phase in their solubility measurements on magnetite in reducing, aqueous alkaline media below 356 K, based on breaks in the solubility curves and partial solid characterization by XPS.

Most solubility-product values are based on fresh precipitates and are therefore upper limits, likely influenced by small particle size and crystalline imperfections such as stacking faults [2000PAR/MAR]. Until the 1950s, most solubility measurements on $Fe(OH)_2$(s) also lacked corrections for ionic activities or for hydrolysis and complexation of Fe^{2+}. Most uncorrected K_s values (*e.g.*, compilations by [1932RAN/FRA], [1953LEU/KOL], and [1963DAU/DAU]) lie between 10^{-13} and 10^{-15}. Leussing and Kolthoff [1953LEU/KOL], who recognized (but apparently over-estimated) the importance of $FeOH^+$, obtained $\log_{10} K_s = -(15.14 \pm 0.32)$ for precipitates aged up to two weeks; this may be the origin of the value of $\Delta_f G^\circ_m$ ($Fe(OH)_2$, s, 298.15 K) $= -492$ kJ·mol^{-1} in some compilations. A more recent, relatively low $\log_{10} K_s$ value of -16.05 at 293 K [1964DAU/DAU] suggests slightly greater stability, $\Delta_f G^\circ_m$ ($Fe(OH)_2$, s, 298.15 K) $= -497$ kJ·mol^{-1}, but this is difficult to evaluate because many chloride complexes are involved in the data analysis.

Refait *et al.* [1999REF/BON] obtained the following saturating conditions for freshly precipitated $Fe(OH)_2$(s), formed as a precursor to green rusts in dilute sulfate solutions: pH = (8.0 ± 0.1); [Fe(II), total] = (15 ± 1) × 10^{-3} M; [SO_4, total] = (113 ± 3) × 10^{-3} M; balancing cation, Na^+. From this they calculated $\Delta_f G^\circ_m$ ($Fe(OH)_2$, s, 298.15 K) = − (490 ± 1) kJ·mol^{-1}.

Randall and Frandsen [1932RAN/FRA] attributed a steady-state potential, $E(298\ \text{K}) = (0.973 \pm 0.005)$ V after ~ 600 days to the reaction:

$$\text{Fe(s)} + \text{HgO(s)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{Hg(l)} + \text{Fe(OH)}_2\text{(s)}\ ,$$

whence $\Delta_f G^\circ_m(\text{Fe(OH)}_2, \text{s}, 298.15\ \text{K}) = -(483.4 \pm 1.0)\ \text{kJ}\cdot\text{mol}^{-1}$.

Ziemniak *et al.* [1995ZIE/JON] estimated a transition temperature of 356 K at an $\text{H}_2\text{(sln)}$ concentration of $2.37 \times 10^{-4}\ \text{mol}\cdot\text{kg}^{-1}$, above and below which Fe_3O_4 and Fe(OH)_2 are the saturating phases, *i.e.*, these transition conditions correspond to the following equilibrium.

$$\text{Fe(OH)}_2\text{(s)} \rightleftharpoons \tfrac{1}{3}\,\text{Fe}_3\text{O}_4\text{(s)} + \tfrac{1}{3}\,\text{H}_2\text{(g)} + \tfrac{2}{3}\,\text{H}_2\text{O(l)}$$

This is consistent with the values $\Delta_f G^\circ_m(\text{Fe(OH)}_2, \text{s}, 298.15\ \text{K}) = -500.16\ \text{kJ}\cdot\text{mol}^{-1}$, $\Delta_f H^\circ_m(\text{Fe(OH)}_2, \text{s}, 298.15\ \text{K}) = -583.39\ \text{kJ}\cdot\text{mol}^{-1}$, and $S^\circ_m(\text{Fe(OH)}_2, \text{s}, 298.15\ \text{K}) = 84.0\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, as tabulated in [1995ZIE/JON], together with an expected value of ~ 90 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for $C^\circ_{p,m}(\text{Fe(OH)}_2, \text{s}, 298.15\ \text{K})$, and thermodynamic values for Fe_3O_4 in this review. No error limits were assigned to the values by Ziemniak *et al.*, but the uncertainties in their reaction enthalpy and entropy contributions were markedly greater (the values are obviously strongly correlated) than for the Gibbs energies of reaction [1995ZIE/JON]. Other processes, such as non-equilibrium incongruent dissolution of magnetite, may have influenced the low-temperature solubility measurements. Other aspects of [1995ZIE/JON], as well as solubilities of other Fe(II) phases, are discussed in Section VII.1.2.

The results from [1995ZIE/JON] imply a rather wide stability field for Fe(OH)_2 in water at 298.15 K, between p_{H_2} boundary values of 4.6×10^2 Pa (oxidation to magnetite) and 3.4×10^9 Pa (reduction to Fe metal). If these results are correct, then it should be feasible to recrystallize Fe(OH)_2 at moderate temperatures with an H_2 overpressure, and thereby obtain better-characterized material for either calorimetric measurements or solubility studies.

Note that, for $\text{Fe(OH)}_2\text{(cr)}$ to have any stability field at all within the Fe–O–H system, $\Delta_f G^\circ_m$ must be negative for the reaction:

$$\text{Fe}_3\text{O}_4\text{(cr)} + \text{Fe(cr)} + 4\ \text{H}_2\text{O(l)} \rightleftharpoons 4\ \text{Fe(OH)}_2\text{(cr)}\ ,$$

i.e., $\Delta_f G^\circ_m(\text{Fe(OH)}_2, \text{s}, 298.15\ \text{K}) < -(490.3 \pm 0.4)\ \text{kJ}\cdot\text{mol}^{-1}$ or $\log_{10} K_s < -(14.91 \pm 0.13)$. The various studies summarized above yielded values for $\Delta_f G^\circ_m(\text{Fe(OH)}_2, \text{s}, 298.15\ \text{K})$ within the range $-(492 \pm 10)\ \text{kJ}\cdot\text{mol}^{-1}$, indicating a much higher uncertainty than some of the individual, reported error limits. No attempt has been made in the current review to adjust or evaluate the foregoing experimental Gibbs energy values, largely because of the limited characterization of the finely divided saturating phase. Particle-size effects have also influenced attempts to study $\text{Fe(OH)}_2\text{(s)}$ by thermal analaysis [1963BER/KOV]. Therefore, no thermodynamic values are recommended for $\text{Fe(OH)}_2\text{(s)}$.

VII.2.19 High-pressure Fe–O–H phases

High-pressure Fe-O phase relationships have attracted interest because of the system's geophysical importance, *e.g.*, [1996STO/GLO], [2000HAA/STO], [2002SHI/DUF], [2004LAZ/SHE]. Hematite transforms at $p > 50$ GPa to a dense polymorph, h-Fe_2O_3, thought to have the Rh_2O_3-II structure [2002SHI/DUF], [2004LAZ/SHE]. The wüstite phase field extends to compositions near stoichiometric FeO at elevated pressures [1986FEI/SAX], [1996STO/GLO]. Wüstite undergoes a displacive cubic-to-rhombohedral phase transition at p between 10 and 18 GPa, the actual transformation pressure being stress-sensitive ([2004LAZ/SHE] and references therein).

Calculations predict magnetite decomposition to (wüstite + hematite) at $p >$ 13.3 GPa (at 298 K), but without experimental confirmation [2004LAZ/SHE]. A high-density polymorph, h-Fe_3O_4 with a $CaTi_2O_4$-type structure, is favoured at $p > 40$ GPa [2004LAZ/SHE]. The h-Fe_2O_3 and h-Fe_3O_4 phases have been estimated to be unstable with respect to hematite and magnetite by about 134 and 50 $kJ \cdot mol^{-1}$, respectively, at 298 K and 0.1 MPa [2004LAZ/SHE], making their formation under ambient conditions highly unlikely.

High-pressure X-ray diffraction studies show that goethite persists at ambient temperature up to at least 24 GPa [2003NAG/KAG]. The stability of goethite with respect to (hematite + water) apparently increases markedly with increasing pressure [1973BAN/BEN]. A high-pressure phase, ε-FeOOH, was obtained from hematite and water at 9 MPa and 673 K, and reported to have the manganite (γ-MnOOH) structure [1972BEN/BAN]. The p–T phase diagram shows an invariant point for the assemblage α-FeOOH + ε-FeOOH + α-Fe_2O_3 + H_2O at about 5.6 GPa and 723 K [1973BAN/BEN]. Chenavas *et al.* obtained a high-pressure modification of FeOOH under similar conditions (8 GPa and 773 K), but identified the InOOH structure type [1973CHE/JOU]. Both γ-MnOOH and InOOH are structurally related to the rutile form of TiO_2 [1973CHE/JOU]. The XRD measurements were apparently made at elevated [1972BEN/BAN] and ambient pressure [1973CHE/JOU]; so it is possible that the same product was obtained by both groups.

VII.2.20 Other mineral names

Various names of the form "hydro-X" or "proto-X", where X is a known oxide mineral, have been coined for either poorly crystallized, hydrous forms of known phases or for intermediate stages of phase conversion reactions. While they may be important in phase-transformation kinetics, *e.g.*, protohematite in the transformation of goethite to hematite [1999GUA/VEN], it is doubtful that they could be isolated for thermodynamic measurements. There are also many archaic and generic names for iron oxide minerals, some of which persist in industrial or mineral-collecting usage. A good example is limonite, a mixture of iron oxyhydroxide phases usually dominated by goethite.

Chapter VIII

Group 17 (halogens) compounds and complexes

VIII.1 Gaseous iron halides

Assessment of thermodynamic quantities for the iron chloride gas-phase species is beyond the scope of the present review. However, short synopses of the literature relevant to the thermodynamic properties for these species are provided below

VIII.1.1 Gaseous iron-chlorine species

Bardi *et al.* [1996BAR/BRU] summarized the earlier experimental work [1958SCH/POR], [1960SIM/GRE], [1969KAN/MCC] on the sublimation of $FeCl_2$(cr) (also see [1976RAT/NOV], [1977LAN/ADA], [1983BUR]). The major gas-phase species on vaporization of $FeCl_3$(cr) is Fe_2Cl_6(g), and the solid-gas and dimer-monomer equilibria also have been the subject of extensive work [1925MAI], [1925STI], [1929JEL/KOO], [1938SAN2], [1942JOH/WEI], [1949RIN], [1950KAN/PET], [1953SCH/OEH], [1958WIL/GRE], [1962COO], [1962HAM/GRE], [1968GAL], [1968MAP/GRE], [1975SHI/GRE], [1982RUS/GRE], [1983RUS/GRE], [2006BLA]. There are many complications involved in carrying out measurements in these systems [1980RUS/GRE], [1982RUS/GRE], [1983RUS/GRE], [2006BLA]. $Fe(H_2O)Cl_3$(g) has also been reported as a major species in the $FeCl_3$-Cl_2-HCl-H_2O system at 500 K [1988GRE].

VIII.1.2 Gaseous iron-bromine species

The literature contains thermodynamic information on $FeBr_2$(g), Fe_2Br_4(g), $FeBr_3$(g) and Fe_2Br_6(g) [1950GRE/THA], [1955GRE/MAC], [1955MAC/GRE], [1959POR/SCH], [1960SIM/GRE], [1967CHR/GRE], [1977LAN/ADA], [1996BAR/BRU]. Bardi *et al.* [1996BAR/BRU] found that measurements of the vapour pressure of $FeBr_2$(cr) from different sources are reasonably consistent, as are the derived enthalpies of sublimation at 298.15 K (and concluded that essentially no Fe_2Br_4(g) forms at temperatures below 833 K). $Fe(H_2O)Br_3$(g) has also been reported as a major species in the $FeBr_3$-H_2O system at 500 K [1988GRE].

VIII.1.3 Gaseous iron-iodine species

The literature contains thermodynamic information on $FeI_2(g)$, $Fe_2I_4(g)$, $FeI_3(g)$ and $Fe_2I_6(g)$. Although many papers have been written [1956SCH/HON], [1956SHC/ORA], [1959SCH/FRI], [1960SIM/GRE], [1966ZAU/GRE], [1966ZAU/GRE2], [1968BAR/BAR], [1977LAN/ADA], [1984GRA/ROS], [1985GRA/ROS], [1985HIL/VIS], [1996SCA/PIA], the reasons for the lack of agreement of the various studies of the equilibria over $FeI_2(cr)$, and especially the lack of consistency with the selected value for $\Delta_f H_m^o$ (FeI_2, cr, 298.15 K), are not completely resolved.

VIII.2 Aqueous iron halide complexes

In the present review, only the aqueous solution interactions between Fe(II) and F^- and Cl^- and between Fe(III) and Cl^- are discussed. Other aspects of the Fe-halide aqueous chemistry are deferred to TDB-Iron Part 2.

VIII.2.1 Aqueous iron(II) fluoride complexes

There are only a very few studies available in which the formation of aqueous fluoride complexes has been investigated. Potentiometric measurements with fluoride-sensitive electrodes and kinetic studies of the oxidation of Fe(II) with $H_2O_2(sln)$ are the methods from which quantitative information on complex formation in aqueous solution is available. Available experimental stability constants are compiled in Table VIII-1.

Table VIII-1: Experimental formation constants for $Fe(II)F_n^{2-n}$ complexes.

Method	Ionic medium	t /°C	β_n	Reference	Comment
sp, kin	0.125 M NaF + 0.875 M $NaClO_4$	0	$\beta_3 = 520\ dm^9\cdot mol^{-3}$	[1967WEL/SAL]	+ 0.004 M $HClO_4$ $k_0 = 35.0\ dm^3\cdot mol^{-1}\cdot s^{-1}$
sp, kin	0.25 M NaF + 0.75 M $NaClO_4$	15	$\beta_2 = 850\ dm^6\cdot mol^{-2}$	[1967WEL/SAL]	+ 0.004 M $HClO_4$ $k_0 = 58.2\ dm^3\cdot mol^{-1}\cdot s^{-1}$
sp, kin	0.094 M NaF + 0.906 M NaClO4	25	$\beta_2 = 198\ dm^6\cdot mol^{-2}$	[1967WEL/SAL]	+ 0.004 M $HClO_4$ $k_0 = 117\ dm^3\cdot mol^{-1}\cdot s^{-1}$
sp, kin	0.15 M NaF + 0.85 M $NaClO_4$	35	$\beta_2 = 57\ dm^6\cdot mol^{-2}$	[1967WEL/SAL]	+ 0.004 M $HClO_4$ $k_0 = 300\ dm^3\cdot mol^{-1}\cdot s^{-1}$
sp, kin	0.25 M NaF + 0.75 M $NaClO_4$	45	$\beta_2 = 21.4\ dm^6\cdot mol^{-2}$	[1967WEL/SAL]	+ 0.004 M $HClO_4$ $k_0 = 490\ dm^3\cdot mol^{-1}\cdot s^{-1}$

(Continued on next page)

Table VIII-1 (continued)

Method	Ionic medium	t /°C	β_n	Reference	Comment
pot	1.0 M $NaClO_4$	25	$\beta_1 = (6.7 \pm 0.3)$ $dm^3\cdot mol^{-1}$	[1972BON/HEF]	Measured with a fluoride sensitive electrode. Conversion to molality using 1.0515 $dm^3\cdot kg^{-1}$ gives $\beta_1 = (6.4 \pm 0.3)$ $kg\cdot mol^{-1}$
pot	0.05 M tetraethylammonium perchlorate	25	$\beta_1 = (28 \pm 4)$ $dm^3\cdot mol^{-1}$	[1983SOL/BON]	Measured with a fluoride sensitive electrode. Conversion to molality using 1.006 $dm^3\cdot kg^{-1}$ and considering an increased uncertainty range of ± 7 $dm^3\cdot mol^{-1}$ produces β_1 = (28 ± 7) $kg\cdot mol^{-1}$
pot	0.05 M tetraethylammonium perchlorate in MeOH	25	$\beta_1 = (6100 \pm 1000)$ $dm^3\cdot mol^{-1}$	[1983SOL/BON]	Measured with a fluoride sensitive electrode.
pot	0.5 M $(Na,H)ClO_4$	25	$\beta_1 < 30$ $dm^3\cdot mol^{-1}$	[1949DOD/ROL]	Indirect method

VIII.2.1.1 FeF^+

There are only two studies that provide quantitative data on the equilibrium

$$Fe^{2+} + F^- \rightleftharpoons FeF^+ \tag{VIII.1}$$

in aqueous solution. Both studies describe potentiometric measurements with a fluoride-sensitive electrode. From the measurements of Bond and Hefter [1972BON/HEF] in 1.0 M $NaClO_4$, (6.4 ± 0.3) $kg\cdot mol^{-1}$ is derived as the molal value of the formation constant β_1((VIII.1), 298.15 K, 1.052 m $NaClO_4$).

The extrapolation to zero ionic strength can be performed using $\log_{10} \beta_1^\circ = \log_{10} \beta_1 + 4D + \Delta\varepsilon \cdot I_m$, with $(4D) = 0.823$ in 1.052 m $NaClO_4$ at 298.15 K and with $\Delta\varepsilon = \varepsilon(FeF^+, ClO_4^-) - \varepsilon(Fe^{2+}, ClO_4^-) - \varepsilon(Na^+, F^-)$. The interaction coefficient $\varepsilon(FeF^+, ClO_4^-)$ is not known. From the corresponding Ni^{2+}-system measured in $NaClO_4$-solutions of variable concentrations, Gamsjäger *et al.* [2005GAM/BUG] derived $\Delta\varepsilon(Ni^{2+}) = \varepsilon(NiF^+, ClO_4^-) - \varepsilon(Ni^{2+}, ClO_4^-) - \varepsilon(Na^+, F^-) = -(0.049 \pm 0.060)$ $kg\cdot mol^{-1}$. The present review uses the analogy $\Delta\varepsilon(Fe^{2+}) \approx \Delta\varepsilon(Ni^{2+})$ and calculates $\log_{10} \beta_1^\circ(\text{VIII.1}) = \{(0.81 \pm 0.02) + 0.823 - (0.049 \pm 0.060)\ 1.052\} = (1.58 \pm 0.07)$.

Solomon and Bond [1983SOL/BON] explored the same equilibrium in 0.05 M tetraethylammonium perchlorate at 298.15 K and found β_1((VIII.1), 298.15 K, 0.05 M

$(\mathrm{Et})_4\mathrm{NClO}_4$) = (28 ± 4) $\mathrm{dm^3{\cdot}mol^{-1}}$. The authors found the formation constant to be very sensitive to the calibration of the fluoride electrode. Based on their sensitivity analysis, the present review accepts the reported formation constant, but with a substantially increased uncertainty of ± 7 $\mathrm{dm^3{\cdot}mol^{-1}}$. Due to the low inert electrolyte concentration, the conversion to the molal scale does actually not make a significant change to the value, and β_1((VIII.1), 298.15 K, 0.05 m $(\mathrm{Et})_4\mathrm{NClO}_4$) = (28 ± 7) $\mathrm{kg{\cdot}mol^{-1}}$, (*i.e.*, $\log_{10}\beta_1$((VIII.1), 298.15 K, 0.05 m $(\mathrm{Et})_4\mathrm{NClO}_4$) = (1.48 ± 0.11)) is accepted. The extrapolation to zero ionic strength can be performed using $\log_{10}\beta_1^{\circ} = \log_{10}\beta_1 + 4D + \Delta\varepsilon I_{\mathrm{m}}$, with $(4D)$ = 0.341 in 0.05 m $(\mathrm{Et})_4\mathrm{NClO}_4$ at 298.15 K and with $\Delta\varepsilon = \varepsilon(\mathrm{FeF^+}, \mathrm{ClO_4^-}) - \varepsilon(\mathrm{Fe^{2+}}, \mathrm{ClO_4^-}) - \varepsilon((\mathrm{Et})_4\mathrm{N^+},\mathrm{F^-})$. Both, $\varepsilon(\mathrm{FeF^+}, \mathrm{ClO_4^-})$ and $\varepsilon((\mathrm{Et})_4\mathrm{N^+},\mathrm{F^-})$ are not known. However, when again using the analogy $\Delta\varepsilon(\mathrm{Fe^{2+}}) \approx \Delta\varepsilon(\mathrm{Ni^{2+}})$ and using $\varepsilon(\mathrm{Na^+},\mathrm{F^-})$ = (0.02 ± 0.02) $\mathrm{kg{\cdot}mol^{-1}}$ [2005GAM/BUG], one obtains

$$\begin{aligned}
\varepsilon(\mathrm{FeF^+}, \mathrm{ClO_4^-}) - \varepsilon(\mathrm{Fe^{2+}}, \mathrm{ClO_4^-}) &\approx \varepsilon(\mathrm{NiF^+}, \mathrm{ClO_4^-}) - \varepsilon(\mathrm{Ni^{2+}}, \mathrm{ClO_4^-}) \\
&\approx -(0.049 \pm 0.060)\ \mathrm{kg{\cdot}mol^{-1}} + (0.02 \pm 0.02)\ \mathrm{kg{\cdot}mol^{-1}} \\
&\approx -(0.029 \pm 0.063)\ \mathrm{kg{\cdot}mol^{-1}}
\end{aligned}$$

and, hence, $\log_{10}\beta_1^{\circ} \approx (1.48 \pm 0.11) + 0.341 - (0.029 \pm 0.063)\,0.05 - \varepsilon((\mathrm{Et})_4\mathrm{N^+},\mathrm{F^-})\,I_m$.

This produces the intermediate result

$$\log_{10}\beta_1^{\circ}\ ((\mathrm{VIII.1}), 298.15\ \mathrm{K}) = (1.82 \pm 0.11) - \varepsilon((\mathrm{Et})_4\mathrm{N^+},\mathrm{F^-})\,0.05.$$

The term $\varepsilon((\mathrm{Et})_4\mathrm{N^+},\mathrm{F^-})\,I_m$ remains to be estimated. Hummel *et al.* [2005HUM/AND] presented a comprehensive discussion on the problems with tetraalkylammonium halide interaction coefficients. In most cases the description of such interaction coefficients requires an ionic strength dependent form, *i.e.*, $\varepsilon(\mathrm{i,k},I_m) = \varepsilon_1(\mathrm{i,k}) + \varepsilon_2(\mathrm{i,k})\log_{10} I_m$, as for example proposed by Ciavatta [1980CIA]. Hummel *et al.* [2005HUM/AND] (Figure V-1 on page 94) compared the ionic strength dependency of $\{\log_{10}\gamma_{\pm} + D(I_m)\}$ of $\mathrm{NH_4Cl}$ and $(\mathrm{Me})_4\mathrm{NCl}$ solutions with that of NaCl and Na-acetate solutions, where the slopes of the curves represent the corresponding interaction coefficients. From this comparison, one may suppose that in the case of $\mathrm{R_4NCl}$ solutions the slopes/interaction coefficients are negative at low ionic strength and that the actual magnitude may become substantially greater with increasing length of the alkyl group R. However, it is very unlikely that the value of $\varepsilon((\mathrm{Et})_4\mathrm{N^+},\mathrm{F^-})$ is outside the interval −0.3 to 0.0 $\mathrm{kg{\cdot}mol^{-1}}$, and so considering this ample range, $\log_{10}\beta_1^{\circ}$ ((VIII.1), 298.15 K) becomes (1.82 ± 0.11) when using $\varepsilon((\mathrm{Et})_4\mathrm{N^+},\mathrm{F^-})$ = 0.0 $\mathrm{kg{\cdot}mol^{-1}}$, and becomes (1.83 ± 0.11) when using $\varepsilon((\mathrm{Et})_4\mathrm{N^+},\mathrm{F^-})$ = − 0.3 $\mathrm{kg{\cdot}mol^{-1}}$.

The results from Bond and Hefter [1972BON/HEF] and from Solomon and Bond [1983SOL/BON] were averaged according to the rules described in Appendix C for two discrepant data to give the selected value:

$$\log_{10}\beta_1^{\circ}\ ((\mathrm{VIII.1}), 298.15\ \mathrm{K}) = (1.7 \pm 0.2).$$

VIII.2.1.2 $FeF_2(aq)$, FeF_3^-

There is only one study in which it was concluded that higher-order iron(II) complexes, FeF_n^{2-n}, are formed [1967WEL/SAL]. The analysis given in this study is unclear, and the results are contradicted by the more recent finding of Vogel Koplitz *et al.* [1987VOG/MCC] in the $FeCl_n^{2-n}$ system that the formation constants of the halide complexes should decrease with decreasing temperature. Further, it is not clear why the dominant complex in solution should change from $FeF_2(aq)$ to FeF_3^- if the temperature decreases from 288.15 to 273.15 K (see Table VIII-1). Finally, the magnitude of β_2 (and of β_3) is incompatible with the measurements of Bond and Hefter [1972BON/HEF] and of Solomon and Bond [1983SOL/BON]. Conditions in both of these studies were such that formation of 2:1 and 3:1 complexes should have been reported if these complexes were dominant under conditions used by Wells and Salam [1967WEL/SAL]. It seems that the formation constants given by Wells and Salam are strongly related to their selection of k'_0, the rate constant in absence of anions different from perchlorate. As mentioned in the corresponding Appendix A entry, values from the Wells and Salam [1967WEL/SAL] paper are not used further in the present review.

VIII.2.1.3 The interaction coefficient $\varepsilon(FeF^+, ClO_4^-)$

To derive a value of $\log_{10}\beta_1^\circ$ (VIII.1) from the data of Bond and Hefter [1972BON/HEF], the present review made use of the analogy

$$\varepsilon(FeF^+, ClO_4^-) - \varepsilon(Fe^{2+}, ClO_4^-) - \varepsilon(Na^+,F^-) \approx \varepsilon(NiF^+, ClO_4^-) - \varepsilon(Ni^{2+}, ClO_4^-) - \varepsilon(Na^+,F^-).$$

Consequently, since

$$\varepsilon(NiF^+, ClO_4^-) - \varepsilon(Ni^{2+}, ClO_4^-) - \varepsilon(Na^+,F^-) = -(0.049 \pm 0.060)\ kg{\cdot}mol^{-1},$$

$$\varepsilon(Na^+,F^-) = (0.02 \pm 0.02)\ kg{\cdot}mol^{-1}\ [2005GAM/BUG],$$

and $\varepsilon(Fe^{2+}, ClO_4^-) = (0.37 \pm 0.04)\ kg{\cdot}mol^{-1}$ [this review, SectionVI.4.4],

the above analogy also leads to

$$\varepsilon(FeF^+, ClO_4^-) \approx \{-(0.049 \pm 0.060) + (0.02 \pm 0.02) + (0.37 \pm 0.04)\}\ kg{\cdot}mol^{-1},$$

or $\varepsilon(FeF^+, ClO_4^-) \approx (0.34 \pm 0.07)\ kg{\cdot}mol^{-1}$.

VIII.2.2 Aqueous iron(II) chloride complexes

Qualitative studies have shown that Fe(II) may form several complexes $FeCl_n^{2-n}$ with chloride. For example, Vogel Koplitz *et al.* [1987VOG/MCC] investigated the formation of Fe(II) chlorido complexes in concentrated LiCl-DCl-D_2O solutions at various temperatures. Using principal factor analysis they found strong indications for higher-order complexes at high chloride concentrations, particularly at elevated temperatures. Their study showed that at 322 K, for example, the complex $FeCl_2(aq)$ seems to become significant in solutions with a chloride molality above 6 to 7; in solutions above 9 m Cl^- the analysis indicated the existence of $FeCl_3^-$. At 345 K and at very high chloride concentrations (> 10 m) Vogel Koplitz *et al.* [1987VOG/MCC] suggested the formation of $FeCl_4^{2-}$. A new IR band at ~ 4000 cm^{-1} was attributed to this tetrahedral complex $FeCl_4^{2-}$ [1987VOG/MCC]. Heinrich and Seward [1990HEI/SEW] found evidence for the formation of $FeCl_2(aq)$, but not at temperatures below 423 to 473 K in chloride solutions ≤ 3.4 m. In his thesis, later summarized in a paper given by Zhao and Pan [2001ZHA/PAN], Zhao [1997ZHA] drew similar conclusions about the existence of higher-order complexes and the tetrahedral $FeCl_4^{2-}$ complex. However, these authors particularly criticized the work of Heinrich and Seward [1990HEI/SEW] because formation of $FeCl_4^{2-}$ had not been considered in the data evaluation. As discussed in Appendix A the high-temperature (≥ 570 K) solubility results from Boctor *et al.* [1980BOC/POP] and Zeng *et al.* [1989ZEN/AI] are not considered to be within the scope of the present review.

Several direct methods (photometric and potentiometric measurements) and indirect methods (kinetic studies of the oxidation of Fe(II) with $H_2O_2(sln)$, and solubility, ligand exchange, osmotic and isopiestic measurements) have been used to determine the formation constants of $FeCl_n^{2-n}$ complexes.

VIII.2.2.1 $FeCl^+$

Most of the authors, with the exception of Dauphin *et al.* [1963DAU/DAU], [1963DAU/DAU], [1964DAU/DAU] who gave a formation constant of 300 to 600 $dm^3 \cdot mol^{-1}$ in their early work, have concluded that the formation constant for the equilibrium

$$Fe^{2+} + Cl^- \rightleftharpoons FeCl^+ \qquad (VIII.2)$$

is well below 10 $kg \cdot mol^{-1}$ at various ionic strengths. Due to the low formation constants all investigations were carried out using solutions with rather high chloride concentrations. This in turn complicates the evaluation, because corresponding SIT interaction coefficients $\varepsilon(Fe^{2+},(Cl^-,X^{n-}))$ and $\varepsilon(FeCl^+,(Cl^-,X^{n-}))$ are not readily available.

Table VIII-2: Experimental/re-evaluated formation constants and related parameters for the iron(II) chlorido complexes.

Method	Ionic medium	t /°C	Reported Value $^{(a)}$	Reference	Re-evaluation $^{(b)}$
E_{cell}, sp	2 M (Na)ClO_4	20	$\beta_1 = 2.3$ $\beta_2 = 2.5$	[1944OLE]	
sol, pH	0.03 – 0.15 M (Ba,Fe(II))Cl_2	RT ?	$\beta_1 = 288$ to 625	[1964DAU/DAU]	
sp, kin	1 M NaCl	10	$\beta_1 = 12.0$	[1967WEL/SAL]	

(Continued on next page)

Table VIII-2 (continued)

Method	Ionic medium	t /°C	Reported Value $^{(a)}$	Reference	Re-evaluation $^{(b)}$
sp, kin	0.3 M NaCl + 0.7 M $NaClO_4$	25	$\beta_1 = 5.54$	[1967WEL/SAL]	
sp, kin	0.7 M NaCl + 0.3 M $NaClO_4$	25	$\beta_1 = 9.8$	[1967WEL/SAL]	
sp, kin	4.0 M NaCl	25	$\beta_1 = 9.8$	[1967WEL/SAL]	
sp, kin	1.0 M NaCl	35	$\beta_1 = 4.0$	[1967WEL/SAL]	
sp, kin	0.5 M NaCl + 0.5 M $NaClO_4$	45	$\beta_1 = 2.8$	[1967WEL/SAL]	
sp, kin	1 M $H(ClO_4,Cl)$	25	$\beta_1 = (0.5 \pm 0.3)$	[1968PO/SUT]	$\beta_1 = (0.48 \pm 0.28)$; does actually not differ from $\beta_1 = (0.5 \pm 0.3)$
sp, kin	1.0 (ClO_4)	25	$\beta_1 = (6.0 \pm 0.3)$	[1969WEL]	$\beta_1 = (5.7 \pm 0.3)$
E_{cell}	$I = 6$ M ($HCl/HClO_4$)	RT	$K_2 = 0.314$	[1976KHA/BEL]	
sp	5 M $(Na/H)ClO_4$	25	$\beta_1 = (0.32 \pm 0.01)$	[1976ASH]	$\beta_1 = 0.24$. Uncertainty is at least ± 0.05. $I = 6.59$ m.
sp	5 M $(Na/H)ClO_4$	60	$\beta_1 = (0.30 \pm 0.02)$	[1976ASH]	$\beta_1 = 0.22$. Uncertainty is at least ± 0.05. $I = 6.75$ m
sp	2.8 M ($NaCl/KNO_3$) 2.96…3.20 m	18.0	$\beta_1 = (0.45 \pm 0.05)$	[1976RAM]	see Appendix A
sp	2.8 M ($NaCl/KNO_3$)	20.0	$\beta_1 = (0.38 \pm 0.05)$	[1976RAM]	
sp	2.8 M ($NaCl/KNO_3$)	22.0	$\beta_1 = (0.37 \pm 0.05)$	[1976RAM]	
sp	2.8 M ($NaCl/KNO_3$) 2.96…3.20 m	26.0	$\beta_1 = (0.29 \pm 0.05)$	[1976RAM]	see Appendix A
sp	2.8 M ($NaCl/KNO_3$) 2.96…3.20 m	32.0	$\beta_1 = (0.37 \pm 0.05)$	[1976RAM]	see Appendix A
sp	2.8 M ($NaCl/KNO_3$) 2.96…3.20 m	37.0	$\beta_1 = (0.39 \pm 0.05)$	[1976RAM]	see Appendix A

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Table VIII-2 (continued)

Method	Ionic medium	t /°C	Reported Value $^{(a)}$	Reference	Re-evaluation $^{(b)}$
sp	2.8 M ($NaCl/KNO_3$)	43.5	$\beta_1 = (0.43 \pm 0.05)$	[1976RAM]	
sp	2.8 M ($NaCl/KNO_3$) 2.96…3.20 m	18.0	$\beta_1 = (0.12 \pm 0.03)$	[1976RAM]	see Appendix A
sp	2.8 M ($NaCl/KNO_3$)	20.0	$\beta_1 = (0.09 \pm 0.03)$	[1976RAM]	
sp	2.8 M ($NaCl/KNO_3$) 2.96…3.20 m	22.0	$\beta_1 =$ (0.095 ± 0.030)	[1976RAM]	see Appendix A
sp	2.8 M ($NaCl/KNO_3$) 2.96…3.20 m	26.0	$\beta_1 = (0.13 \pm 0.03)$	[1976RAM]	see Appendix A
sp	2.8 M ($NaCl/KNO_3$)	32.0	$\beta_1 = (0.13 \pm 0.03)$	[1976RAM]	
sp	2.8 M ($NaCl/KNO_3$) 2.96…3.20 m	37.0	$\beta_1 = (0.12 \pm 0.03)$	[1976RAM]	see Appendix A
sp	2.8 M ($NaCl/KNO_3$)	43.5	$\beta_1 = (0.15 \pm 0.03)$	[1976RAM]	
sp	Var (Cl) → 0	25	$\beta_1^{\circ} = (0.69 \pm 0.04)$ $\Delta_r H^{\circ} = 5.6$ $\Delta_r S^{\circ} = 16$	[1990HEI/SEW]	$\log_{10} \beta_{1m}^{\circ} = -(0.111 \pm 0.064)$ $\varepsilon(FeCl^+,Cl^-) - \varepsilon(Fe^{2+},Cl^-) - \varepsilon(H^+,Cl^-)$ $= -(0.075 \pm 0.031)\ kg\cdot mol^{-1}$
sp	Var (Cl) → 0	50	$\beta_1^{\circ} = (0.95 \pm 0.04)$ $\Delta_r H^{\circ} = 9.4$ $\Delta_r S^{\circ} = 28$	[1990HEI/SEW]	
sp	Var (Cl) → 0	100	$\beta_1^{\circ} = (1.64 \pm 0.03)$ $\Delta_r H^{\circ} = 18.6$ $\Delta_r S^{\circ} = 54$	[1990HEI/SEW]	
sp	Var (Cl) → 0	150	$\beta_1^{\circ} = (4.6 \pm 0.2)$ $\Delta_r H^{\circ} = 30.0$ $\Delta_r S^{\circ} = 83$	[1990HEI/SEW]	

(Continued on next page)

Table VIII-2 (continued)

Method	Ionic medium	t /°C	Reported Value $^{(a)}$	Reference	Re-evaluation $^{(b)}$
sp	Var (Cl) $\rightarrow$ 0	200	β_1° = (12.7 ± 1.7) $\Delta_r H^{\circ}$ = 43.1 $\Delta_r S^{\circ}$ = 112	[1990HEI/SEW]	
				This review	$\Delta_r H^{\circ}$ (FeCl$^+$) = (10.7 ± 7.9) in the temperature range 25 to 100 °C, based on ($1/T_0$–$1/T$) regression of $\log_{10} \beta_{1m}^{\circ}$. $\Delta_r H^{\circ}$ (FeCl$^+$) = (28.9 ± 8.9) in the temperature range 100 to 200 °C, based on ($1/T_0$–$1/T$) regression of $\log_{10} \beta_{1m}^{\circ}$.
E_{cell}	1 m sodium – trifluoromethane–sulfonate	125 to 295	$\log_{10} \beta_1^{\circ}$ 25 °C: −0.125 50 °C: −0.026 100 °C: 0.266 150 °C: 0.648 200 °C: 1.09 250 °C: 1.58 300 °C: 2.10 $\Delta_r H^{\circ}$ 25 °C: 5.4 50 °C: 9.4 100 °C: 18.3 150 °C: 28.5 200 °C: 40.0 250 °C: 52.8 300 °C: 66.9	[1993PAL/HYD]	Regression of molal formation quotients against ($1/T_0$ – $1/T$): $\log_{10} \beta_{1m}$(FeCl$^+$, 1 m, 25 °C) = −(1.74 ± 0.33) $\Delta_r H^{\circ}$ (FeCl$^+$, 1 m) = (29.1 ± 4.8) valid in the range from 120 to 300 °C
sp	(Cl$^-$) $\rightarrow$ 0	10	$\log_{10} \beta_1^{\circ}$ = −(0.648 ± 0.082) $\log_{10} \beta_2^{\circ}$ = −(2.16 ± 0.10)	[2001ZHA/PAN] [1997ZHA]	$\log_{10} \beta_{1m}$ = −(1.095 ± 0.105) at I_m = 4.49 m (NaCl/FeCl$_2$), assuming that only FeCl$^+$ is formed
sp	(Cl$^-$) $\rightarrow$ 0	25	$\log_{10} \beta_1^{\circ}$ = −(0.366 ± 0.059) $\log_{10} \beta_2^{\circ}$ = −(1.74 ± 0.02)	[2001ZHA/PAN] [1997ZHA]	$\log_{10} \beta_{1m}$ = −(0.918 ± 0.082) at I_m = 4.47 m (NaCl/FeCl$_2$), assuming that only FeCl$^+$ is formed.

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Table VIII-2 (continued)

Method	Ionic medium	t /°C	Reported Value [(a)]	Reference	Re-evaluation [(b)]
sp	$(\mathrm{Cl}^-) \rightarrow 0$	40	$\log_{10}\beta_1^\circ = -(0.200 \pm 0.130)$ $\log_{10}\beta_2^\circ = -(1.56 \pm 0.01)$	[2001ZHA/PAN] [1997ZHA]	$\log_{10}\beta_{1m} = -(0.772 \pm 0.069)$ at I_m = 4.46 m ($NaCl/FeCl_2$), assuming that only $FeCl^+$ is formed.
sp	$(\mathrm{Cl}^-) \rightarrow 0$	60	$\log_{10}\beta_1^\circ = (0.015 \pm 0.016)$ $\log_{10}\beta_2^\circ = -(1.25 \pm 0.02)$ $\log_{10}\beta_4^\circ = -4.1$	[2001ZHA/PAN] [1997ZHA]	
sp	$(\mathrm{Cl}^-) \rightarrow 0$	80	$\log_{10}\beta_1^\circ = (0.233 \pm 0.014)$ $\log_{10}\beta_2^\circ = -(0.967 \pm 0.044)$ $\log_{10}\beta_4^\circ = -3.5$	[2001ZHA/PAN] [1997ZHA]	
sp	$(\mathrm{Cl}^-) \rightarrow 0$	100	$\log_{10}\beta_1^\circ = -(0.509 \pm 0.035)$ $\log_{10}\beta_2^\circ = -(0.512 \pm 0.10)$ $\log_{10}\beta_4^\circ = -2.9$	[2001ZHA/PAN] [1997ZHA]	
sp	$(\mathrm{Cl}^-) \rightarrow 0$		$FeCl^+$: $\Delta_r H^\circ = (24.7 \pm 1.2)$ $\Delta_r S^\circ = (75.0 \pm 3.6)$ $FeCl_2(aq)$: $\Delta_r H^\circ = (9.9 \pm 1.5)$ $\Delta_r S^\circ = (6.1 \pm 4.7)$ $FeCl_4^{2-}$: $\Delta_r H^\circ = (71.4 \pm 2.5)$ $\Delta_r S^\circ = (136 \pm 7)$	[2001ZHA/PAN] [1997ZHA]	Regression against $(1/T_0 - 1/T)$ produces $\log_{10}\beta_{1m}(FeCl^+$, 4.5 m, 25 °C$) = -(0.923 \pm 0.049)$ $\Delta_r H^\circ$ ($FeCl^+$, 4.5 m, 25 °C) = 18.1 ± 6.9
isop	$FeCl_2$ (0 to 5 m)	25		[2004MOO/HAG] + this review	$\log_{10}\beta_{1m}^\circ(FeCl^+) = -(2.05 \pm 0.15)$ $\varepsilon(Fe^{2+},Cl^-) = (0.17 \pm 0.01)$ kg·mol^{-1} $\varepsilon(FeCl^+,Cl^-) = (0.16 \pm 0.01)$ kg·mol^{-1}

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Table VIII-2 (continued)

Method	Ionic medium	t /°C	Reported Value $^{(a)}$	Reference	Re-evaluation $^{(b)}$
calc				this review +[2005GAM/BUG] + [1988MAR]	$\varepsilon(\mathrm{Fe^{2+},Cl^-}) = (0.15 \pm 0.02)\ \mathrm{kg \cdot mol^{-1}}$

(a) Molar constants (*i.e.*, β_{1c}) unless specifically identified as molal constants (β_{1m}); values of $\Delta_r H_m$ in $\mathrm{kJ \cdot mol^{-1}}$, of $\Delta_r S_m$ in $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$.

(b) Molal constants; when necessary, molar values were converted to molal values using the factors in Table II-5.

There are only two studies [1990HEI/SEW], [2004MOO/HAG] that systematically vary chloride concentrations and allow the value of β_1(VIII.2) to be evaluated according to the SIT formalism. Following the conclusion of Vogel Koplitz *et al.* [1987VOG/MCC] that no higher-order complexes are formed at ambient temperature below ~5 m chloride, *i.e.*, making the assumption that only the complex $\mathrm{FeCl^+}$ is formed at $m_{\mathrm{Cl^-}} < 5$, the 298.15 K Heinrich and Seward data lead to (Figure VIII-1):

$$\log_{10} \beta_1^{\circ}\ ((\mathrm{VIII.2}), 298.15\ \mathrm{K}) = -(0.11 \pm 0.03)$$

and

$$\varepsilon(\mathrm{FeCl^+,Cl^-}) - \varepsilon(\mathrm{Fe^{2+},Cl^-}) - \varepsilon(\mathrm{H^+,Cl^-}) = -(0.08 \pm 0.01)\ \mathrm{kg \cdot mol^{-1}}.$$

The data points measured at low ionic strength must not be used in a simple ($\log_{10} \beta_1 + 4D$) *vs.* I_m regression because the implicit approximation $I_m \approx m_{\mathrm{Cl^-}} \approx m_{\mathrm{H^+}}$ is no longer valid at low ionic strength, and because at $I_m < 0.1$ m the doubly charged cation $\mathrm{Fe^{2+}}$ may contribute significantly to the ionic strength, and may thus induce a medium effect.

The resulting difference $\varepsilon(\mathrm{FeCl^+,Cl^-}) - \varepsilon(\mathrm{Fe^{2+},Cl^-}) = (0.05 \pm 0.03)\ \mathrm{kg \cdot mol^{-1}}$ indicates that the two interaction coefficients are nearly identical, but their absolute values cannot be calculated without further information.

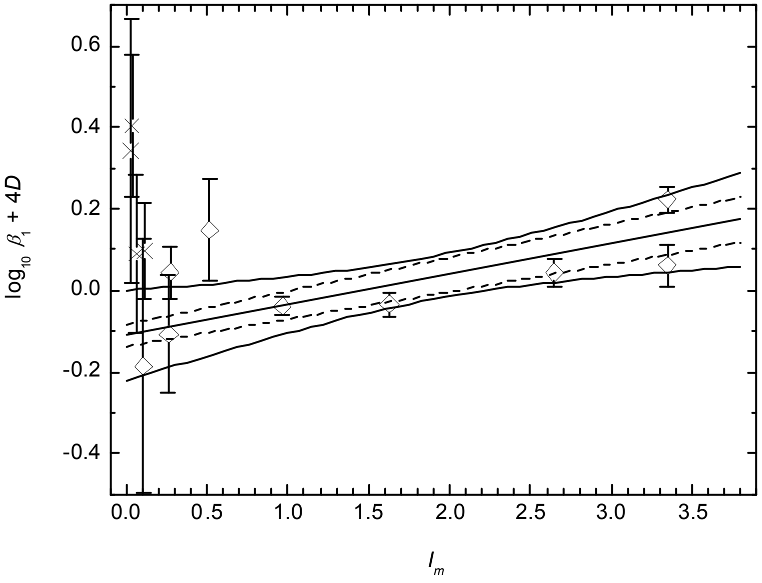
A detailed description of the re-evaluation of the Moog *et al.* [2004MOO/HAG] isopiestic (osmotic) data is given in Appendix A. The simplest model assuming only the complex $\mathrm{FeCl^+}$ to be formed produces

$$\log_{10} \beta_1^{\circ}\ ((\mathrm{VIII.2}), 298.15\ \mathrm{K}) = -(2.05 \pm 0.15),$$

$$\varepsilon(\mathrm{Fe^{2+},Cl^-}) = (0.17 \pm 0.01)\ \mathrm{kg \cdot mol^{-1}},$$

$$\text{and } \varepsilon(\mathrm{FeCl^+,Cl^-}) = (0.16 \pm 0.01)\ \mathrm{kg \cdot mol^{-1}}.$$

Figure VIII-1: Weighted linear regression of ($\log_{10} \beta_1$ + 4*D*) for data measured by Heinrich and Seward [1990HEI/SEW] in hydrochloric acid solutions against ionic strength. Data points marked with a cross were not used in the calculation due to a significant contribution of Fe^{2+} to the ionic strength. The dashed-line pair delimits the 2σ uncertainty band and the thin solid-line pair defines the 95% confidence band.



Hence, the Moog *et al.* [2004MOO/HAG] data confirm the result from the Heinrich and Seward [1990HEI/SEW] data that the interaction coefficients $\varepsilon(Fe^{2+},Cl^-)$ and $\varepsilon(FeCl^+,Cl^-)$ are nearly identical. In addition, the osmotic data produce an absolute value for $\varepsilon(Fe^{2+},Cl^-)$ (and for $\varepsilon(FeCl^+,Cl^-)$). Further, the resulting interaction coefficient $\varepsilon(Fe^{2+},Cl^-) = (0.17 \pm 0.01)$ kg·mol^{-1} is confirmed by an interesting analogy.

If known interaction coefficients $\varepsilon(Me^{2+},Cl^-)$ are regressed against the reciprocal mean ion-water distance as published by Marcus [1988MAR] one finds $\varepsilon(Fe^{2+},Cl^-) = (0.15 \pm 0.02)$ kg·mol^{-1} (Table VIII-3 and Figure VIII-2).

However, the formation constants from the two studies disagree by nearly two orders of magnitude. The higher value of Heinrich and Seward [1990HEI/SEW] is in principle confirmed by the study of Zhao and Pan [2001ZHA/PAN], which suggests $\log_{10} \beta_1^{\circ}$ ((VIII.2), 298.15 K) = $-(0.44 \pm 0.06)$ and by the study of Raman [1976RAM], from which $\log_{10} \beta_1^{\circ}$ ((VIII.2), 298.15 K) = $-(0.06 \pm 0.33) + 3.18\,\varepsilon(FeCl^+, NO_3^-)$ can be derived—the latter expression being useful only if iron(II) nitrate interactions are negligible compared to iron(II) chloride interactions[1]. The low value derived from the study of Moog *et al.* is partly supported by the high-temperature determinations performed by Palmer and Hyde [1993PAL/HYD], which lead to $\log_{10} \beta_1$ ((VIII.2), 298.15 K, $I = 1$ m) = $-(1.74 \pm 0.17)$ on extrapolation down to 298.15 K.

Table VIII-3: Literature data on published SIT interaction coefficients $\varepsilon(\mathrm{Me}^{2+},\mathrm{Cl}^-)$ [2005GAM/BUG], mean metal-water distances and ionic radii in solution of selected divalent cations in aqueous solution (Table XIII of Marcus [1988MAR]).

Cation	$\varepsilon(\mathrm{Me}^{2+},\mathrm{Cl}^-)$/ $\mathrm{kg \cdot mol^{-1}}$	Mean metal-water distance [nm]	Ionic radius in solution [nm]
Mn^{2+}	0.13 ± 0.01	0.2192 ± 0.0013	0.080 ± 0.001
Co^{2+}	0.16 ± 0.02	0.2106 ± 0.0022	0.072 ± 0.002
Ni^{2+}	0.17 ± 0.02	0.2061 ± 0.0014	0.067 ± 0.001
$\mathrm{Cu}^{2+}{}_{\mathrm{(axial)}}$	0.08 ± 0.01	0.240 ± 0.010	
Fe^{2+}		0.2114 ± 0.0010	0.072 ± 0.001

It is not clear at present which value should be selected for $\log_{10} \beta_1^{\circ}$ ((VIII.2), 298.15 K). Any selection is difficult to justify. The SIT corrections from the experimental conditions to zero ionic strength are as much as an order of magnitude in $\log_{10} \beta_1^{\circ}$, and the values found for $\log_{10} \beta_1^{\circ}$ differ greatly from study to study, and are all negative. Thus, it is clear that FeCl^+ is a very weak complex. Hence, no formation constant $\log_{10} \beta_1^{\circ}$ ((VIII.2), 298.15 K) value is selected. To provide some assistance to modellers who must select a constant due to the specifics of their speciation code, the present review suggests use of $\log_{10} \beta_1^{\circ}$ ((VIII.2), 298.15 K) = $-(1.0 \pm 0.8)$, with $\varepsilon(\mathrm{Fe}^{2+},\mathrm{Cl}^-)$ = (0.17 ± 0.01) $\mathrm{kg \cdot mol^{-1}}$, and $\varepsilon(\mathrm{FeCl}^{+},\mathrm{Cl}^-)$ = (0.16 ± 0.01) $\mathrm{kg \cdot mol^{-1}}$ as discussed above.

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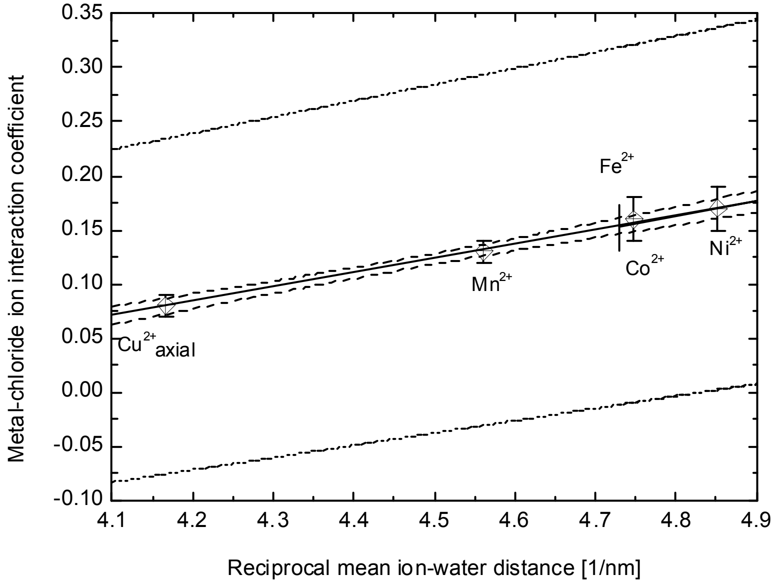
[1] There is sufficient evidence that iron(II)-chloride interactions become significant at high chloride concentrations and/or at elevated temperatures (see also further discussions below). No such evidence is available for iron(II) nitrate solutions. From this absence of evidence, and from the fact that nitrate interactions with divalent transition metals in general are very weak to non-existent, we draw the conclusion by analogy that at ambient temperature iron(II)-nitrate interactions are negligible if compared to iron(II)-chloride interactions.

Figure VIII-2: Weighted linear regression of chloride SIT coefficients $\varepsilon(\mathrm{Me}^{2+},\mathrm{Cl}^-)$ against the reciprocal ion-water distance (data from Table VIII-3). The dashed-line pair delimits the 2σ uncertainty band and the thin solid-line pair defines the 95% confidence band. Although the confidence interval is quite small and the linearity is good, a large uncertainty in estimated values arises from the small number of data points.



VIII.2.2.2 $FeCl_2$(aq)

At elevated temperatures and higher chloride concentrations the neutral complex $FeCl_2$(aq) may become important. For the formation constant β_2° ($FeCl_2$, aq) Heinrich and Seward [1990HEI/SEW] gave the ranges ≤ 0.16 (423.15 K; units correspond to $(\mathrm{kg \cdot mol^{-1}})^2$) and 0.17…2.0 (473.15 K; same units). Palmer and Hyde [1993PAL/HYD] did not report on the neutral complex, obviously the chloride concentration in their experiments was too low (*i.e.*, < 1 m) to allow the complex to be detected. Zhao and Pan [2001ZHA/PAN] performed measurements only up to 373.15 K, but these authors varied the chloride concentration up to 15.2 m using LiCl. For $\log_{10} \beta_2^{\circ}$ ($FeCl_2$, aq) they evaluated temperature dependent formation constants as given in Table VIII-2. At 373.15 K their formation constant β_2° ($FeCl_2$, aq) = (0.31 ± 0.07) compares well with the available constants from Heinrich and Seward [1990HEI/SEW]. Khachaturyan and Belyakov [1976KHA/BEL] gave β_2° ($FeCl_2$, aq, room temperature, I = 6 M) = 0.314, in principle in accordance with [2001ZHA/PAN] and [1990HEI/SEW], but the reliability of this value is very unclear. Available data clearly demonstrate that substantially high chloride concentrations and/or elevated temperatures are necessary to form $FeCl_2(aq)$. Therefore, the present review does not attempt to give a formation constant for 298.15 K.

VIII.2.2.3 Heat of reaction for $Fe^{2+} + Cl^- \rightleftharpoons FeCl^+$

Raman [1976RAM], Heinrich and Seward [1990HEI/SEW], Zhao and Pan [2001ZHA/PAN] as well as Palmer and Hyde [1993PAL/HYD] performed experiments at different temperatures, which in principle allows a value for the heat of reaction to be derived.

The experiments of Raman [1976RAM] cover a temperature range of only 20 K, and for reasons discussed in Appendix A, cannot be used in the present review. Heinrich and Seward [1990HEI/SEW] gave experimental results at 298.15, 323.15, 373.15, 423.15 and 473.15 K. Interestingly, a regression of their three "high temperature" points against $1/T$ gives $\Delta_r H_m^\circ$ (298.15 K, $I = 0$) = (28.7 ± 8.9) kJ·mol^{-1}, very similar to the slope derived from the results of Palmer and Hyde [1993PAL/HYD] (and similar to the slope from Zhao and Pan [2001ZHA/PAN] at lower temperatures). The two lower temperature experiments of Heinrich and Seward [1990HEI/SEW] deviate from this linearity and their data from 298.15 to 373.15 K (3 experimental points) would produce $\Delta_r H_m^\circ$ (298.15 K, $I = 0$) = (10.7 ± 7.9) kJ·mol^{-1}. If a regression of all points from the work of Heinrich and Seward is done against $1/T$, one still obtains a more or less linear relationship with

$$\Delta_r H_m^\circ (\mathrm{FeCl^+}, 298.15\ \mathrm{K}, I = 0) = (18.8 \pm 3.7)\ \mathrm{kJ\cdot mol^{-1}},$$

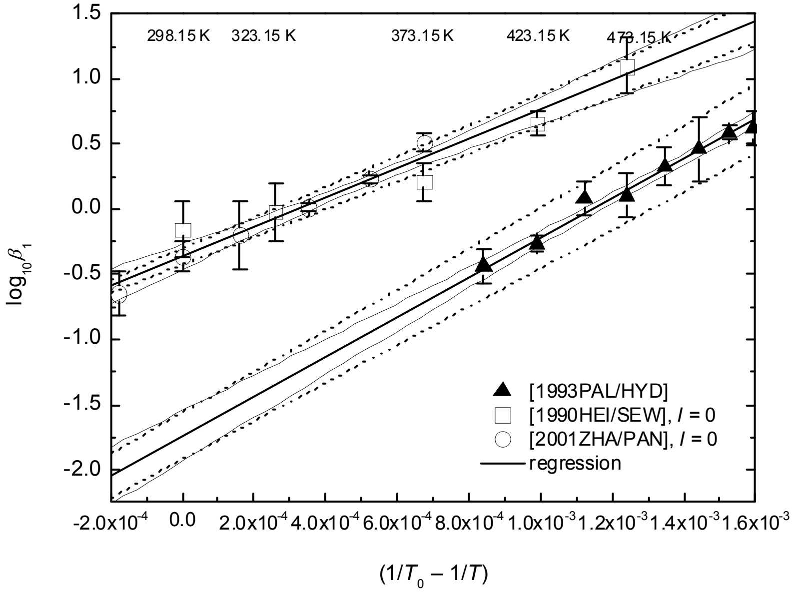
and it is noted that that the value of R^2 decreases from almost unity to 0.93. The authors themselves used an empirical function of T to express their formation constants ($\log_{10} \beta_1^\circ(T) = 24.355 + 0.0215\,T - 5.429\ln(T)$; T in K), which, through differentiation according to van't Hoff leads to $\Delta_r H_m^\circ (T) = 0.4116\,T^2 - 103.94\,T$ [J·mol^{-1}], resulting in 5.6 kJ·mol^{-1} at 298.15 K.

Palmer and Hyde performed experiments in the temperature range 393.15 K to 573.15 K in 1 molal sodium trifluoromethanesulfonate (tfms ≡ trifluoromethanesulfonate anion). Their $\log_{10} \beta_{1m}$ ($FeCl^+$, 1 m Na(tfms), T) data show very good linearity with $1/T$ as is demonstrated in Figure VIII-3. The enthalpy of reaction in 1 m Na(tfms) is

$$\Delta_r H_m^\circ (\mathrm{FeCl^+}, 298.15\ \mathrm{K, Na(tfms)\ 1\ m}) = (29.1 \pm 2.5)\ (2\sigma)\ \mathrm{kJ\cdot mol^{-1}}.$$

Interestingly, and as mentioned above, $\log_{10} \beta_1$ ((VIII.2), 298.15 K, $I_m = 1$) = – (1.74 ± 0.17) results from extrapolation of the Palmer and Hyde data down to 298.15 K. The Debye-Hückel term $4D$ for this reaction at $I_m = 1$ and 298.15 K is + 0.81. Hence, $\log_{10} \beta_1^\circ$ ((VIII.2), 298.15 K) = $-(0.93 \pm 0.17) - 1.0(0.03 \pm 0.01) + 1.0\,(\varepsilon(\mathrm{FeCl^+},\mathrm{tfms}) - \varepsilon(\mathrm{Fe^{2+}},\mathrm{tfms}))$.

Figure VIII-3: Weighted linear regression —— of zero ionic strength formation constants from Heinrich and Seward [1990HEI/SEW] (□) and Zhao and Pan [2001ZHA/PAN] (○) as a function of inverse temperature. Formation constants (and a linear regression on the values -----) from Palmer and Hyde [1993PAL/HYD] (Δ) in 1 m sodium trifluoromethanesulfonate are also shown in the lower part of the diagram. The dashed-line pairs delimit the 2σ uncertainty band and the thin solid-line pairs define the 95% confidence band.



If a regression of the Zhao and Pan [2001ZHA/PAN] data (as given in their table 2) is done against $1/T$, one obtains

$$\Delta_r H^\circ_m\ (\text{FeCl}^+,\ 298.15\ \text{K},\ I = 0) = (24.9 \pm 2.5)\ (2\sigma)\ \text{kJ·mol}^{-1}.$$

The experimental data of [2001ZHA/PAN] were re-evaluated (*cf.* Appendix A) and the $\log_{10} \beta_{1m}$ values of $-(1.095 \pm 0.105)$, $-(0.918 \pm 0.082)$ and $-(0.772 \pm 0.069)$ at 283.15, 298.15 and 313.15 K and the single ionic strength (4.5 m, (4.3 m NaCl)), respectively, were obtained. Regression of these formation constants under the assumption of a constant molar enthalpy of reaction over this narrow temperature range produces $\Delta_r H_m$ (FeCl$^+$, 298.15 K, I_m = 4.5) = (18.2 ± 6.9) kJ·mol^{-1}.

If a linear regression is carried out on the zero ionic strength formation constant values (as provided by the authors) from Heinrich and Seward

[1990HEI/SEW] and from Zhao and Pan [2001ZHA/PAN] against inverse temperature, we obtain the selected value

$$\Delta_r H_m (\text{FeCl}^+, 298.15 \text{ K}, I_m = \text{var}) = (21.55 \pm 1.77)\ (2\sigma)\ \text{kJ}\cdot\text{mol}^{-1}.$$

The resulting coefficient of determination is 0.95. If the formation constants from Palmer and Hyde [1993PAL/HYD] in 1 m sodium trifluoromethanesulfonate are used for a similar regression[1] (coefficient of determination 0.99), a value of (29.1 ± 2.5) (1 σ) $\text{kJ}\cdot\text{mol}^{-1}$ is obtained for $\Delta_r H_m$ (FeCl^+, 298.15 K, I_m = 1.0). Within 2σ uncertainty limits, these values are in marginal agreement, and the high-temperature results of Palmer and Hyde at an ionic strength of 1.0 $\text{mol}\cdot\text{kg}^{-1}$ corroborate the results from the work of Heinrich and Seward [1990HEI/SEW] and Zhao and Pan [2001ZHA/PAN].

VIII.2.2.4 Discussion on the entropy of reaction for $\text{Fe}^{2+} + \text{Cl}^- \rightleftharpoons \text{FeCl}^+$

When we assume, as indicated above, that $\log_{10} \beta_1$ depends linearly on $1/T$ we can also alternately derive a value for $\Delta_r S$ from the linear fit of $\log_{10} \beta_1$ against $1/T$. From the combined data of Heinrich and Seward [1990HEI/SEW], and Zhao and Pan [2001ZHA/PAN] as corrected to zero ionic strength by the authors one obtains $\Delta_r S^\circ$ = (65.3 ± 6.0) (2σ) $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. The data of Palmer and Hyde [1993PAL/HYD], measured at I_m = 1.0 (sodium trifluoromethanesulfonate), lead to a value of (64.3 ± 8.8) $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for $\Delta_r S^\circ$ (1 m Na(tfms)). Using 21.6 $\text{kJ}\cdot\text{mol}^{-1}$ for $\Delta_r H_m$ (FeCl^+,298.15 K) from the combined data of Heinrich and Seward, and Zhao and Pan, with the value of -1.0 for $\log_{10} \beta_1^\circ$ ((VIII.2), 298.15 K) would lead to an entropy of reaction of 53 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. The present review suggests use of this value when modelers are forced to select a number due to the specific requirements of their speciation model.

VIII.2.2.5 Higher chlorido complexes

Vogel Koplitz *et al.* [1987VOG/MCC] gave spectroscopic evidence that several higher-order species with octahedral or tetrahedral geometry may form at very high chloride concentrations and Heinrich and Seward [1990HEI/SEW] reported a value of 0.77 $\text{kg}^2\cdot\text{mol}^{-2}$ for β_2 at 473.15 K (only). Zhao and Pan [2001ZHA/PAN] reported values of β_2 and β_4 at five temperatures from 298.15 to 373.15 K, and the maximum values (at 373.15 K) were 0.3 $\text{kg}^2\cdot\text{mol}^{-2}$ and 0.0013 $\text{kg}^4\cdot\text{mol}^{-4}$, respectively. The latter authors also provided enthalpies and entropies of the formation reactions based on these measurements. However, considering the small size of their formation constants, it is considered that any estimation of the enthalpies or entropies of formation would be highly speculative.

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[1] In the case of the points from Palmer and Hyde, values at individual temperatures represent weighted averages of individual measurements.

VIII.2.3 Aqueous iron(III) chlorido complexes

Chlorido complexes of iron(III) in aqueous solutions have been investigated by many workers from the beginning of the twentieth century to the present. Thermodynamic, spectroscopic and kinetics investigations have been published, and the following species have been claimed:

- $Fe^{3+}\cdot 6H_2O\cdot Cl^-$, octahedral outer-sphere ion pair, the Fe^{3+} ion first coordination sphere has six water molecules; represented in this review by $FeCl^{2+}_{(out)}$.
- $FeCl^{2+}\cdot 5H_2O$, inner-sphere monochlorido complex, the Fe^{3+} ion first coordination sphere has five water molecules and one chloride anion; represented in this review as $FeCl^{2+}_{(in)}$.
- $FeCl_2^+\cdot 4H_2O$, inner-sphere dichlorido complex, the Fe^{3+} ion first coordination sphere has four water molecules and two chloride anions; represented in this review as $FeCl_2^+$.
- $FeCl_3\cdot 3H_2O$, octahedral inner-sphere trichlorido complex, the Fe^{3+} ion first coordination sphere has three water molecules and three chloride anions; represented in this review as $FeCl_3(aq)$.
- $FeCl_3\cdot 2H_2O$, this trigonal bipyramidal species has been quoted as a possible complex of iron(III) in concentrated LiCl solutions as shown by EXAFS and XANES spectroscopy [2006LIU/ETS].
- $FeCl_4^-\cdot 2H_2O$ inner-sphere tetrachlorido complex, the Fe^{3+} ion first coordination sphere has two water molecules and four chloride anions. However this octahedral species has not been verified by any method other than solution X-ray diffraction.
- $FeCl_4^-$ tetrahedral species has been claimed as the limiting species in aqueous solutions in concentrated hydrochloric acid. $FeCl_4^-$ in equilibrium with the octahedral $FeCl_4^-\cdot 2H_2O$ hydrated complex also has been claimed to exist [1964BRA/ROB] in concentrated iron(III) chloride aqueous solutions; represented in this review as $FeCl_4^-$. However, polymeric species, possibly partially hydrolysed, also may exist [1967BAL].
- $FeCl_5^{2-}\cdot H_2O$ has been claimed in solids such as $Cs_2\cdot FeCl_5\cdot H_2O$ obtained by evaporation of an aqueous solution of $FeCl_3$ also containing CsCl, and as the extracted species in organic solutions after equilibration with aqueous chloride solutions containing tertiary amine hydroxidochlorides or quaternary ammonium chlorides.
- $FeCl_6^{3-}$ has been found to be octahedral in solids. It is less common than $FeCl_4^-$ or FeF_6^{3-}. The hexachloridoferrate(III) anion, $FeCl_6^{3-}$, needs the presence of large cations such as $Co(NH_3)_6^{3+}$ or $Co(pn)_3^{3+}$ (pn = 1,3-diaminopropane) to be stabilized in solids [1987NEL]. It has not been found in

aqueous solutions in which the higher-order complex is the tetrahedral species $FeCl_4^-$ [1952FRI].

- $FeClOH^+ \cdot 4H_2O$ has been reported; represented in this review as $FeClOH^+$. Because chloride ions have been found in solid intermediate species in the precipitation of Fe(III) hydroxide from aqueous chloride solution, it has been proposed that this species is stable in weakly acidic solutions containing low concentrations of chloride. However the stability of $FeClOH^+$, if it exists, is very low, and this species is not considered to be important in sea water [2001WAI] or natural waters [1995MIL/YAO].

VIII.2.3.1 Monochlorido $FeCl^{2+}_{(in)}$, $FeCl^{2+}_{(out)}$, $FeClOH^+$ formation constants

VIII.2.3.1.1 General literature review

The aqueous chlorido complexes of Fe(III) have been investigated with great care using many physical-chemical techniques, especially for the monochlorido $FeCl^{2+}$. The effects of varying ionic strength and temperature on the formation constant have been investigated.

The outer-sphere and inner-sphere $FeCl^{2+}$ complexes were not distinguished in early publications dealing with iron(III) aqueous chlorido complexes. The existence of the two types of complexes was proven for the first time by a kinetics investigation using the pressure-jump method [1962WEN/STR].

Table VIII-4 contains a summary of the main publications concerning the monochlorido complex of iron(III). We have separated the reports dealing with the monochlorido species because many studies focused only on the 1:1 species. The outer- and inner-sphere complexes are rather weak, and even if the stability constants reported by the various authors are different (for example: $2.0 < \beta_1 < 5$ $mol^{-1} \cdot kg$ at ionic strength ~ 1 m), this difference probably has a limited impact for the modelling of the behaviour of nuclear waste. However, in view of the quality of most of the experimental work and its interpretation, this difference is too high and is probably due to unidentified systematic errors. The existence of an outer-sphere complex with a large uncertainty in its formation constant, (and thus the effect of this complex on the different types of measurements used for the determination of β_1) is surely one of them. In the spectrophotometric investigations that used the charge-transfer band of $FeCl^{2+}$, the contributions of $FeCl^{2+}_{(in)}$ and $FeCl^{2+}_{(out)}$ to the measured optical densities are unknown. In potentiometry the influence of the outer-sphere species for the electron exchange to the electrodes is an open question. These questions address the fundamental properties of the aqueous solutions, and more profound answers are beyond the scope of this review. In the SIT model, weak interactions such as those that lead to outer-sphere complexes can be part of the values of the interaction coefficients. So they are considered as medium effects. Doing so probably changes the interaction coefficients values, which then no longer simply reflect just the long distance interactions. In the case of the $FeCl^{2+}$ complex, the formation constant values determined by several authors, [1962WOO/GAL], [1976BYR/KES2], [1981BYR/KES], either by spectrophotometry or potentiometry, are not clearly different. That invalidates the idea that all the complexes (inner plus outer) influence the electrode potentials. A charge-transfer band is used for the determination of the formation constant of $FeCl^{2+}$ by UV-visible spectrophotometry. Based on the work of Schwarz and Dodson [1976SCH/DOD], the absorption of the outer-sphere complex at 340 nm is negligible, so spectrophotometry leads to characterization of the inner-sphere complex. The similarity of these results to those from potentiometric investigations demonstrates that the same applies to results from potentiometry. In principle, the formation constants determined by redox potentiometry are underestimated if the Fe^{2+} associates are neglected. Estimation of the formation constant of $FeCl^{+}$ is difficult. However, using the value given in this chapter one finds that $FeCl^{+}$ cannot play a sufficient role to compensate for the presence of an outer-sphere complex, $FeCl^{2+}_{(out)}$, in changing the electrode potential.

Table VIII-4: Summary of experimental conditions and experimental and re-evaluated formation constants for the iron(III) monochlorido complexes. For discussion of the re-evaluations, see the corresponding Appendix A entries.

Reference	Method	Ionic medium	t /°C	Reported value $^{(a)}$	Re-evaluation $^{(b)}$
$Fe^{3+} + Cl^- \rightleftharpoons FeCl^{2+}$					
[1937MOL]	E_{cell}	0.1 M HCl(sln) + 0.0 to 3.00 M KCl(sln)	25	$\beta_1 = 4.1$ (avg.)	———
[1941BEN/FRE]	sp	$I = 0.665$ M ($NaClO_4$/NaCl in the presence of small amounts of NaSCN and HCl)	RT?	$\beta_1 = (1.28 \pm 0.13)$	———
[1941BRO]	pot	0.53 M KNO_3	25	$\beta_1 = 2.3$	
[1942RAB/STO]	sp	1 M $HClO_4$ $I_c = 0.61$ M (mainly $HClO_4$)	26.7 20–50	$\beta_1 = (4.2 \pm 0.2)$ $\Delta_rH_1 = (35.6 \pm 0.8)$	$\beta_1 = (4.0 \pm 0.2)$
[1944OLE]	sp	2 M $HClO_4$	20 25	$\beta_1 = 5.7$	$\beta_1 = (5.2 \pm 0.9)$ $\beta_1 = (6.1 \pm 1.0)$

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Table VIII-4 (continued)

Reference	Method	Ionic medium	t /°C	Reported value $^{(a)}$	Re-evaluation $^{(b)}$
[1959COL/NAU]	sp	2.50 M $HClO_4$	25	$\beta_1 = (4.2 \pm 0.1)$	$\beta_1 = (3.7 \pm 0.1)$
		3.00 M $HClO_4$		$\beta_1 = (5.8 \pm 0.1)$	(5.0 ± 0.1)
		4.00 M $HClO_4$		$\beta_1 = (12.5 \pm 0.2)$	(10.3 ± 0.2)
		4.95 M $HClO_4$ +		$\beta_1 = (28.0 \pm 0.3)$	Not used.
		0.775 M $NaClO_4$		$\beta_1 = (52.0 \pm 0.5)$	I_m beyond the
		+ 1.55 M $NaClO_4$		$\beta_1 = (97.0 \pm 1.4)$	limits of validity o
		+ 2.32 M $NaClO_4$6.00 M		$\beta_1 = (184.0 \pm$	SIT.
		$HClO_4$		$3.0)$	
		7.00 M $HClO_4$		$\beta_1 = (92.0 \pm 1.2)$	
		8.00 M $HClO_4$		$\beta_1 = (329.0 \pm$	
		8.50 M $HClO_4$		$4.0)$	
		9.00 M $HClO_4$		$\beta_1 = (1340 \pm 20)$	
		3 M $HClO_4$	25–45	$\beta_1 = (2060 \pm 50)$	
		8.5 M $HClO_4$		$\beta_1 = (6100 \pm$	
				$100)$	
				$\Delta_r H = 15.9$	
				$\Delta_r S = 66.9$	
				$\Delta_r H = -9.62$	
				$\Delta_r S = 34.3$	
[1959CON/COP]	sp	1.3 M $HClO_4$ (I_c = 1.38 M)	22–45	$\Delta_r H = (25.1 \pm$	$I_m = 1.48$,
				$0.4)$	$\beta_1 = (4.4 \pm 0.4)$
[1961SUT/ROW]	sp	0.5 M $HClO_4$	25	$\beta_1 = 4.4$	$I_m = 0.51$,
			16.5–35.5	$\Delta_r H = 20.92$	$\beta_1 = (4.3 \pm 0.2)$
			25		
		0.5 M $DClO_4$	16.5–35.5	$\beta_1 = 8.7$	
				$\Delta_r H = 17.57$	
[1961WHI/KEL]	ix	0.2 M $HCl/HClO_4$	25	$\beta_1 = 6.03$	$\beta_1 = (6.0 \pm 0.6)$
		0.3 M $HCl/HClO_4$		$\beta_1 = 5.13$	$\beta_1 = (5.5 \pm 0.5)$
		1.0 M $HCl/HClO_4$		$\beta_1 = 4.57$	$\beta_1 = (4.6 \pm 0.5)$
[1962WEN/STR]	kin/pj	2.6 M $HClO_4$	25	$\beta_{1\text{in}} = (1.0 \pm 0.5)$	———
				$\beta_{1\text{out}} = (2 \pm 1)$	
[1962WOO/GAL]	sp	1.0 M $HClO_4$	25	$\beta_1 = (2.95 \pm$	$\beta_1 = 2.86$
			25–45	$0.09)$	
				$\Delta_r H = 16.9$	

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Table VIII-4 (continued)

Reference	Method	Ionic medium	t /°C	Reported value $^{(a)}$	Re-evaluation $^{(b)}$
[1962WOO/GAL]	pot	0.1 M $HClO_4$	25	$\beta_1 = 7.\ 4$	$\beta_1 = (7.34 \pm 0.50)$
		0.3 M $HClO_4$		$\beta_1 = 3.75$	$\beta_1 = (3.7 \pm 0.3)$
		0.5 M $HClO_4$		$\beta_1 = 3.16$	$\beta_1 = (3.1 \pm 0.3)$
		0.7 M $HClO_4$		$\beta_1 = 2.96$	$\beta_1 = (2.9 \pm 0.3)$
		0.9 M $HClO_4$		$\beta_1 = 2.92$	$\beta_1 = (2.8 \pm 0.3)$
		1.0 M $HClO_4$		$\beta_1 = 2.86$	$\beta_1 = (2.7 \pm 0.3)$
			14.3−44.3	$\Delta_r H = 18.4$	
		1.2 M $HClO_4$	25	$\beta_1 = 3.01$	$\beta_1 = (2.84 \pm 0.30)$
		1.4 M $HClO_4$		$\beta_1 = 3.09$	$\beta_1 = (2.89 \pm 0.30)$
		1.6 M $HClO_4$		$\beta_1 = 3.28$	$\beta_1 = (3.04 \pm 0.30)$
		2.0 M $HClO_4$		$\beta_1 = 3.86$	$\beta_1 = (3.50 \pm 0.30)$
		3.0 M $HClO_4$		$\beta_1 = 6.6$	$\beta_1 = (5.70 \pm 0.50)$
		3.7 M $HClO_4$		$\beta_1 = 10.7$	$\beta_1 = (8.91 \pm 0.80)$
[1962WOO/GAL]	cal	1.0 M $HClO_4$	25	$\Delta_r H = 17.6$	
		3.7 M $HClO_4$	25	$\Delta_r H = 14.2$	
[1963HEI/CLE]	sp	1.0 M $HClO_4$	25	$\beta_1 = (3.9 \pm 0.7)$	$\beta_1 = (3.7 \pm 0.7)$
		+ 1.0 M $NaClO_4$		$\beta_1 = (4.1 \pm 1.0)$	$\beta_1 = (3.8 \pm 0.9)$
		+ 2.0 M $NaClO_4$		$\beta_1 = (5.2 \pm 0.8)$	$\beta_1 = (4.6 \pm 0.7)$
		+ 3.0 M $NaClO_4$		$\beta_1 = (10 \pm 2)$	$\beta_1 = (8.5 \pm 1.7)$
		+ 4.0 M $NaClO_4$		$\beta_1 = (20 \pm 4)$	———
		1.0 M $HClO_4$		$\beta_1 = (3.9 \pm 0.7)$	$\beta_1 = (3.7 \pm 0.7)$
		2.0 M $HClO_4$		$\beta_1 = (5.0 \pm 1.0)$	$\beta_1 = (4.5 \pm 0.9)$
		3.0 M $HClO_4$		$\beta_1 = (7.8 \pm 2.0)$	$\beta_1 = (6.7 \pm 0.7)$
		4.0 M $HClO_4$		$\beta_1 = (20 \pm 4)$	$\beta_1 = (16.1 \pm 3.2)$
		5.0 M $HClO_4$		$\beta_1 = (48 \pm 7)$	———
[1967VAS/LOB2]	cal	0 (extrap)	10	$\Delta_r H = (19.41 \pm 0.84)$	
		2.15 m $HClO_4$		$\Delta_r H = (13.81 \pm 0.84)$	
		3.40 m $HClO_4$		$\Delta_r H = (12.13 \pm 0.63)$	
		4.73 m $HClO_4$		$\Delta_r H = (10.21 \pm 0.63)$	
		6.29 m $HClO_4$		$\Delta_r H = (7.70 \pm 0.25)$	
		9.72 m $HClO_4$		$\Delta_r H = -\ (0.01 \pm 0.10)$	
		0 (extrap)	18	$\Delta_r H = (21.51 \pm 0.84)$	
		2.15 m $HClO_4$		$\Delta_r H = (15.36 \pm 0.63)$	
		3.40 m $HClO_4$		$\Delta_r H = (13.35 \pm 0.42)$	
		4.73 m $HClO_4$		$\Delta_r H = (11.05 \pm 0.59)$	
		6.29 m $HClO_4$		$\Delta_r H = (8.58 \pm 0.25)$	

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Table VIII-4 (continued)

Reference	Method	Ionic medium	t /°C	Reported value [(a)]	Re-evaluation [(b)]
		9.72 m $HClO_4$	25	$\Delta_rH = (0.95 \pm 0.13)$	
		0 (extrap)		$\Delta_rH = (23.43 \pm 0.84)$	
		2.15 m $HClO_4$		$\Delta_rH = (16.65 \pm 0.67)$	
		3.40 m $HClO_4$		$\Delta_rH = (13.93 \pm 0.63)$	
		4.73 m $HClO_4$		$\Delta_rH = (12.09 \pm 0.63)$	
		6.29 m $HClO_4$		$\Delta_rH = (8.95 \pm 0.33)$	
		9.72 m $HClO_4$		$\Delta_rH = (1.66 \pm 0.08)$	
		0 (extrap)	35	$\Delta_rH = (25.77 \pm 0.84)$	
		2.15 m $HClO_4$		$\Delta_rH = (17.82 \pm 0.50)$	
		3.40 m $HClO_4$		$\Delta_rH = (15.73 \pm 0.42)$	
		4.73 m $HClO_4$		$\Delta_rH = (13.39 \pm 0.63)$	
		6.29 m $HClO_4$		$\Delta_rH = (9.75 \pm 0.29)$	
		9.72 m $HClO_4$		$\Delta_rH = (2.31 \pm 0.08)$	
		0 (extrap)	45	$\Delta_rH = (27.95 \pm 0.84)$	
		2.15 m $HClO_4$		$\Delta_rH = (19.37 \pm 0.63)$	
		3.40 m $HClO_4$		$\Delta_rH = (17.74 \pm 0.75)$	
		4.73 m $HClO_4$		$\Delta_rH = (14.60 \pm 0.54)$	
		6.29 m $HClO_4$		$\Delta_rH = (11.05 \pm 0.33)$	
		9.72 m $HClO_4$		$\Delta_rH = (3.30 \pm 0.10)$	
		0 (extrap)	55	$\Delta_rH = (30.125 \pm 0.840)$	
		2.15 m $HClO_4$		$\Delta_rH = (21.05 \pm 0.54)$	
		3.40 m $HClO_4$		$\Delta_rH = (18.74 \pm 0.50)$	
		4.73 m $HClO_4$		$\Delta_rH = (15.94 \pm 0.59)$	
		6.29 m $HClO_4$		$\Delta_rH = (12.01 \pm 0.25)$	
		9.72 m $HClO_4$		$\Delta_rH = (4.13 \pm 0.15)$	
[1969FOR]	sp	0.15 M $HClO_4$	20	$\beta_1 = (4.0 \pm 1.1)$	———
[1969MOR/WIL]	ix	1 M $HClO_4$/HCl	25	$\beta_1 = (4.3 \pm 0.5)$	$\beta_1 = (4.2 \pm 0.5)$
[1969NIK/PAL]		1.0 M $HClO_4$/HCl	25	$\beta_1 = (3.7 \pm 0.2)$	$\beta_1 = (3.5 \pm 0.2)$
		4.0 M $HClO_4$/HCl		$\beta_1 = (10.5 \pm 0.2)$	$\beta_1 = (9.1 \pm 0.5)$
[1969PAL/STR]		6.0 M $HClO_4$/HCl	25.0	$\beta_1 = (80.0 \pm 0.2)$	———
[1970ROW/SUT][(c)]	sp,kin	1 M $HClO_4$	25	$\beta_1 = (5.2 \pm 0.4)$	(see Appendix A for the discussion about these values)
		3 M $HClO_4$		$\beta_1 = (9.8 \pm 0.7)$	
		4 M $HClO_4$		$\beta_1 = (17.3 \pm 1.0)$	
		5 M $HClO_4$		$\beta_1 = (36.3 \pm 1.5)$	

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Table VIII-4 (continued)

Reference	Method	Ionic medium	t /°C	Reported value $^{(a)}$	Re-evaluation $^{(b)}$
		6 M $HClO_4$		$\beta_1 = (110 \pm 3)$	
			2.4−44.6	$\Delta_rH = (0.0 \pm 3.3)$	
		0.5 M $HClO_4$		$\beta_1 = 5.6^{(d)}$	
[1972KOR/PER]	kin,Tj	$I = 0.4$ M (Li,K, Cs)NO_3	10.0−33.6	$K = (1.2 \pm 0.2)\times10^{-2}$ ($^*K = c_{\mathrm{FeClOH^+}}c_{\mathrm{H^+}}/c_{\mathrm{FeCl^{2+}}}$)	———
[1972SEK/TET]	dist	3 M $NaClO_4$ + 1 M $HClO_4$	25	$\beta_1 = 7.58$	$\beta_1 = (6.2 \pm 1.0)$
[1976ASH]	sp	1 M $HClO_4$ + 4 M $NaClO_4$	22	$\beta_1 = 10.2$	
			34	$\beta_1 = 13.1$	
			47	$\beta_1 = 17.4$	
			60	$\beta_1 = 22.3$	
		3 M $HClO_4$ + 2 M $NaClO_4$	25	$\beta_1 = 17.6$	
			34	$\beta_1 = 20.4$	
			47	$\beta_1 = 25.9$	
			60	$\beta_1 = 21.0$	
		2 M $HClO_4$			$I_m = 2.2$
			25	$\beta_1 = 3.3$	$\beta_1 = (3.0 \pm 0.2)$
			34	$\beta_1 = 4.8$	$\beta_1 = (4.4 \pm 0.3)$
			47	$\beta_1 = 6.1$	$\beta_1 = (5.5 \pm 0.5)$
			60	$\beta_1 = 7.6$	$\beta_1 = (6.9 \pm 0.5)$
		3M $HClO_4$			$I_m = 3.47$
			25	$\beta_1 = 6.0$	$\beta_1 = (5.2 \pm 0.4)$
			34	$\beta_1 = 6.6$	$\beta_1 = (5.7 \pm 0.4)$
			47	$\beta_1 = 9.9$	$\beta_1 = (8.6 \pm 0.6)$
			60	$\beta_1 = 11.9$	$\beta_1 = (10.3 \pm 0.8)$
		4 M $HClO_4$			$I_m = 4.87$
			25	$\beta_1 = 10.9$	$\beta_1 = (9.0 \pm 0.7)$
			34	$\beta_1 = 13.3$	$\beta_1 = (10.9 \pm 0.8)$
			47	$\beta_1 = 16.4$	$\beta_1 = (13.5 \pm 1.0)$
		5 M $HClO_4$	60	$\beta_1 = 20.8$	$\beta_1 = (17.1 \pm 1.5)$
			25	$\beta_1 = 29.1$	———
			34	$\beta_1 = 30.7$	
			47	$\beta_1 = 36.6$	
			60	$\beta_1 = 44.8$	

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Table VIII-4 (continued)

Reference	Method	Ionic medium	t /°C	Reported value $^{(a)}$	Re-evaluation $^{(b)}$
[1976BYR/KES2]	pot	0.68 m H/$NaNO_3$/NaCl	25	$\beta_{1m} = 2.76$	———
[1976KHA/BEL]	pot	1 M $HClO_4$/HCl	RT?	$\beta_1 = 3.3$	———
		3 M $HClO_4$/HCl		$\beta_1 = 5.7$	———
		6 M $HClO_4$/HCl		$\beta_1 = 56$	———
[1976SCH/DOD]	kin	1 M $HClO_4$	25	$\beta_{1\text{in}} = 3.0$ $\beta_{1\text{out}} = 2.2$	$\beta_1 = (2.9 \pm 0.3)$
[1976SCH/DOD], reinterpretation of [1970ROW/SUT]	kin,sp	1 M $HClO_4$	25	$\beta_{1\text{in}} = 2.9$ $\beta_{1\text{out}} = 2.3$	$\beta_1 = (2.8 \pm 0.2)$
		3 M $HClO_4$		$\beta_{1\text{in}} = 6.4$ $\beta_{1\text{out}} = 3.4$	$\beta_1 = (5.6 \pm 0.5)$
		4 M $HClO_4$		$\beta_{1\text{in}} = 13.5$ $\beta_{1\text{out}} = 3.8$	$\beta_1 = (11.1 \pm 1.0)$
		5 M $HClO_4$		$\beta_{1\text{in}} = 33.5$ $\beta_{1\text{out}} = 2.8$	———
		6 M $HClO_4$		$\beta_{1\text{in}} = 107$	———
[1978PER/TAP]	kin	1 M $HClO_4$	25	$\beta_{1\text{in}} = (2.95 \pm 0.14)$	———
[1979STR/PAT]	kin,sp	1 M $HClO_4$ + 1.6 M	25	$\beta_1 = 7.6$ ($\beta_{1\text{in}} = 6.5$; $\beta_{1\text{out}} = 1.1$)	$\beta_1 = (5.7 \pm 0.4)$
	kin, sp, Tj	$NaClO_4$/NaCl	21−25	$\Delta H_{1\text{in}} = 13.39$ $\Delta H_{1\text{out}} = 11.72$ $\Delta H_1 = 17.15$	
[1981BYR/KES]	sp	2.74 M HCl/$HClO_4$		$\beta_{1m} = (5.34 \pm 0.14)$	$\beta_{1m} = (4.9 \pm 0.1)$
[1981BYR/KES]	sp	0.68 m NaCl		$K = 1.8\times10^{-4}$ ($K = (c_{FeClOH^+}c_{H^+})/(c_{Cl^-}c_{Fe^{3+}})$)	———
[1988FEN/WAK]	sp	$I_c = 0.4$ M	20	$\beta_1 = 7.6$ (“absolute” constant with a formation constant of 2.1 for the simple iron(III) perchlorato complex)	
[1989BRU/PET]	sp	$I = 1.05$ m $HClO_4$	25	$\beta_{1m} = 4.9$ (recalc.)	
			25−125	$\Delta_r H_1 = (24.3 \pm 0.8)$ (from paper)	
[1999INA/FUN]	EXAFS	$I = 1.0$ M $HClO_4$	25	$\beta_1 = (3.8 \pm 0.4)$	

(Continued on next page)

Table VIII-4 (continued)

Reference	Method	Ionic medium	t /°C	Reported value $^{(a)}$	Re-evaluation $^{(b)}$
[2000TAG/DIA]	pot	0.196 m HCl	25	$\beta_{1m} = 5.47$	Direct use for determination of $\varepsilon(\mathrm{FeCl^{2+},Cl^-})$
		0.259 m HCl		$\beta_{1m} = 4.76$	
		0.523 m HCl		$\beta_{1m} = 3.82$	
		0.624 m HCl		$\beta_{1m} = 3.74$	
		0.839 m HCl		$\beta_{1m} = 3.52$	
		1.067 m HCl		$\beta_{1m} = 3.29$	
		1.276 m HCl		$\beta_{1m} = 3.34$	
		0 (extrap)	25	$\Delta H_1 = 21.8$	
		0.196 m HCl	35	$\beta_{1m} = 7.10$	
		0.259 m HCl		$\beta_{1m} = 5.97$	
		0.523 m HCl		$\beta_{1m} = 4.87$	
		0.624 m HCl		$\beta_{1m} = 4.70$	
		0.839 m HCl		$\beta_{1m} = 4.48$	
		1.067 m HCl		$\beta_{1m} = 4.45$	
		1.276 m HCl		$\beta_{1m} = 4.32$	
		0 (extrap)	35	$\Delta H_1 = 24.3$	
		0.196 m HCl	50	$\beta_{1m} = 10.54$	
		0.259 m HCl		$\beta_{1m} = 9.00$	
		0.523 m HCl		$\beta_{1m} = 7.43$	
		0.624 m HCl		$\beta_{1m} = 7.31$	
		0.839 m HCl		$\beta_{1m} = 7.00$	
		1.067 m HCl		$\beta_{1m} = 6.66$	
		1.276 m HCl		$\beta_{1m} = 6.92$	
		0 (extrap)	50	$\Delta H_1 = 27.6$	
		0.196 m HCl	70	$\beta_{1m} = 19.95$	
		0.259 m HCl		$\beta_{1m} = 17.68$	
		0.523 m HCl		$\beta_{1m} = 14.40$	
		0.624 m HCl		$\beta_{1m} = 14.12$	
		0.839 m HCl		$\beta_{1m} = 13.80$	
		1.067 m HCl		$\beta_{1m} = 13.40$	
		1.276 m HCl		$\beta_{1m} = 14.11$	
		0 (extrap)	70	$\Delta H_1 = 32.6$	
		0.196 m HCl	90	$\beta_{1m} = 35.49$	
		0.259 m HCl		$\beta_{1m} = 31.79$	
		0.523 m HCl		$\beta_{1m} = 26.34$	
		0.624 m HCl		$\beta_{1m} = 25.98$	
		0.839 m HCl		$\beta_{1m} = 25.84$	

(Continued on next page)

Table VIII-4 (continued)

Reference	Method	Ionic medium	t /°C	Reported value $^{(a)}$	Re-evaluation $^{(b)}$
		1.067 m HCl		$\beta_{1m} = 25.51$	
		1.276 m HCl		$\beta_{1m} = 27.24$	
		0 (extrap)	90	$\Delta H_1 = 37.7$	

(a) Molar constants (*i.e.*, β_{1c}) unless specifically identified as molal constants (β_{1m}); values of $\Delta_r H$ in $kJ\cdot mol^{-1}$; values of $\Delta_r S$ in $J\cdot K^{-1}\cdot mol^{-1}$.

(b) Molal constants; when necessary, molar values were converted to molal values using the factors in Table II-5.

(c) The paper also mentions $HClO_4$/$NaClO_4$ mixtures, but does not seem to provide any details on the H/Na ratios.

(d) Recalculation of earlier results from the same laboratory [1961SUT/ROW].

The recalculated formation constants given in the last column of Table VIII-4 are probably the inner-sphere formation constants in the molal scale with uncertainties depending on the method of investigation at the date of publication. It is obvious that instrumentation and fitting methods have improved markedly between 1942 [1942RAB/STO] and the present (*e.g.*, [2006LIU/ETS]).

The values for the other thermodynamic quantities, $\Delta_r H_m^o$ and $\Delta_r S_m^o$, generally based on the variation of the formation constants with the temperature, are rather scattered and often the value for $\Delta_r C_{p,m}^o$ has been arbitrarily set to zero.

More recent studies [2006LIU/ETS], [2000TAG/DIA] indicate that, as for many electrolytes [1971NAU/RYZ], there is strong stabilization of the chlorido complexes at high temperature, and this might change the mechanism for dissolution of the iron oxides and hydroxides in some natural waters rich in chlorides.

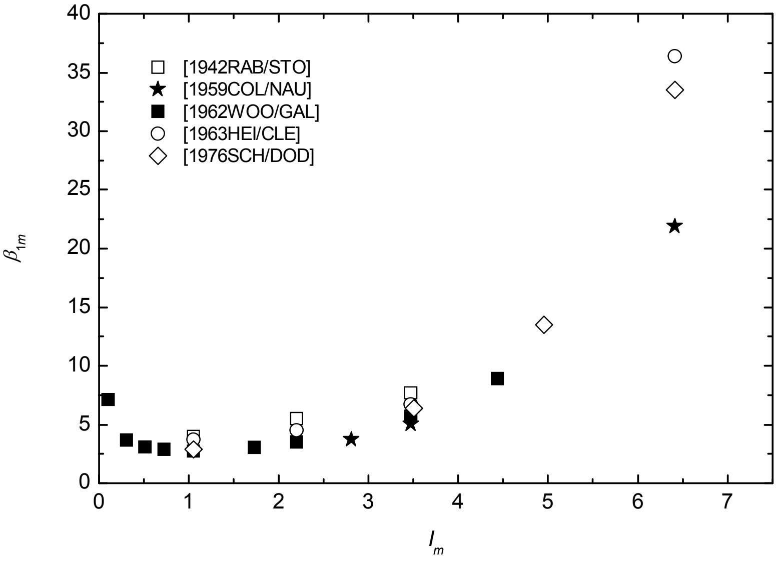
VIII.2.3.1.2 $FeCl^{2+}_{(out)}$, $FeCl^{2+}_{(in)}$ stability constant variation as a function of the ionic strength and the medium composition

Several authors have investigated the influence of ionic strength on the overall formation constant of $FeCl^{2+}$. The results of Rabinowitch and Stockmayer [1942RAB/STO], Coll *et al.* [1959COL/NAU], Woods *et al.* [1962WOO/GAL], Heistand and Clearfield [1963HEI/CLE] and Schwartz and Dodson [1976SCH/DOD] plotted in Figure VIII-4 show that the value of β_{1m} decreases as a function of the ionic strength from 0 to 1 m, and thereafter increases.

The stabilisation of the complex at very low and high ionic strengths is important.

It has also been shown that at constant ionic strength the formation constant of $FeCl^{2+}$, is strongly dependent on the medium. For example, the replacement of Na^+ ions by H^+ or Li^+ shifts the formation constant towards higher values. This has been correlated with the water activity, which is lower in perchloric acid than in sodium perchlorate at the same concentrations. The low activity of water favors the removal of inner-sphere water from $Fe^{3+}\cdot 6H_2O$.

Figure VIII-4: Formation constant of $FeCl^{2+}$ as a function of the ionic strength in aqueous $HClO_4$ or $NaClO_4$ at 298.15 K as found by various authors.



Investigations of the kinetics of complex formation have shown that at high ionic strengths the rate of the Fe^{3+}-Cl^- association is strongly accelerated, and this is responsible for the variation of the equilibrium constant. The rate of $FeCl^{2+}$ dissociation does not change as much with ionic strength [1970ROW/SUT] and has less influence on the stability of the complex.

VIII.2.3.1.3 SIT treatment for the determination of β_1° from the ionic strength dependence of the formation constant of $FeCl^{2+}$

The SIT model can be applied to calculate β_1° and the $\Delta\varepsilon_1$ from the numerous values of β_{1m} contained in the literature.

$$Fe^{3+} + Cl^- \rightleftharpoons FeCl^{2+} \qquad \text{(VIII.3)}$$

As discussed in Appendix B, for a reaction in a single swamping electrolyte the SIT relation between the experimental values of β_1° at 298.15 K, in molal units and the ionic strength, I_m, is given by Eq. (VIII.4) (from Eq. B.5):

$$\log_{10}\beta_1 + 6D = \log_{10}\beta_1^\circ - \Delta\varepsilon I_m. \qquad \text{(VIII.4)}$$

In this equation: D is the Debye-Hückel term

$$D = 0.509 I_m^{½} / (1 + 1.5 I_m^{½}). \quad \text{(VIII.5)}$$

According to Eq. (VIII.4) a plot of $\log_{10}\beta_1 + 6D$ as a function of I_m yields a straight line, with $\log_{10}\beta_1^{\circ}$ as ordinate at $I_m = 0$ and a slope $\Delta\varepsilon$.

If the sole major supporting electrolyte is $HClO_4$ one has:

$$\Delta\varepsilon = \varepsilon(\mathrm{FeCl}^{2+},\mathrm{ClO}_4^-) - \varepsilon(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-) - \varepsilon(\mathrm{H}^+,\mathrm{Cl}^-) \quad \text{(VIII.6)}$$

If the sole major supporting electrolyte is $NaClO_4$ one gets:

$$\Delta\varepsilon = \varepsilon(\mathrm{FeCl}^{2+},\mathrm{ClO}_4^-) - \varepsilon(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-) - \varepsilon(\mathrm{Na}^+,\mathrm{Cl}^-) \quad \text{(VIII.7)}$$

Equation (VIII.4) is not valid in the general case of mixed $NaClO_4$, $HClO_4$ media because the interaction coefficients are multiplied by different factors and I_m is no longer a common factor.

In this case the proper expression corresponding to Eq. (VIII.4) is:

$$\log_{10}\beta_1 + 6D - (\varepsilon(\mathrm{H}^+,\mathrm{Cl}^-)\, m_{\mathrm{H}^+} + \varepsilon(\mathrm{Na}^+,\mathrm{Cl}^-)\, m_{\mathrm{Na}^+}) = \log_{10}\beta_1^{\circ} - (\varepsilon(\mathrm{FeCl}^{2+},\mathrm{ClO}_4^-) - \varepsilon(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-))\, m_{\mathrm{ClO}_4^-} \quad \text{(VIII.8)}$$

Equation (VIII.8) shows that in the case of a mixed medium one must fit $\log_{10}\beta_1 + 6D - (\varepsilon(\mathrm{H}^+,\mathrm{Cl}^-)\, m_{\mathrm{H}^+} + \varepsilon(\mathrm{Na}^+,\mathrm{Cl}^-)\, m_{\mathrm{Na}^+})$ as a linear function of $m_{\mathrm{ClO}_4^-}$ to get $\log_{10}\beta_1^{\circ}$ for $m_{\mathrm{ClO}_4^-} = 0$ and $\varepsilon(\mathrm{FeCl}^{2+},\mathrm{ClO}_4^-) - \varepsilon(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-)$ from the slope.

Many early investigations of Fe^{3+} chlorido complexes were focused on the determination of β_1, and therefore dilute chloride solutions in perchlorate medium, with Fe^{3+} in excess, were used. In such cases the chloride interactions with the dilute cationic iron complex species can be neglected. Even the interaction of Cl^- with Fe^{3+} (aside from complex formation) is small when compared with the interaction of Cl^- with the cation of the supporting electrolyte. So Eqs. (VIII.6), (VIII.7) or (VIII.8) can apply in perchlorate medium for which $m_{\mathrm{ClO}_4^-} >> m_{\mathrm{Fe}^{3+}}$.

If the major electrolyte is HCl(sln):

$$\log_{10}\beta_1 + 6D = \log_{10}\beta_1^{\circ} - (\varepsilon(\mathrm{FeCl}^{2+},\mathrm{Cl}^-) - \varepsilon(\mathrm{Fe}^{3+},\mathrm{Cl}^-) - \varepsilon(\mathrm{H}^+,\mathrm{Cl}^-))\, m_{\mathrm{Cl}^-} \quad \text{(VIII.9)}$$

The results of the SIT calculations based on the experimental data found in selected papers are listed in Table VIII-5. These papers are those which can be treated separately because they dealt with the determination of β_1 as a function of the ionic strength in media having perchloric acid or perchloric acid-sodium perchlorate mixtures as the major electrolyte(s). The recalculated values of $\log_{10}\beta_1^{\circ}$ range from (1.55 ± 0.04) to (1.29 ± 0.09).

Table VIII-5: Formation constants of $FeCl^{2+}$ at $I = 0$ and $\Delta'\varepsilon = \varepsilon(FeCl^{2+}, ClO_4^-) - \varepsilon(Fe^{3+}, ClO_4^-)$ values from studies in which the authors carried out investigations at several ionic strengths (obtained by applying the SIT model to the literature data).†

reference	method	medium	$\log_{10} \beta^{\circ}_{1,m}$	$\Delta'\varepsilon$ / $kg \cdot mol^{-1}$	r*
[1942RAB/STO]	sp	0.13 to 2.2 m (H,Na) ClO_4^- ; $Fe(ClO_4)_3$ >> Cl^- ‡	1.55 ± 0.04	– 0.13 ± 0.03	0.97
[1959COL/NAU]	sp	2.8 to 6.4 m $HClO_4$ 4 points (Eq. (VIII.6))	1.29 ± 0.09	– 0.14 ± 0.02	0.999
[1962WOO/GAL]	pot, sp, cal	0.1 to 4.46 m $HClO_4$ (Eq. (VIII.6))	1.44 ± 0.02 (pot)	– 0.11 ± 0.02	0.988
[1963HEI/CLE]	sp	1 to 6.5 m $HClO_4$ (Eq. (VIII.6))	1.49 ± 0.05	– 0.13 ± 0.02	0.994
[1963HEI/CLE]	sp	1 to 6.6 m ClO_4^- (1 to 4 M $HClO_4$ + 0 to 5.56 m $NaClO_4$) (Eq. (VIII.8))	1.49 ± 0.04	– 0.13 ± 0.02	0.99
[1976SCH/DOD]	sp, reinterpretation of [1970ROW/SUT]	1 to 6.4 m $HClO_4$ (Eq. (VIII.6))	1.39 ± 0.03	– 0.13 ± 0.02	0.997
[2000TAG/DIA]	pot	HCl 0.196 to 1.276 m	1.51 ± 0.03	– 0.11 ± 0.02	0.99

* r is the linear correlation coefficient

† Several papers mentioned previously have not been reworked using the SIT and are omitted from Table VIII-2.

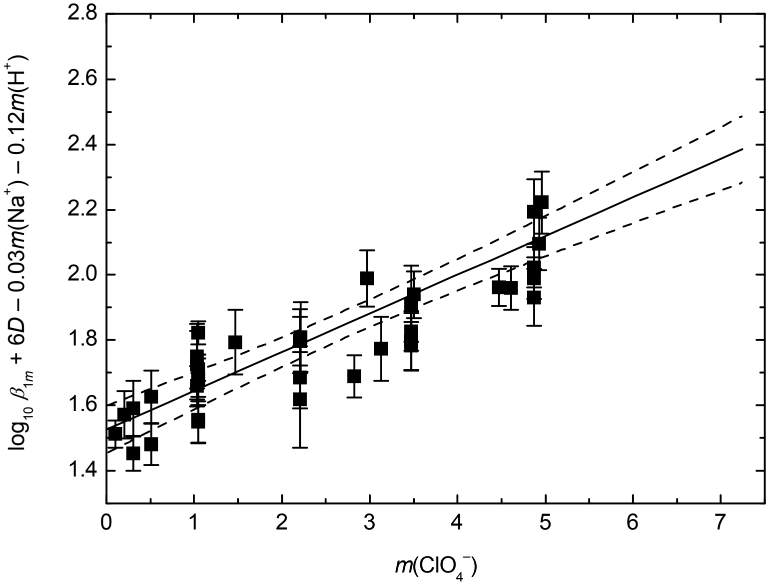
‡ The values of m_{Na^+} and m_{H^+} were not given (only the ionic strength). It was assumed that $m_{Na^+} = m_{H^+}$).

There is one paper [2000TAG/DIA] dealing with the determination of the $FeCl^{2+}$ formation constant in HCl(sln) medium by potentiometry. Only the β_1 values as a function of the molal ionic strength are available. From these, application of the SIT formalism leads to $\log_{10} \beta_1^{\circ} = (1.51 \pm 0.03)$, a value in good agreement with the value given in the original paper and that found from the overall data in perchlorate medium as discussed below.

a) The kinetic investigations of complex formation: [1962WEN/STR], [1976SCH/DOD], [1979STR/PAT] showed that at low ionic strength a non-negligible proportion of the Fe(III) 1:1 chlorido complex is an outer-sphere ion pair. This complex has a rather weak (perhaps non-existent) charge-transfer absorption band. Therefore, spectrophotometry can be considered as a specific method for the measurement of concentrations of inner-sphere complexes. The values from potentiometry or distribution data for Fe^{3+} species, likely refer to the overall complex formation. The spectrophotometric data must be interpreted with no or minimal changes in the molar absorption coefficients as a function of changes in the medium; this was not the case in [1970ROW/SUT], so the results of that paper have been discarded.

b) Part of the work of [1959COL/NAU] was carried out at very high ionic strengths, generally beyond the ionic-strength range for application of the SIT (1 to 6 m). The SIT treatment of this work led to lower values of $\log_{10} \beta_1^{\circ}$, 1.29 for the study in aqueous $HClO_4$ solutions and 1.05 for mixed $NaClO_4$-$HClO_4$ media. We discarded the values obtained from the mixture studies because of the limited number of usable points (2). Nevertheless, their values from studies in aqueous $HClO_4$ alone (m ≤ 6.5) have been included in the general plot (Figure VIII-5).

Figure VIII-5: Linear fit of all $FeCl^{2+}$ data obtained from experiments in $HClO_4$(sln) + $NaClO_4$(sln) at 298.15 K according to Eq. (VIII.6). Data from [1942RAB/STO], [1944OLE], [1959COL/NAU], [1959CON/COP], [1961SUT/ROW], [1962WOO/GAL], [1963HEI/CLE], [1976SCH/DOD], [1976ASH], [1981BYR/KES], [1989BRU/PET].



c) For the redox potentiometric investigations the interaction of Fe(II) with chloride (sometimes described in terms of formation of weak chlorido complexes) must be taken into account. That was done by the authors in the study of Tagirov *et al.* [2000TAG/DIA], but not by Woods *et al.* [1962WOO/GAL]. The method used to calculate the corrected formation constants of the Fe^{3+} chlorido complexes from the potentiometric data and the formation constant of $FeCl^+$ is described in the Appendix A entry for the work of Nikol'skii *et al.* [1969NIK/PAL]. That yielded negligible corrections because we used the β_1° value for $FeCl^+$ suggested in this review (0.1 $mol^{-1}\cdot kg$), which is small when compared with the value (0.7 $mol^{-1}\cdot kg$) from the work of Heinrich and Seward [1990HEI/SEW] used by Tagirov *et al.* [2000TAG/DIA].

d) The general problems of interference from the 2:1 Fe(III) chlorido complex and from $FeOH^{2+}$ have been addressed by taking various precautions in most of the papers listed in Tables VIII-4 and VIII-5.

e) The values for inner- or (inner + outer)-sphere $FeCl^{2+}$ complex formation constants are similar at ionic strengths close to 1 $mol\cdot kg^{-1}$. It has been demonstrated that the percentage of outer-sphere complex is relatively important for ionic strengths close to 1, for which $\log_{10}\beta_1$ is close to its minimum value, 0.35. It becomes negligible at high ionic strengths for which one has $\log_{10}\beta_1$ values close to 3.35 and an outer-sphere complex with a stability constant mainly independent of the ionic strength. If that independence is also true for the low ionic strength region, then it is understandable that the inner-sphere complex, stabilized by and sensitive to the ionic strength, again becomes predominant at zero ionic strength. The relative stability of the inner- and outer-sphere complexes has been investigated as a function of ionic strength by Schwarz and Dodson [1976SCH/DOD] (see Appendix A). In this review we choose to consider as a complex only the inner-sphere species. Doing so, the outer-sphere interactions are taken into account with other ionic strength effects when the SIT formalism is applied to the Fe^{3+}/Fe^{2+} potentiometric data obtained in HCl medium (see Section VI.1.2.1.1.2). The various techniques for investigation of complexes have different sensitivities for the detection of the two kinds of complexes. UV-visible spectrophotometry of $FeCl^{2+}$, the most frequently used method, relies on the intensity of a charge-transfer band, and so only the inner-sphere species might absorb. The EXAFS signals also are related to the number of Fe^{3+}-Cl^- at short distances, and so the method is specific to inner-sphere species. The two kinds of complexes could have a different effect upon the electrode potentials. The similar values of β_1 found using potentiometry and spectrophotometry by several authors [1962WOO/GAL], [1976BYR/KES2], [1981BYR/KES] seem to show that the outer-sphere complexes are incorporated in the ionic strength effects. The distribution of Fe(III) between aqueous phases containing chlorides and immiscible organic solvents or solid ion exchangers has not been investigated in sufficient detail to conclude whether the results differ from those from spectrophotometric studies, or not.

To determine the values of β_1° (VIII.3) and $\Delta\varepsilon$(VIII.3) from all the literature data we carried out three fits: one dealing with all the data obtained in $HClO_4$-$NaClO_4$ mixtures (see Figure VIII-5); one with the data obtained in aqueous solutions of $HClO_4$ as the sole supporting electrolyte (see Figure VIII-6) and one with the data obtained in $NaClO_4$-$HClO_4$-HCl mixtures (see Figure VIII-7). The latter has been carried out by considering the results of Section VI.1.2.1.2.2, which show that the $\varepsilon(Fe^{3+}, ClO_4^-)$ and $\varepsilon(Fe^{3+},Cl^-)$ values are very close to each other.

Figure VIII-6: Plot of $\log_{10} \beta_{1m}$ + 6D *vs.* $m_{ClO_4^-}$ for the complex $FeCl^{2+}$ in aqueous solutions of $HClO_4$ at 298.15 K. Data from: [1942RAB/STO], [1944OLE], [1959COL/NAU], [1959CON/COP], [1961SUT/ROW], [1962WOO/GAL], [1963HEI/CLE], [1976SCH/DOD], [1976ASH], [1981BYR/KES], [1989BRU/PET].

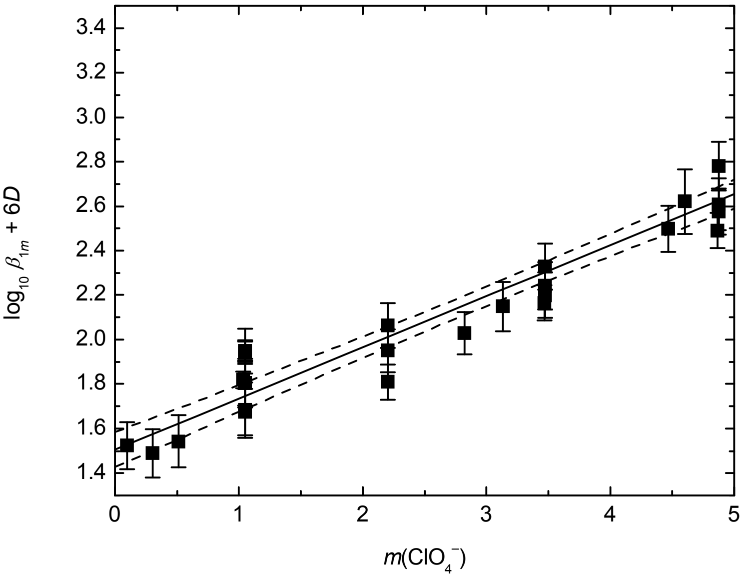
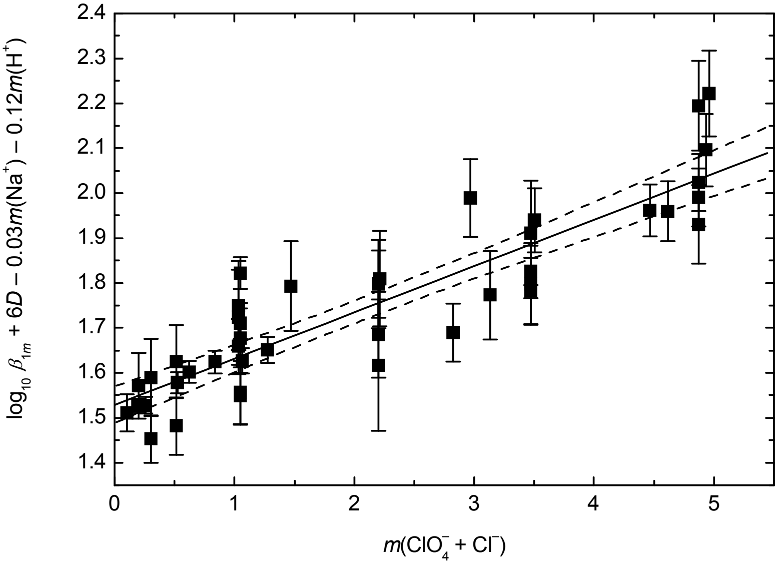


Figure VIII-7: Linear fit of all $FeCl^{2+}$ data at 298.15 K in $HClO_4$(sln) + HCl(sln) + $NaClO_4$(sln) according to Eq. (VIII.8). Data from [1942RAB/STO], [1944OLE], [1959COL/NAU], [1959CON/COP], [1961SUT/ROW], [1961WHI/KEL], [1962WOO/GAL], [1963HEI/CLE], [1969MOR/WIL], [1969NIK/PAL], [1972SEK/TET], [1976SCH/DOD], [1976ASH], [1981BYR/KES], [1989BRU/PET], [2000TAG/DIA].



The linear fit of all the 298.15 K data in $NaClO_4$, $HClO_4$ media produces: $\log_{10}\beta_1^{\circ}$ = (1.51 ± 0.07), and $\Delta'\varepsilon = \varepsilon(\text{FeCl}^{2+}, \text{ClO}_4^-) - \varepsilon(\text{Fe}^{3+}, \text{ClO}_4^-) = -(0.11 \pm 0.02)$ kg·mol^{-1}, $R^2 = 0.769$.

The linear fit of the 298.15 K data in perchloric acid yields: $\log_{10}\beta_1^{\circ}$ = (1.52 ± 0.06); and $\Delta\varepsilon = \varepsilon(\text{FeCl}^{2+}, \text{ClO}_4^-) - \varepsilon(\text{Fe}^{3+}, \text{ClO}_4^-) - \varepsilon(\text{H}^+, \text{Cl}^-) = -(0.22 \pm 0.02)$ kg·mol^{-1}, $R^2 = 0.94$.

All the experimental data for formation of $FeCl^{2+}$, including data from investigations in which the medium was mixed chloride-perchlorate solutions, have been fitted to a straight line (Figure VIII-7). This leads to: $\log_{10}\beta_1^{\circ}$ = (1.53 ± 0.04); and $\Delta'\varepsilon = \varepsilon(\text{FeCl}^{2+}, \text{ClO}_4^-) - \varepsilon(\text{Fe}^{3+}, \text{ClO}_4^-) = -(0.10 \pm 0.02)$ kg·mol^{-1}, $R^2 = 0.82$ at 298.15 K.

The three SIT treatments give results that are quite consistent with each other despite the scatter of the data. The treatment of the data obtained from investigations in mixed chloride-perchlorate solutions and results from the investigations in perchlorate medium lead to very similar results. This is consistent with the very similar values of $\varepsilon(\text{Fe}^{3+}, \text{ClO}_4^-)$ and $\varepsilon(\text{Fe}^{3+},\text{Cl}^-)$ found from redox potentials, and it also indicates that $\varepsilon(\text{FeCl}^{2+}, \text{ClO}_4^-)$ and $\varepsilon(\text{FeCl}^{2+},\text{Cl}^-)$ should have similar values.

The average value of $\log_{10} \beta_1^{\circ}$ at 298.15 K from the analysis of results obtained from investigations using aqueous perchlorate solutions (from the plot in Figure VIII-5—not using the results from experiments in mixed chloride-perchlorate solutions) is recommended, but with a slightly increased uncertainty:

$$\log_{10} \beta_1^{\circ} = (1.52 \pm 0.10).$$

The agreement with the value from a previous review, (1.52 ± 0.10) [2000TAG/DIA], is fortuitous.

The slope of the straight line of the function $\log_{10} \beta_{1m} + 6D = \text{f}(m_{\text{ClO}_4^-})$ given by the SIT treatment of measurements in HClO_4(sln) solutions (Figure VIII-6) gives a value of $\Delta\varepsilon$ that is related to $\varepsilon(\text{FeCl}^{2+}, \text{ClO}_4^-)$ by:

$$\varepsilon(\text{FeCl}^{2+}, \text{ClO}_4^-) = \varepsilon(\text{Fe}^{3+}, \text{ClO}_4^-) + \varepsilon(\text{H}^+,\text{Cl}^-) + \Delta\varepsilon \qquad \text{(VIII.10)}$$

Using the SIT_2 $\varepsilon(\text{Fe}^{3+}, \text{ClO}_4^-)$ value (see Chapter VI) yields:

$$\begin{aligned}\varepsilon(\text{FeCl}^{2+}, \text{ClO}_4^-) = {} & \{(0.78 \pm 0.05) - (0.41 \pm 0.05) \log_{10} I_m\} + (0.12 \pm 0.01) \\ & - (0.22 \pm 0.02)\end{aligned}$$

$$\varepsilon(\text{FeCl}^{2+}, \text{ClO}_4^-) = ((0.68 \pm 0.05) - (0.41 \pm 0.05) \log_{10} I_m)\ \text{kg·mol}^{-1}$$

Using the SIT_1 $\varepsilon(\text{Fe}^{3+}, \text{ClO}_4^-)$ value (again see Chapter VI, especially Section VI.4.1) yields:

$$\varepsilon(\text{FeCl}^{2+}, \text{ClO}_4^-) = (0.63 \pm 0.05)\ \text{kg·mol}^{-1}.$$

The slope of the straight line generated by the linear fit of the function $\log_{10} \beta_{1m} + 6D - 0.03\ m_{\text{Na}^+} - 0.12\ m_{\text{H}^+} = \text{f}(m_{\text{ClO}_4^-})$ from the SIT treatment of all the data for 298.15 K yields a value of $\Delta\varepsilon$ that is related to $\varepsilon(\text{FeCl}^{2+}, \text{ClO}_4^-)$ by:

$$\varepsilon(\text{FeCl}^{2+}, \text{ClO}_4^-) = \varepsilon(\text{Fe}^{3+}, \text{ClO}_4^-) + \Delta\varepsilon \qquad \text{(VIII.11)}$$

For the fittings shown in Figures VIII-5 and VIII-7 one also gets, respectively:

SIT_2: $\varepsilon(\text{FeCl}^{2+}, \text{ClO}_4^-) = ((0.67 \pm 0.05) - (0.41 \pm 0.05) \log_{10} I_m)\ \text{kg·mol}^{-1}$ and

$\varepsilon(\text{FeCl}^{2+}, \text{ClO}_4^-) = ((0.68 \pm 0.05) - (0.41 \pm 0.05) \log_{10} I_m)\ \text{kg·mol}^{-1}$

SIT_1: $\varepsilon(\text{FeCl}^{2+}, \text{ClO}_4^-) = (0.62 \pm 0.05)\ \text{kg·mol}^{-1}$ and

$\varepsilon(\text{FeCl}^{2+}, \text{ClO}_4^-) = (0.63 \pm 0.05)\ \text{kg·mol}^{-1}$

The values of $\varepsilon(\text{H}^+,\text{Cl}^-)$ and $\varepsilon(\text{Na}^+,\text{Cl}^-)$ are those reported in the NEA TDB Tables [2005GAM/BUG].

The scatter in the experimental β_{1m} values is too great to establish whether SIT_1 or SIT_2 better describes the experimental data. In addition most of the stability constant measurements were carried out at medium or rather high ionic strengths for which the SIT_1 and SIT_2 yield comparable values of $\varepsilon(FeCl^{2+}, ClO_4^-)$ (1.325 m is the ionic strength for equal $\varepsilon(FeCl^{2+}, ClO_4^-)$ values).

There is no significant difference between the $\varepsilon(FeCl^{2+}, ClO_4^-)$ values yielded by the three treatments.

The value of $\varepsilon(FeCl^{2+}, ClO_4^-)$ is greater than that estimated for a comparable complex, $AmCl^{2+}$, $\varepsilon(AmCl^{2+}, ClO_4^-) = (0.39 \pm 0.04)$ kg·mol^{-1} [1995SIL/BID]. However, the key to this difference is the corresponding difference in the values for $\varepsilon(Fe^{3+}, ClO_4^-)$ and $\varepsilon(Am^{3+}, ClO_4^-)$ (the latter was estimated by analogy from values for the 3+ lanthanide ions).

The interaction coefficient $\varepsilon(FeCl^{2+},Cl^-)$ can also be estimated approximately from the potentiometric data of [2000TAG/DIA] obtained in aqueous HCl solutions. The SIT analysis of $\log_{10} \beta_1 + 6D$ as a function of m_{Cl^-} leads to $\log_{10} \beta_1^o = (1.51 \pm 0.10)$ (in good agreement with the result given above based on all the data in perchlorate media) and $\Delta\varepsilon = -(0.237 \pm 0.014)$ kg·mol^{-1}. The value of $\varepsilon(FeCl^{2+},Cl^-)$ is calculated by applying Eq. (VIII.12).

$$\varepsilon(FeCl^{2+},Cl^-) = \varepsilon(Fe^{3+},Cl^-) + \varepsilon(H^+,Cl^-) + \Delta\varepsilon \qquad \text{(VIII.12)}$$

$$\varepsilon(FeCl^{2+},Cl^-) - \varepsilon(Fe^{3+},Cl^-) = -(0.12 \pm 0.05)\ \text{kg·mol}^{-1}$$

Using the $\varepsilon(Fe^{3+},Cl^-)$ values determined by the SIT_1 and SIT_2 fits to the data of Popoff and Kunz [1929POP/KUN] (see Section VI.1.2.1.1.2 (case (a), assuming no Fe(II)-chloride association)) the values obtained are:

$$\varepsilon(FeCl^{2+},Cl^-) = (0.64 \pm 0.06)\ \text{kg·mol}^{-1}\ \ (SIT_1)$$

and

$$\varepsilon(FeCl^{2+},Cl^-) = \{(0.72 \pm 0.06) - (0.55 \pm 0.05)\log_{10} I_m\}\ \text{kg·mol}^{-1}\ \ (SIT_2).$$

Here again one observes rather high values for $\varepsilon(FeCl^{2+},Cl^-)$, not very different from $\varepsilon(Fe^{3+},Cl^-)$ and $\varepsilon(FeCl^{2+}, ClO_4^-)$. The fact that the fittings in Figures VIII-5 and VIII-7 lead to similar results (well within the estimated uncertainties) means that the $\Delta'\varepsilon$ values: $\varepsilon(FeCl^{2+},Cl^-) - \varepsilon(Fe^{3+},Cl^-)$ and $\varepsilon(FeCl^{2+}, ClO_4^-) - \varepsilon(Fe^{3+}, ClO_4^-)$ have similar values. That is confirmed by the treatment of the Tagirov *et al.* [2000TAG/DIA] data in HCl(sln) by the SIT formalism.

VIII.2.3.1.4 $FeCl^{2+}_{(out)}$, $FeCl^{2+}_{(in)}$ formation constant variation as a function of the temperature

All the workers [1942RAB/STO], [1959COL/NAU], [1959CON/COP], [1963HEI/CLE], [1967VAS/LOB2], [1976SCH/DOD], [2000TAG/DIA], [2006LIU/ETS] who have investigated the influence of temperature upon the formation constant of $FeCl^{2+}$ found that it increases with increasing T. Almost all literature values for the enthalpy of formation of the complex have been derived from the variation of β_1 with T (Table VIII-4).

Most of these $\Delta_r H^o$ values are scattered, even those from measurements done under similar experimental conditions. The value of $\Delta_r C^o_{p,m}$ which is present in the expression of the variation of $\Delta_r G^o_m$ as a function of the temperature (Eq. (VIII.13)) was often considered to be zero.

$$\Delta_r G^o(T) = \Delta_r H^o(T_0) + \int_{T_0}^{T} \Delta_r C^o_p(T)\mathrm{d}T - T\left\{\Delta_r S^o(T_0) + \int_{T_0}^{T} \Delta_r C^o_p(T)/T\mathrm{d}T\right\} \qquad \text{(VIII.13)}$$

Tagirov *et al.* [2000TAG/DIA] discussed the problem of the value of $\Delta_r C^o_p(T)$ and also used the experimental calorimetric values of $\Delta_r H^o(T_0)$ of Vasil'ev and Lobanov [1967VAS/LOB2]. With an equation proposed by Khodakovskii [1975KHO] for the extrapolation to zero ionic strength and the computer DIANIK code [1992KHO2], they were able to fit all the results at various temperatures by:

$$\log_{10} \beta^o_1 = 0.018\ T + 420.12/T - 5.23 \qquad \text{(VIII.14)}$$

$$\Delta_r H^o(T)\ /\mathrm{kJ\cdot mol^{-1}} = -\ 8.024 + 0.0003431\ (T/\mathrm{K})^2 \qquad \text{(VIII.15)}$$

$$\Delta_r C^o_p(T)\ /\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = 0.682\ T/\mathrm{K} \qquad \text{(VIII.16)}$$

Other direct measurements of $\Delta_r H^o(T)$ by calorimetry have been carried out [1962WOO/GAL] but they were limited to a single ionic strength (1 M $HClO_4$) and it was not possible to extrapolate to $I = 0$. So the value of $\Delta_r H^o$ (298.15 K) given by Tagirov *et al.* [2000TAG/DIA] (22.5 ± 4.6) kJ·mol^{-1} is alone based on a complete treatment of the experimental data, and is in agreement with several other results [1961SUT/ROW], [1962WOO/GAL], [1967VAS/LOB2], [1989BRU/PET] which claimed values of $\Delta_r H^o$ (298.15 K) in the range 15 to 25 kJ·mol^{-1} based on sparser data. Therefore, we recommend the value as recalculated by Tagirov *et al.* [2000TAG/DIA] as the best available current value.

If $\log_{10} \beta^o_1$ = (1.52 ± 0.10) from the SIT treatment is accepted, − (8.68 ± 0.06) kJ·mol^{-1} is obtained for $\Delta_r G^o$ (298.15 K). Taking the value (22.48 ± 4.60) kJ·mol^{-1} for $\Delta_r H^o$ (298.15 K) one gets $\Delta_r S^o$ (298.15 K) = (104.50 ± 15.55) J·K^{-1}·mol^{-1}.

Taking into account the values of $\Delta_f G^o_m$ (Fe^{3+}, 298.15 K) (this review), $\Delta_f G^o_m$ (Cl^-, 298.15 K) (from NEA TDB Table) and $\Delta_r G^o_m$ (298.15 K) = − (8.68 ± 0.06) kJ·mol^{-1}

$$\Delta_f G^o_m(\mathrm{FeCl^{2+}}) = -\ (156.1 \pm 0.9)\ \mathrm{kJ\cdot mol^{-1}}$$

is obtained.

With the same process one obtains $\Delta_f H^o_m$ ($FeCl^{2+}$, 298.15 K) = − (194.7 ± 4.7) kJ·mol^{-1} and S^o_m ($FeCl^{2+}$, 298.15 K) = − (121.3 ± 16.0) J·K^{-1}·mol^{-1}.

The $\Delta_r C_p^\circ(T)$ values were derived from the variation of $\Delta_r H^\circ(T)$ as a function of the temperature. As $\Delta_r C_p^\circ$ (298.15 K) we recommend the value of [2000TAG/DIA] (203 ± 20) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$.

VIII.2.3.1.5 $Fe^{3+}_{(ou)}$, $FeCl^{2+}_{(in)}$ formation constant as function of the pressure

Horne *et al.* [1964HOR/MYE] showed that the application of high pressure leads to the dissociation of the $FeCl^{2+}$ complex, probably because the water activity increases with pressure and stabilizes the more hydrated species ($Fe(H_2O)_6^{3+}$ and Cl^-) rather than the less hydrated complex.

VIII.2.3.1.6 About the existence and the stability of $FeClOH^+$

Two publications [1972KOR/PER], [1981BYR/KES] dealing with the stability of $FeClOH^+$ are cited in Table VIII-4. If stable, this complex could be a non-negligible species in weakly acidic natural media containing chloride ions. Byrne and Kester [1981BYR/KES] did not detect significant concentrations of this complex by spectrophotometry between pH 2.16 and 4.17 in 0.68 m chloride, so they estimated $^*K$ (VIII.17) = $(c_{FeClOH^+} c_{H^+})/(c_{Fe^{3+}} c_{Cl^-})$ for

$$Fe^{3+} + Cl^- + H_2O(l) \rightleftharpoons FeClOH^+ + H^+ \qquad \text{(VIII.17)}$$

to be as small as 1.8×10^{-4}, a value 200 times lower than that given in the paper of Koren and Perlmutter-Hayman [1972KOR/PER].

Calculations of the percentage of $FeClOH^+$ as a function of pH, in solutions 0.68 or 2 molal in Cl^-, using formation-constant values similar to those determined by Byrne and Kester [1981BYR/KES], are given in Table VIII-6. The model takes into account the species $FeCl^{2+}$, $FeCl_2^+$, $FeOH^{2+}$ and $Fe(OH)_2^+$ which compete with $FeClOH^+$. The formation constants of all the species are calculated for the two ionic strengths considered using the values of equilibrium constants and $\Delta\varepsilon$ recommended in this volume. Some numerical values are given in Table VIII-6 and the proportion of $FeClOH^+$ with regard to the other species is plotted as a function of $-\log_{10} m_{H^+}$ in Figure VIII-8. Evidently this species is marginal if its stability constant value is 1.8×10^{-4}. It would be very difficult to detect unless an important spectral change arises from the mixed-ligand binding.

Based on the results of Byrne and Kester [1981BYR/KES], the occurrence of $FeClOH^+$ reaches a maximum at a pH value around 3.5 and for rather high chloride concentrations, 2 m, it can be as much as 3% of the total iron(III) species.

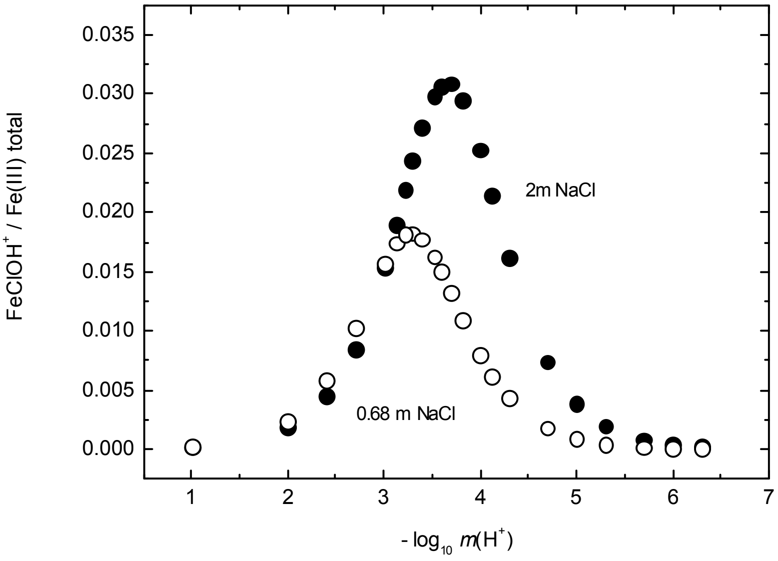
Table VIII-6 Percentage of total iron(III) calculated to be present in solution as FeClOH^+ as a function of $-\log_{10} m_{\mathrm{H}^+}$, for $^*K_m$ (VIII.17) (≈ $^*K_c$ (VIII.17)) = 1.8×10^{-4}. $^*\beta_{1,1}(\mathrm{FeOH}^{2+}) = 0.00164$ mol·kg^{-1} (at 0.68 m Cl^-) and 0.00291 mol·kg^{-1} (at 2 m Cl^-); $^*K_{2,1}(\mathrm{Fe(OH)}_2^+)$ = 1.33×10^{-6} mol·kg^{-1} (at 0.68 m Cl^-) and 9×10^{-7} mol·kg^{-1} (at 2 m Cl^-)[1]; $\beta_1(\mathrm{FeCl}^{2+})$ = 3.21 kg·mol^{-1} (at 0.68 m Cl^-) and 2.8 kg·mol^{-1} (at 2 m Cl^-); $\beta_2(\mathrm{FeCl}_2^+)$ = 3.56 kg^2·mol^{-2} (at 0.68 m Cl^-) and 3.19 kg^2·mol^{-2} (at 2 m Cl^-); trace molalities of total iron(III); no multinuclear hydroxido species taken into account.

% iron(III) as FeClOH^+	$-\log_{10} m_{\mathrm{H}^+}$	m_{Cl^-}	% iron(III) as FeClOH^+	$-\log_{10} m_{\mathrm{H}^+}$	m_{Cl^-}
0.24	2	0.68	0.18	2	2
1.0	2.7	0.68	0.85	2.7	2
1.6	3	0.68	1.5	3	2
1.8 (maximum yield)	3.2	0.68	2.7	3.4	2
1.6	3.5	0.68	3.1 (maximum yield)	3.7	2
0.8	4	0.68	2.5	4	2
0.18	4.7	0.68	0.38	5	2

---

[1] These calculations were carried out before the values of the hydrolysis constants had been selected in the present review. Use of selected values from Table III-2 would lead to even lower calculated relative amounts of FeClOH^+.

Figure VIII-8: Fraction of the total Fe(III) as $FeClOH^+$ at 298.15 K in NaCl medium as a function of the acidity, calculated using the constants shown in the caption of Table VIII-6. Soluble polymers and $Fe(OH)_3$ precipitation are not taken into account because of the low total Fe(III) concentrations, $Fe(III)_{total} < 10^{-6}$ m.



VIII.2.3.2 Aqueous iron(III) chlorido complexes with more than one chloride

VIII.2.3.2.1 Literature data

Although considerable attention has been paid to the characterization and measurement of the thermodynamic constants for formation of $FeCl^{2+}$, fewer studies have been devoted to the higher-order complexes. The 2:1, 3:1, and 4:1 chlorido complexes have been claimed to exist in aqueous solutions. The even higher chlorido 5:1 and 6:1 species have been found in solids or in organic media, but not in aqueous media. This subsection is a review of the literature for the aqueous chlorido complexes with more than one chloride. The main studies are listed in Table VIII-7. The precision claimed for the constants is lower than for the 1:1 species.

Table VIII-7: Summary of experimental conditions and experimental and re-evaluated formation constants for the higher iron(III) chlorido complexes $FeCl_2^+$, $FeCl_3(aq)$ and $FeCl_4^-$. For discussion of the re-evaluations, see the corresponding Appendix A entries.

Reference	Method	Ionic medium	t / °C	Reported Value $^{(a)}$	Re-evaluation $^{(b)}$
$FeCl^{2+} + Cl^- \rightleftharpoons FeCl_2^+$					
[1942RAB/STO]	sp	1 M $HClO_4$	26.7	$K_2 = (1.3 \pm 0.4)$	$K_2 = (1.2 \pm 0.5)$
[1943OLE]		2 M $HClO_4$	20	$K_2 = 2$	$K_2 = (2.1 \pm 0.5)$
[1955LIS/RIV3]	sp	1.2 M $HClO_4$/HCl/ $NaClO_4$/NaCl	25	$K_2 = 1.5$	$K_2 = (1.4 \pm 0.5)$
[1969MOR/WIL]	ix	1 M $HClO_4$ + HCl	25	$\beta_2 = (5.5 \pm 2.5)$	$K_2 = (1.2 \pm 0.6)$
[1969NIK/PAL]	pot	4.0 M	25	$K_2 = (0.95 \pm 0.19)$	$K_2 = (1.1 \pm 1.0)$
[1969PAL/STR]	pot	6.0 M	25.0	$K_2 = (2.85 \pm ?)$	———
[1972SEK/TET]	dist	3 M $NaClO_4$ + 1 M $HClO_4$	25	$\beta_2 = 6.3$	$K_2 = (0.8 \pm 1.0)$
[1976ASH]		1 M $HClO_4$ + 4 M $NaClO_4$	22	$\beta_2 = 3.6$	———
			34	$\beta_2 = 9.1$	
			47	$\beta_2 = 15.4$	
			60	$\beta_2 = 21.1$	
[1976BYR/KES2]	pot	0.68 m H/$NaNO_3$/NaCl	25	$\beta_{2m} = 0.44$	———
[1976KHA/BEL]	pot	3 M $HClO_4$/HCl	RT?	$K_2 = 0.43$	———
		6 M $HClO_4$/HCl		$K_2 = 2.45$	
[1976SCH/DOD]	kin	1 M $HClO_4$	25	$K_2 = 1.3$	$K_2 = (1.24 \pm 0.50)$
[1979STR/PAT]	kin,sp.	1 M $HClO_4$ + 1.6 M $NaClO_4$ /NaCl	25	$K_2 = 1.8$	$K_2 = (1.58 \pm 0.50)$
	kin,sp.,Tj		21 to 25	$\Delta H_2 = 8.79$	
[1981BYR/KES]	sp	2.74 M $HClO_4$,HCl	25	$K_2 = (0.340 \pm 0.046)$	$K_2 = (0.3 \pm 0.1)$
[2000TAG/DIA]	review	$I = 0$ (extrap.)	25	$K_2^\circ = (7.9 \pm 3.7)$	$K_2^\circ = (7.9 \pm 3.7)$
[2006LIU/ETS]	sp	$I = 0$ (extrap. based on I = 0.107 m HCl + 0 to 15.0 m LiCl)	25	$\log_{10} K_2^\circ = (0.32 \pm 0.25)$	———
			60	$\log_{10} K_2^\circ = (0.49 \pm 0.25)$	———
			90	$\log_{10} K_2^\circ = (0.95 \pm 0.45)$	———

(Continued on next page)

Table VIII-7 (continued)

Reference	Method	Ionic medium	t / °C	Reported Value $^{(a)}$	Re-evaluation $^{(b)}$
$FeCl_2^+ + Cl^- \rightleftharpoons FeCl_3(aq)$					
[1942RAB/STO]	sp	1 M $HClO_4$	26.7	$K_3 = (0.04 \pm 0.02)$	$K_3 = (0.038 \pm 0.019)$
[1953GAM/JOR]	sp	3.3 to 5.1 M HCl	20	$K'^{\circ}_3 = 0.73$ see Appendix A	$K^{\circ}_3 = 0.73$ see Appendix A
[1960MAR]	iex	$I = 0$ (extrap. based on $I = 1$ to 12 m HCl + LiCl)	25	$\log_{10} K^{\circ}_3 = -(1.40 \pm 0.06)$	$K^{\circ}_3 = 0.040$
[1969PAL/STR]		6.0 M	25.0	$K_{3m} = (0.10 \pm ?)$	———
[1979STR/PAT]	kin,sp	1 M $HClO_4$ + 1.6 M $NaClO_4$ /NaCl	25	$K_3 = 6.0$	———
[2006LIU/ETS]	sp	$I = 0$ (extrap. based on $I = 0.107$ m HCl + 0 to 15.0 m LiCl)	25	$\log_{10} K^{\circ}_3 = -(1.11 \pm 0.40)$	———
			60	$\log_{10} K^{\circ}_3 = -(0.97 \pm 0.30)$	———
			90	$\log_{10} K^{\circ}_3 = -(0.63 \pm 0.55)$	———
$FeCl_3(aq) + Cl^- \rightleftharpoons FeCl_4^-$					
[1953GAM/JOR]	sp	8.2 to 11.3 M HCl	20	$K'^{\circ}_4 = 0.0105$ see Appendix A	$K^{\circ}_4 = 0.0105$ see Appendix A
[1960MAR]	iex	$I = 0$ (extrap. based on $I = 1$ to 12 m HCl + LiCl)	25	$\log_{10} K^{\circ}_4 = -(1.92 \pm 0.08)$	$K^{\circ}_4 = 0.012$
[2006LIU/ETS]	sp	$I = 0$ (extrap. based on $I = 0.107$ m HCl + 0 to 15.0 m LiCl)	25	$\log_{10} K^{\circ}_4 = -(2.03 \pm 0.30)$	———
			60	$\log_{10} K^{\circ}_4 = -(1.93 \pm 0.30)$	———
			90	$\log_{10} K^{\circ}_4 = -(1.79 \pm 0.45)$	———

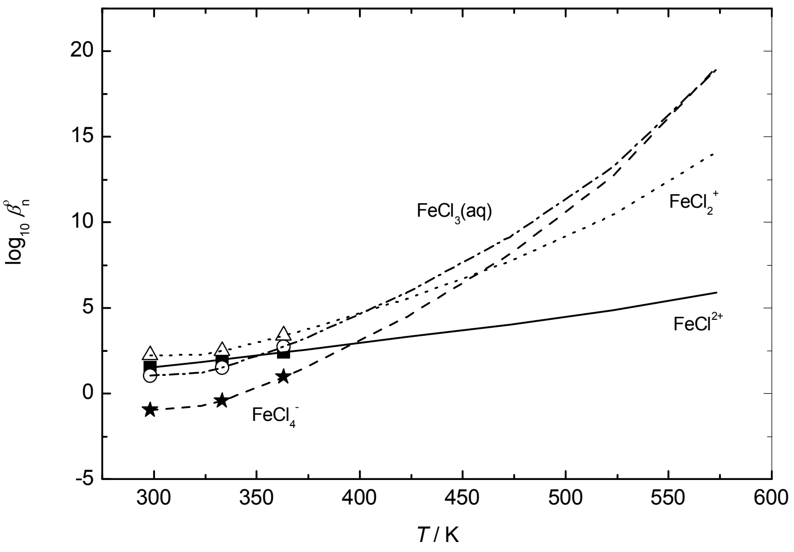
(a) Molar constants (*i.e.*, β_{1c}) unless specifically identified as molal constants (β_{1m}); values of $\Delta_r H$ in $kJ \cdot mol^{-1}$; values of $\Delta_r S$ in $J \cdot K^{-1} \cdot mol^{-1}$.

(b) Molal constants.

At 298.15 K, there is a strong decrease in the values of the stability constants as the complexes become richer in Cl^-. The values are rather scattered, as one would expect with such small constants, especially considering the difficulties in avoiding the interference from the lower- and higher-order complexes. As seen before, and also as confirmed by Liu *et al.* [2006LIU/ETS], all the complexes are stabilized in high ionic-strength solutions, the higher-order complexes more than the lower-order complexes.

These constants were determined primarily at temperatures near 298.15 K. The recent work of Liu *et al.* [2006LIU/ETS] addresses the previous lack of reliable data for higher temperatures. They obtained values of K_2 to K_4 from 298.15 to 363.15 K and extrapolated their values to 373.15 K by applying a formula suggested by Anderson *et al.* [1991AND/CAS] (see Appendix A). It can be seen in Figure VIII-9 that higher-order complexes might be stabilized at high temperatures. For example, $FeCl_4^-$, a minor species at 298.15 K, may well become the predominant complex at 573.15 K. If this extrapolation procedure is used, the predominance of $FeCl_3(aq)$ and $FeCl_4^-$ at 573.15 K instead of $FeCl^{2+}$ and $FeCl_2^+$ at 298.15 K, is clear. However, such extrapolations far beyond the range of the experimental points are not recognised sources for TDB values and must be taken only to suggest probable trends.

Figure VIII-9: Formation constants of the Fe^{3+} chlorido complexes as a function of temperature for zero ionic strength. Experimental points 298.15 to 363.15 K for the 1:2 △, 1:3 ○, and 1:4 ★ complexes [2006LIU/ETS]. Extrapolations to higher temperatures were done using the Anderson equation [1991AND/CAS], [2006LIU/ETS] (*cf.* Appendix A). The data for the 1:1 complex are from Tagirov *et al.* [2000TAG/DIA]. The β_n° values at 298.15 K are the values recommended in the present review.



VIII.2.3.2.2 Application of the SIT formalism to the calculation of the standard formation constants of the Fe^{3+} chlorido complexes with more than one Cl^- ion

VIII.2.3.2.2.1 $FeCl_2^+$

Values of K_2 reported in several of the papers listed in Table VIII-7 and in Table 11 and Figure 10 of the paper of Tagirov *et al.* [2000TAG/DIA] were reassessed in this review in terms of the reaction $FeCl^{2+} + Cl^- \rightleftharpoons FeCl_2^+$.

We applied an equation similar to Eq. (VIII-8) to prepare the graph shown in Figure VIII-9; here the value of Δz^2 is -4 instead of -6 for the formation of the 1:1 complex.

The scatter in the data is much greater than was the case for the data for formation of $FeCl^{2+}$. The uncertainties are not those given by the authors. Instead, they have been estimated taking into account the scatter in the published values. However the results of the fittings depend much more on which studies are chosen for the analysis. This is illustrated in Table VIII-8 which shows three sets of studies and the result of carrying out a linear fitting for each set.

Table VIII-8: Effect of the selection of papers upon the fit of $FeCl_2^+$ data.

List 1 (6 papers)	List 2 (8 papers)	List 3 (9 papers)
[1942RAB/STO]	[1942RAB/STO]	[1942RAB/STO]
[1943OLE]	[1943OLE]	[1943OLE]
[1955LIS/RIV3]	[1955LIS/RIV3]	[1955LIS/RIV3]
[1969MOR/WIL]	[1969MOR/WIL]	[1969MOR/WIL]
[1976SCH/DOD]	[1969NIK/PAL]	[1969NIK/PAL]
[1979STR/PAT]	[1972SEK/TET]	[1972SEK/TET]
	[1976SCH/DOD]	[1976SCH/DOD]
	[1979STR/PAT]	[1979STR/PAT]
		[1981BYR/KES]
$\log_{10} K_2^\circ = (0.673 \pm 0.065)$	$\log_{10} K_2^\circ = (0.845 \pm 0.160)$	$\log_{10} K_2^\circ = (0.84 \pm 0.37)$
$\Delta'\varepsilon = (0.115 \pm 0.036)$ kg·mol^{-1}	$\Delta'\varepsilon = -(0.005 \pm 0.064)$ kg·mol^{-1}	$\Delta'\varepsilon = -(0.05 \pm 0.26)$ kg·mol^{-1}
$R^2 = 0.907$	$R^2 = 0.004$	$R^2 = 0.08$

In contrast to the plot based on references in list 1 of Table VIII-8, a plot of values from list 2 (not shown) is far from linear because the small values from the work of Sekine and Tetsuka [1972SEK/TET] and of Nikol'skii *et al.* [1969NIK/PAL] are included. Similarly, if the results from the references in list 3 are considered, the low K_2 values from [1981BYR/KES], [1972SEK/TET], and [1969NIK/PAL] lead to erratic fits. When a linear fitting with the values of these last three papers is carried out, the linearity is rather good, R^2 = 0.984, but the $\log_{10} K_2^\circ = -(0.66 \pm 0.28)$ value is incredibly low. Therefore, the papers from list 1 were selected for the determination of $\log_{10} K_2^\circ$ and $\Delta'\varepsilon$. The values $\log_{10} K_2^\circ = (0.673 \pm 0.065)$ and $\Delta'\varepsilon = -(0.115 \pm 0.036)$ kg·mol^{-1} are obtained.□ After rounding, we propose the values:

$$\log_{10} K_2^\circ = (0.7 \pm 0.2) \text{ and } \Delta'\varepsilon = -(0.11 \pm 0.04)\ \text{kg·mol}^{-1},$$

where $\Delta'\varepsilon$ is defined below (Eq. (VIII.18)).

Tagirov *et al.* [2000TAG/DIA] used values for K_2 found in the literature (see Appendix A) to deduce the value of K_2° by applying a Debye-Hückel-type equation for extrapolation to the standard state. They found $\log_{10} K_2^\circ = (0.9 \pm 0.2)$, a value close to that proposed in the present review by applying the SIT method, $\log_{10} K_2^\circ = (0.7 \pm 0.2)$.

Liu *et al.* [2006LIU/ETS] recently published a study leading to $\log_{10} \beta_2^\circ = (1.87 \pm 0.25)$. The rounded SIT value from the present review, $\log_{10} \beta_2^\circ = (2.22 \pm 0.22)$, is in marginal agreement, and is between the value from Liu *et al.* and that of [2000TAG/DIA], $\log_{10} \beta_2^\circ = (2.4 \pm 0.3)$. Therefore, the rounded K_2° value resulting from the SIT treatment of the data from the studies in list 1 is recommended for the NEA TDB tables as the best available value for K_2°.

$$\log_{10} K_2^\circ = (0.7 \pm 0.2)$$

The slope of the straight line in the lower graph of Figure VIII-10 represents the value of

$$\Delta'\varepsilon = \varepsilon(\text{FeCl}_2^+, \text{ClO}_4^-) - \varepsilon(\text{FeCl}^{2+}, \text{ClO}_4^-) = -(0.11 \pm 0.04)\ \text{kg·mol}^{-1}. \qquad \text{(VIII.18)}$$

That allows calculation of a value for $\varepsilon(\text{FeCl}_2^+, \text{ClO}_4^-)$ using the values of $\varepsilon(\text{FeCl}^{2+}, \text{ClO}_4^-)$ given above

SIT_1:

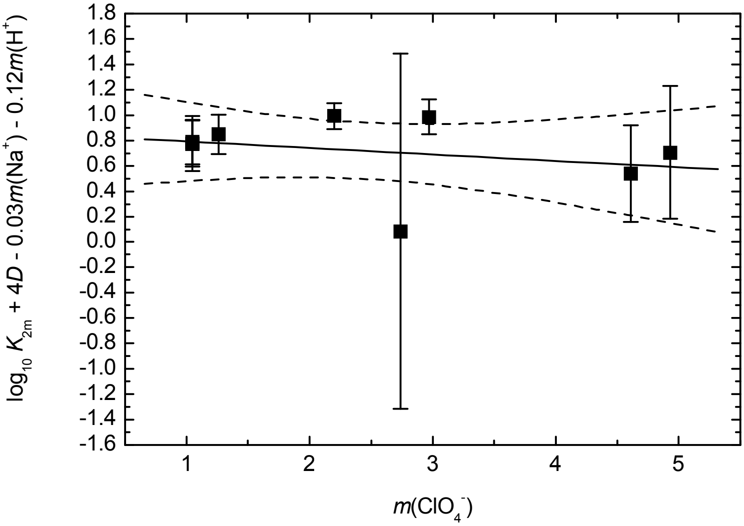
$$\varepsilon(\text{FeCl}_2^+, \text{ClO}_4^-) = (0.52 \pm 0.05)\ \text{kg·mol}^{-1}$$

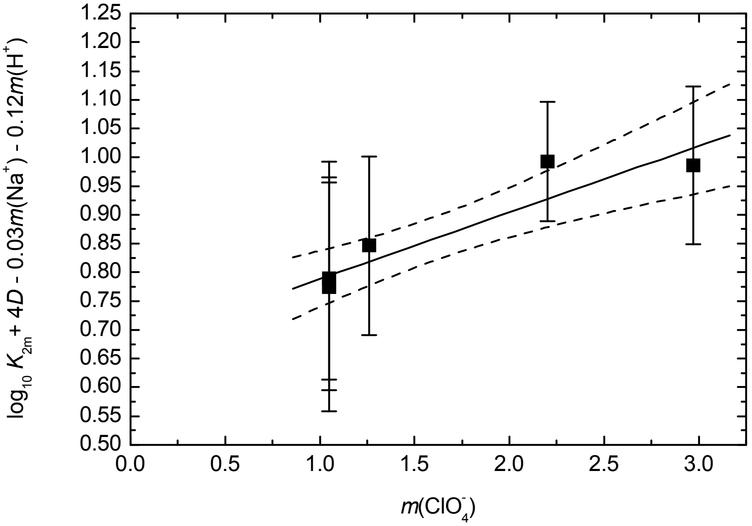
and SIT_2:

$$\varepsilon(\text{FeCl}_2^+, \text{ClO}_4^-) = ((0.57 \pm 0.05) - (0.41 \pm 0.05) \log_{10} I_m)\ \text{kg·mol}^{-1}.$$

Of the data used for this optimisation, the results from only one paper [1969MOR/WIL] are based on experiments in mixed HCl-HClO_4 media, and in view of the uncertainty in the values proposed, the small differences due to the differences in ClO_4^- and Cl^- interaction coefficients with the cations are limited, and probably masked.

Figure VIII-10: SIT treatment for values of the equilibrium constant K_2 ($FeCl^{2+} + Cl^- \rightleftharpoons FeCl_2^+$) in mixed $HClO_4$ / $NaClO_4$ media as a function of the perchlorate molality at 298.15 K. Sets of literature references as in Table VIII-8. Upper graph: Table VIII-8, List 3: [1942RAB/STO], [1943OLE], [1955LIS/RIV3], [1969MOR/WIL], [1969NIK/PAL], [1972SEK/TET], [1976SCH/DOD], [1979STR/PAT], [1981BYR/KES]. Lower graph: Table VIII-8, List 1: [1942RAB/STO], [1943OLE], [1955LIS/RIV3], [1969MOR/WIL], [1976SCH/DOD], [1979STR/PAT].





VIII.2.3.2.2.2 $FeCl_3(aq)$

Literature values of K_3 for the formation of $FeCl_3(aq)$ are listed in Table VIII-7. Some of these have been noted by Tagirov *et al.* [2000TAG/DIA] in their Table 11 and Liu *et al.* [2006LIU/ETS] in their Table 6.

Because of the limited information and the various media used for the experimental measurements, the SIT formalism cannot be applied.

The estimation of $\log_{10} K_3^\circ$ has been carried out by averaging the results of Rabinowitch and Stockmayer [1942RAB/STO], Marcus [1960MAR], and Liu *et al.* [2006LIU/ETS]; all for 298.15 K and $I = 0$. The value $K_3 = 6$ of Strahm *et al.* [1979STR/PAT] for $I_c = 2.6$ appears to be much too high, and has been rejected in this review. The value given by Gamlen and Jordan [1953GAM/JOR] is also significantly higher than the three chosen values and has not been used. The averaged value obtained is $\log_{10} K_3^\circ = -(1.17 \pm 0.15)$ which has been been rounded to:

$$\log_{10} K_3^\circ = -(1.2 \pm 0.2).$$

VIII.2.3.2.2.3 $FeCl_4^-$

The status of the studies on the tetrachlorido complex is similar to that for the trichlorido complex. These two weak complexes exist only in very concentrated chloride solutions; so the experimental work has been carried out primarily at high ionic strengths, out of the range of applicability of the SIT. We averaged the results of Gamlen and Jordan (the uncertainty in $\log_{10} K_4^\circ$ is estimated in the present review as ± 0.7) [1953GAM/JOR] (293.15 K), Marcus [1960MAR], and Liu *et al.* [2006LIU/ETS], both for 298.15 K and $I = 0$, and found, after rounding :

$$\log_{10} K_4^\circ = -(2.0 \pm 0.7).$$

VIII.2.3.2.3 Formation constants of the higher chlorido complexes of Fe(III) as a function of the temperature

The variation of the formation constant K_2 with temperature has been measured in several studies. The variation of K_3 and K_4 with the temperature has been reported only in the paper of Liu *et al.* [2006LIU/ETS]. Results from the literature concerning the thermodynamic constants of the higher chlorido complexes of iron(III) are given in Table VIII-9.

The K_2° value of Tagirov *et al.* [2000TAG/DIA] leads to a value of $\Delta_r G_m^\circ = -(5.1 \pm 1.1)\ kJ\cdot mol^{-1}$. To determine the other thermodynamic constants they relied on theoretical relations because of the lack of experimental measurements. Their results are reported here for general information only and cannot be considered for use as TDB values. The standard entropy, $\Delta_r S_m^\circ$ and heat capacity $\Delta_r C_{p,m}^\circ$ at 298.15 K and 100 kPa for the reaction $Fe^{3+} + 2\ Cl^- \rightleftharpoons FeCl_2^+$ were estimated [2000TAG/DIA] using an *ab initio* calculation of ionic association proposed by Akinfiev [1995AKI]. The model uses the thermodynamic properties of $FeCl^{2+}$, the interionic distance of the Fe-Cl bond and the frequency of bond oscillation. The calculation resulted in the values $\Delta_r S^\circ_m$ = 149.8 J·K^{-1}·mol^{-1} and $\Delta_r C^\circ_{p,m}$ = 378.65 J·K^{-1}·mol^{-1}. With these values and appropriate auxiliary values, a complete set of thermodynamic constants for the formation of $FeCl_2^+$ was tabulated (*cf.* the Appendix A entry for [2000TAG/DIA] and calculated corrections to the $\Delta_f G^\circ_m$ and $\Delta_f H^\circ_m$ values).

Table VIII-9: The thermodynamic constants related to the temperature dependence of the reactions $FeCl^{2+} + Cl^- \rightleftharpoons FeCl_2^+$; $FeCl_2^+ + Cl^- \rightleftharpoons FeCl_3(aq)$ and $FeCl_3(aq) + Cl^- \rightleftharpoons FeCl_4^-$.

reference	I /M	t /°C	K_q	$\Delta_r G^\circ_m$ /kJ·mol^{-1}	$\Delta_r H^\circ_m$ /kJ·mol^{-1}	$\Delta_r S^\circ_m$ /J·K^{-1}·mol^{-1}
$FeCl^{2+} + Cl^- \rightleftharpoons FeCl_2^+$						
[1979STR/PAT]	2.6 (1.6 M $NaClO_4$, 1 M $HClO_4$)	25	1.8	− 1.46	8.76	34.28
[2000TAG/DIA]	$HClO_4 \rightarrow 0$	25	7.9 ± 3.7	− 5.12 ± 1.14		
			{for β_2°	− 13.7 ± 1.7	30.87 ± 4.79	149 ± 15 † ($\Delta_r C^\circ_{p,m}$ = (378.65 ± 40.00)†}
[2006LIU/ETS]	HCl/LiCl → 0	25	2.1 ± 1.2	− 1.8 ± 1.4	19.35 ± 7.30 *	
This review	0	25	5.0 ± 2.3	− 4.0 ± 1.1	No recommended value ($\Delta_r H_2^\circ > \Delta_r H_1^\circ$)	
$FeCl_2^+ + Cl^- \rightleftharpoons FeCl_3(aq)$						
[2006LIU/ETS]	HCl/LiCl → 0		0.078 ± 0.071	6.3 ± 2.3	14.8 ± 7.3 *	
This review	0	25	0.73	6.8 ± 1.1	No recommended value ($\Delta_r H_3^\circ > \Delta_r H_2^\circ$)	
$FeCl_3(aq) + Cl^- \rightleftharpoons FeCl_4^-$						
[2006LIU/ETS]	HCl/LiCl → 0	25	0.0093 ± 0.0064	11.6 ± 1.7	7.5 ± 1.5 *	
This review	0		0.010 ± 0.005	11.4 ± 1.1	No recommended value ($\Delta_r H_4^\circ > \Delta_r H_3^\circ$)	

* A rough estimate from the three formation constants values at 298.15, 333.15 and 363.15 K.

† No uncertainty value was listed [2000TAG/DIA]; it is estimated in the present review.

By using the values of $\Delta_r S^\circ_m$ and the heat-capacity $\Delta_r C^\circ_{p,m}$ values proposed by Tagirov *et al.* with the cumulative formation constant selected in the present review, the auxiliary constants found in the NEA-TDB tables, and the values for Fe^{3+} as selected in the present review, the following values are obtained for

$$Fe^{3+} + 2\,Cl^- \rightleftharpoons FeCl_2^+ \qquad \text{(VIII.19)}$$

$\Delta_r G^\circ_m$ (VIII.19) = – (12.7 ± 0.8) kJ·mol^{-1} and $\Delta_r H^\circ_m$ (VIII.19) = (31.99 ± 4.65) kJ·mol^{-1} at 298.15 K, and hence, $\Delta_f G^\circ_m$ ($FeCl_2^+$, 298.15 K) = – (291.3 ± 1.4) kJ·mol^{-1}; $\Delta_f H^\circ_m$ ($FeCl_2^+$, 298.15 K) = – (352.2 ± 4.8) kJ·mol^{-1}; S°_m ($FeCl_2^+$, 298.15 K) = – (19.4 ± 15.5) J·K^{-1}·mol^{-1}; $C^\circ_{p,m}$ ($FeCl_2^+$, 298.15 K) = (24 ± 46) J·K^{-1}·mol^{-1}.

In Table VIII-9 $\Delta_r H^\circ_m$ values for the formation reaction of the 2:1, 3:1 and 4:1 complexes as reported by Liu *et al.* [2006LIU/ETS] are listed. These were calculated by applying the van't Hoff relation ($\mathrm{d}\ln K^\circ_n/\mathrm{d}(1/T) = -\Delta_r H^\circ_m/R$) to the experimental values of K°_n at 298.15, 333.15 and 363.15 K.

The three points available for each complex did not fall on a straight line. This could mean that $\Delta_r H^\circ$ varies with the temperature even in the narrow range of temperatures investigated (298.15 to 363.15 K), but uncertainties in the K°_n values also could be responsible. The experimental work of Vassilev and Lobanov [1967VAS/LOB2] dealing with calorimetric measurements at different ionic strengths and temperatures for the formation of the 1:1, Fe^{3+}-chlorido complex showed that $\Delta_r H_1$ varies with both the temperature and the ionic strength. So the literature data are too sparse to indicate any precise values of $\Delta_r H^\circ_n$ when $n > 1$. However it seems well established that an increase in temperature stabilizes the higher-order Fe^{3+} chlorido complexes with respect to the monochlorido complex, following the general rule for all such complexes. The variation of $\log_{10} \beta^\circ_n$ as a function of temperature (Figure VIII-9) appears to indicate that:

$$\Delta_r H^\circ_4 > \Delta_r H^\circ_3 > \Delta_r H^\circ_2 > \Delta_r H^\circ_1$$

where $\Delta_r H^\circ_n$ is the molar enthalpy change for formation of the n:1 complexes from Fe^{3+} and Cl^- ions.

VIII.2.3.3 Conclusions and recommended thermodynamic values

The literature dealing with the thermodynamics of the aqueous iron(III) chlorido complexes is voluminous but most of the papers have dealt only with the 1:1 complex. They address all aspects of chloride-iron(III) association in aqueous solutions. The presence of an outer-sphere complex, $FeCl^{2+}_{(out)}$, has been demonstrated. To treat all the data with the SIT formalism one considers that this association interaction is encompassed within the ionic strength effects, and so only the formation constants of the inner-sphere species have been analysed by the SIT.

Recent papers have been more oriented to environmental problems, and considered the formation of higher-order complexes and the variation of the formation constants as a function of ionic strength and temperature. Calorimetric investigations are very scarce, and for thermodynamic constants other than the complex formation constants agreement between the published values is rather poor.

The SIT formulation yielded formation constants in good agreement with those in the original literature but its application was limited to $FeCl^{2+}$ and $FeCl_2^+$.

The recommended values for the thermodynamic constants are collected in Table VIII-10.

Table VIII-10: Thermodynamic constants for the aqueous iron(III) chlorido complexes

Species	$\log_{10} K_q^\circ$	$\log_{10} \beta_q$	$\Delta_r G_m^\circ$ / kJ·mol^{-1} (cumulative)	$\Delta_r H_m^\circ$ / kJ·mol^{-1} (stepwise)	$\Delta_r H_m^\circ$ / kJ·mol^{-1} (cumulative)
$FeCl^{2+}$	1.52 ± 0.10	1.52 ± 0.10	− 8.68 ± 0.57	22.48 ± 4.60	22.48 ± 4.60
$FeCl_2^+$	0.7 ± 0.2	2.22 ± 0.22	− 12.67 ± 1.28	9.51 ± 6.54 (a)	31.99 ± 4.65 (a)
$FeCl_3$(aq)	− 1.2 ± 0.2	1.02 ± 0.30			
$FeCl_4^-$	− 2.0 ± 0.2	− 0.98 ± 0.36			

Selected values

Species	$\Delta_f G_m^\circ$ / kJ·mol^{-1}	$\Delta_f H_m^\circ$ / kJ·mol^{-1}	$\Delta_f S_m^\circ$ / J·K^{-1}·mol^{-1}
$FeCl^{2+}$	− 156.12 ± 0.87	− 194.7 ± 4.7	− 121.3 ± 16.0
$FeCl_2^+$	− 291.3 ± 1.4		
$FeCl_3$(aq)	− 415.7 ± 1.8		
$FeCl_4^-$	− 535.5 ± 4.4		

(a) This value was calculated in the present review based on estimated values of 149.8 J·K^{-1}·mol^{-1} for $\Delta_r S_m^\circ$ and 378.65 J·K^{-1}·mol^{-1} for $\Delta_r C_{p,m}^\circ$ [2000TAG/DIA] for the cumulative reaction to form the dichlorido complex, but was not used to obtain a selected value for the dichlorido complex.

It can be seen that the chlorido complexes, although weak at 298.15 K, are rather well characterized. The SIT treatment, when sufficient data are available, does not lead to large discrepancies with literature interpretations in which several other kinds of extrapolations to zero ionic strength have been used. That is different from the case when the SIT was applied to the Fe^{3+}/Fe^{2+} standard potential and determination of $\varepsilon(Fe^{3+}, ClO_4^-)$ from redox data (Section VI.1.2.1.1.1). One reason for the better agreement could be the unavailability of lower ionic strength data from investigations of chlorido complexes. Relatively high choride concentrations (and hence ionic strengths) are necessary to observe the weak 1:1 chloride complex, and even higher chloride molalities are needed to obtain information concerning the 2:1, 3:1 and 4:1 species.

VIII.2.4 Mixed iron(II)-iron(III) complexes in chloride solutions

Mixed iron(II)-iron(III) chlorido complexes have been proposed in solutions with high concentrations of iron and chloride [1950MCC/DAV], but no quantitative thermodynamic data for such species have been found.

VIII.3 Iron halide compounds

VIII.3.1 Iron fluoride compounds

VIII.3.1.1 Iron(II) fluoride FeF_2(cr)

VIII.3.1.1.1 Entropy and heat capacity of FeF_2(cr)

Stout and Catalano [1954STO/CAT] reported heat-capacity values from a set of careful adiabatic calorimetry experiments carried out on a sample of FeF_2(cr) at temperatures between 11 and 310 K. Macheteau and Barberi [1974MAC/BAR] reported a limited set of heat-capacity values for FeF_2(cr) (473 to 673 K) from differential-calorimetry measurements. As discussed in Appendix A, a single function was fit to the results of the two studies

$$[C^{\circ}_{p,\mathrm{m}}]^{675\,\mathrm{K}}_{250\,\mathrm{K}}(\mathrm{FeF_2, cr}, T)/\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}} = 68.7299 + 2.69560 \times 10^{-2}\,(T/\mathrm{K}) - 7.70919 \times 10^{5}\,(T/\mathrm{K})^{-2}.$$

The value at 298.15 K is

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{FeF_2, cr, 298.15\ K}) = (68.09 \pm 0.50)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}},$$

and is based primarily on the work of Catalano and Stout [1955CAT/STO2]. The value for S°_{m} (FeF_2, cr, 298.15 K) reported by Catalano and Stout is also accepted with an estimated uncertainty of 0.20 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$:

$$S^{\circ}_{\mathrm{m}}(\mathrm{FeF_2, cr, 298.15\ K}) = (86.99 \pm 0.20)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}.$$

VIII.3.1.1.2 Enthalpy of formation of FeF_2(cr)

Several groups have determined values for $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ (FeF_2, cr) from enthalpies of reaction at temperatures between 500 and 1000 K. Jellinek and Rudat [1928JEL/RUD] investigated the reaction

$$\mathrm{H_2(g) + FeF_2(cr) \rightleftharpoons Fe(cr) + 2\,HF(g)} \qquad \text{(VIII.20)}$$

by a transpiration method (673 to 873 K). However, most of the studies [1966LOF/MCI], [1967MAR/BON], [1968MAR], [1970VEC/ROG], [1972BAG], [1973SKE/PAT], [1975CHA/KAR], [1975SCH2], [1988AZA/SRE] have involved galvanic-cell measurements to determine equilibrium constants for the reaction

$$\mathrm{NiF_2(cr) + Fe(cr) \rightleftharpoons FeF_2(cr) + Ni(cr)} \qquad \text{(VIII.21)}$$

at temperatures between 500 and 1000 K. There also have been studies [1975CHA/KAR], [1978PET/VEC] that reported measurements of galvanic potentials for cells of the type Co,CoF_2 | CaF_2 | FeF_2,Fe. However, use of these data to determine a value for $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ (FeF_2, cr, 298.15 K) would require assessment of thermodynamic quantities for CoF_2(cr), and this falls outside the scope of the present review.

The study of Vecher and Rogach [1970VEC/ROG] cannot be used for reasons discussed in Appendix A, and Markin *et al.* [1967MAR/BON] reported only a single value at one temperature. The potentials from the other studies (Figure VIII-11) show only a slight temperature dependence, but there appear to be systematic differences between the measurements of different groups. A value of $\Delta_f H^\circ_m$ (FeF$_2$, cr, 298.15 K) can be obtained by using the thermodynamic quantities for Ni(cr) and NiF$_2$(cr) as assessed by Gamsjäger *et al.* [2005GAM/BUG], for Fe(cr) from this review, Section V.2, together with the values accepted above for S°_m (FeF$_2$, cr, 298.15 K) and $C^\circ_{p,m}$ (FeF$_2$, cr, T). Schaefer and Gokcen [1975SCH2], [1981SCH/GOK] tabulated the measured potential at each temperature, and the average value for $\Delta_f H^\circ_m$ (FeF$_2$, cr, 298.15 K) based on these data is listed in Table VIII-11. However, the primary data were not reported in the other studies, or were shown only as points in figures. In those cases it has been necessary to rely on the reported linear functions for $E(T)$, and values $\Delta_f H^\circ_m$ (FeF$_2$, cr, 298.15 K) were calculated at the extrema of the reported temperature ranges.

Figure VIII-11: Results of high-temperature cell-potential studies of Reaction (VIII.21). The curve for E_{calc} is based on a value of − 712.1 kJ·mol^{-1} for $\Delta_f H^\circ_m$ (FeF$_2$, cr, 298.15 K) and other values as assessed in the present review and in Gamsjäger *et al.* [2005GAM/BUG].

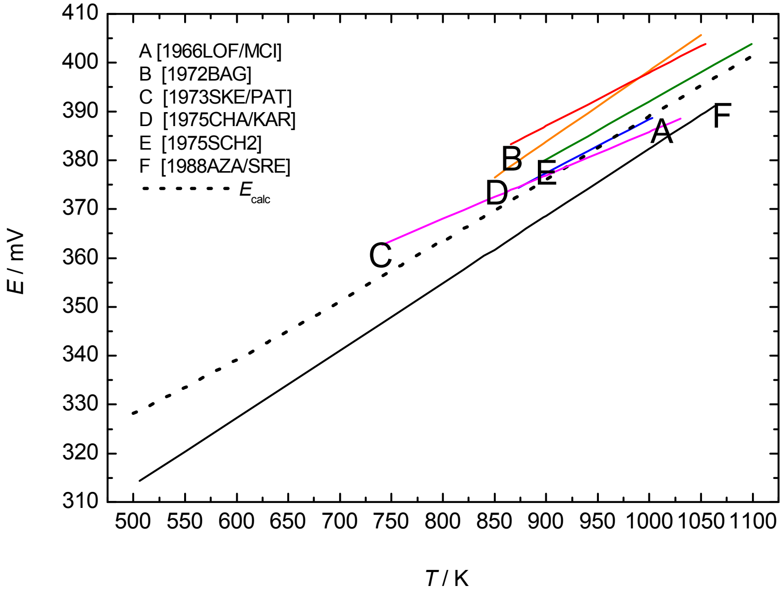


Table VIII-11: Enthalpy of formation values for FeF_2(cr) from galvanic-cell measurements

T / K	$\Delta_f H_m^o$ (FeF_2, cr, 298.15 K)/kJ·mol^{-1}	reference
873, 1003	− 712.4, − 712.0	[1966LOF/MCI]
866, 1051	− 710.5, − 711.8	[1972BAG]
741, 1030	− 713.4, − 711.3	[1973SKE/PAT]
850, 1050	− 713.4, − 714.1	[1975CHA/KAR]
897.5 to 1098.7 (14 measurements)	− (712.7 ± 0.2)	[1975SCH2], [1981SCH/GOK]
506, 1063	− 709.3, − 711.0	[1988AZA/SRE]

If the values of Schaefer and Gokcen [1981SCH/GOK] are assigned a double weight (because their careful measurements were described in detail and tabulated) and averaged with the mid-value from each of the other five sets, the value of $\Delta_f H_m^o$ (FeF_2, cr, 298.15 K) is − (712.1 ± 2.0) kJ·mol^{-1}. The uncertainty spans the average values, but does not include the uncertainties in the auxiliary data. The equation for $C_{p,m}^o$ (FeF_2, cr, T) is based on very sparse data at temperatures above 300 K, and it is estimated that uncertainties in the function selected in Section VIII.3.1.1.1 introduce an uncertainty of 1 - 2 kJ·mol^{-1} in the value for $\Delta_f H_m^o$ (FeF_2, cr, 298.15 K). However, this is outweighted by the much larger uncertainty introduced from the uncertainty (± 8.0 kJ·mol^{-1}) in the value of $\Delta_f H_m^o$ (NiF_2, cr, 298.15 K).

As discussed in Appendix A, the results of the transpiration experiments of Jellinek and Rudat [1928JEL/RUD] are questionable. However, when combined with CODATA auxiliary data (and values for Fe(cr) selected in Section V.2), values of − 704, − 711, and − 713 kJ·mol^{-1} are calculated for $\Delta_f H_m^o$ (FeF_2, cr, 298.15 K). These are independent of the value of $\Delta_f H_m^o$ (NiF_2, cr, 298.15 K), and are in moderately good agreement with the value calculated from the galvanic-cell results.

In the present review

$$\Delta_f H_m^o (FeF_2, \text{cr}, 298.15\ \text{K}) = -(712.1 \pm 8.5)\ \text{kJ·mol}^{-1}$$

is selected.

VIII.3.1.2 Iron(III) fluoride FeF_3(cr)

VIII.3.1.2.1 Entropy and heat capacity of FeF_3(cr)

There appears to be a limited amount of information on the heat capacity of FeF_3(cr). Bizette *et al.* [1965BIZ/MAI] presented a plot of the molar heat capacity of FeF_3(cr) for temperatures between 102 and 445 K, and reported a small, rather broad, thermal anomaly with a peak at 367 K. Differential calorimetry was used by Macheteau and Barberi [1974MAC/BAR] to determine the heat-capacity values of FeF_3(cr) at 473, 573 and 673 K. The reported value of $C^{\circ}_{p,\mathrm{m}}$ (FeF_3, cr) for 473.15 K does not mesh especially well with those for temperatures above 420 K from [1965BIZ/MAI], being ~ 5 J·K^{-1}·mol^{-1} greater than would be expected based on the earlier work.

A polynomial fit to the values of [1965BIZ/MAI] for temperatures from 250 to 320 K leads to 91.3 J·K^{-1}·mol^{-1} for $C^{\circ}_{p,\mathrm{m}}$ (FeF_3, cr, 298.15 K). This value is selected in the present review with an estimated uncertainty of 2.0 J·K^{-1}·mol^{-1}.

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{FeF_3(cr, 298.15\ K)}) = (91.3 \pm 2.0)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}.$$

However, the available data do not appear to be of sufficient consistency to select an equation for $C_p(T)$ for higher temperatures. Also, the lack of low-temperature heat-capacity measurements precludes evaluation of S°_{m} (FeF_3, cr, 298.15 K) by integration of C_p/T.

VIII.3.1.2.2 Enthalpy of formation of FeF_3(cr)

There have been several attempts to measure the enthalpy of formation of FeF_3(cr). Johnson [1981JOH] reported $\Delta_f H^{\circ}_{\mathrm{m}}$ (FeF_3, cr, 298.15 K) = − (989.6 ± 2.2) kJ·mol^{-1} from fluorine bomb-calorimetry measurements. Purvov *et al.*, who did similar measurements, reported $\Delta_f H^{\circ}_{\mathrm{m}}$ (FeF_3, cr, 298.15 K) = −(993.7 ± 2.5) kJ·mol^{-1}. Earlier, Jellinek and Rudat [1928JEL/RUD] studied the equilibrium

$$2\ \mathrm{FeF_3(cr)} + \mathrm{H_2(g)} \rightleftharpoons 2\ \mathrm{FeF_2(cr)} + 2\ \mathrm{HF(g)} \qquad \text{(VIII.22)}$$

at 623, 723 and 823 K, and Domange [1937DOM] reported equilibrium constants between 573 and 723 K for

$$2\ \mathrm{FeF_3(cr)} + 3\ \mathrm{H_2O(g)} \rightleftharpoons \mathrm{Fe_2O_3(cr)} + 6\ \mathrm{HF(g)}. \qquad \text{(VIII.23)}$$

Schaefer and Gokcen [1975SCH2], [1981SCH/GOK] reported measurements of the potential of the galvanic cell $\mathrm{Ni, Pt, (MgO + MgF_2) | CaF_2 | (FeF_3 + Fe_2O_3), Pt, Ni}$ for temperatures between 881 and 935 K. These were really measurements of the potential difference related to the quotient of the equilibrium constant $((K = p_{\mathrm{F_2}} / p_{\mathrm{O_2}}{}^{½}))$ for the reactions

$$½\ \mathrm{O_2(g)} + \mathrm{MgF_2(cr)} \rightleftharpoons \mathrm{MgO(cr)} + \mathrm{F_2(g)}$$

and

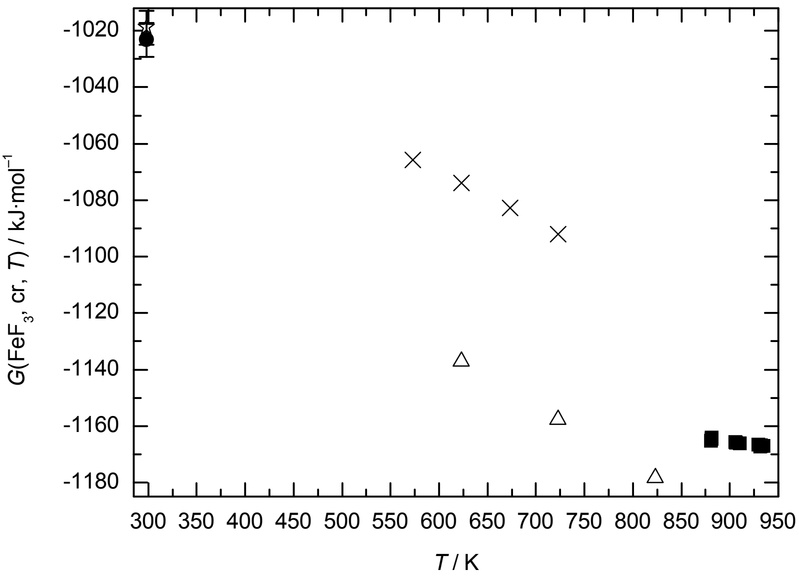
$$½\ \mathrm{O_2(g)} + ⅔\ \mathrm{FeF_3(cr)} \rightleftharpoons ⅓\ \mathrm{Fe_2O_3(cr)} + \mathrm{F_2(g)}$$

and required that $p_{\mathrm{O_2}}$ over the two compartments be equal and constant.

As discussed above, the entropy and heat-capacity values for FeF_3(cr) that are required for a good third-law extrapolation of the high-temperature results to 298.15 K are not available. However, the values of $G(T)$ calculated from the results of Domange [1937DOM] are much less negative than those from Jellinek and Rudat [1928JEL/RUD] at 623 and 723 K (by ~ 60 kJ·mol^{-1}, see Figure VIII-12 and Appendix A). The values of $G(T)$ from Schaefer and Gokcen [1981SCH/GOK] are fairly consistent with those of Jellinek and Rudat [1928JEL/RUD] for slightly lower temperatures, though the plots of $G(\text{FeF}_3, \text{cr}, T)$ *vs.* temperature show very different slopes.

Estimated entropies used with the enthalpy of formation values from the two calorimetry studies lead to values for $G(\text{FeF}_3, \text{cr}, 298.15\ \text{K})$ that are also shown in Figure VIII-12. However, there is no reasonable selection of values for $S^{\circ}_{m}(\text{FeF}_3, \text{cr}, 298.15\ \text{K})$ and $C_p(\text{FeF}_3, \text{cr}, T)$ that can make the bomb-calorimetry results of Johnson [1981JOH] and Pervov *et al.* [1981PER/MUR] compatible with the results of Jellinek and Rudat, and Schaefer and Gokcen. The results of Domange seem to be marginally compatible with the bomb-calorimetry results (within 10 kJ·mol^{-1}), though the differences are greater when CODATA [1989COX/WAG] thermodynamic quantities are used for HF(g), rather than the older JANAF values [1971STU/PRO], [1981JOH].

Figure VIII-12: Gibbs-energy values for $\text{FeF}_3(\text{cr})$ from 298.15 to 935 K based on bomb-calorimetric and equilibrium studies: Δ: [1928JEL/RUD], ×: [1937DOM], ✯: [1981JOH], ●: [1981PER/MUR], ■: [1981SCH/GOK]. Plotted values for 298.15 K from the bomb-calorimetry results include a contribution of $-(29.3 \pm 6.0)\ \text{kJ·mol}^{-1}$ based on an estimated value of $(98.3 \pm 20)\ \text{J·K}^{-1}\text{·mol}^{-1}$ for $S^{\circ}_{m}(\text{FeF}_3, \text{cr}, 298.15\ \text{K})$.



In the present review, for $\Delta_f H_m^\circ$ (FeF$_3$, cr, 298.15 K), the average value from the two bomb-calorimetry studies is selected and an uncertainty of ± 10 kJ·mol^{-1} is assigned because of the lack of agreement with the results of the other studies.

$$\Delta_f H_m^\circ (\mathrm{FeF_3, cr, 298.15\ K}) = -(991.7 \pm 10.0)\ \mathrm{kJ \cdot mol^{-1}}$$

Further corroboration of this selected value would be useful.

VIII.3.1.3 Iron fluoride hydrates

Information in the literature on solid iron-fluoride hydrates is limited. The Gmelin Handbook [1932GME] lists a tetrahydrate and octahydrate of FeF_2, but no thermodynamic data. For iron(III), there are two well-established polymorphs of $FeF_3 \cdot 3H_2O$ [1940NIE]; α-$FeF_3 \cdot 3H_2O$ is metastable with respect to β-$FeF_3 \cdot 3H_2O$ [1987DEZ/PAN] in saturated aqueous iron(III) fluoride solutions at and above room temperature. The β-trihydrate is converted to the monohydrate at ~450 K under nitrogen at 100 kPa [1972MAC/CHA]. Tananaev and Deichman carried out an extensive series of measurements [1946TAN/DEI] to establish the phase diagram for the FeF_3-HF-H_2O system at 298.15 K. At equilibrium in contact with $FeF_3 \cdot 3H_2O$ a solution containing no added HF(sln) was reported to contain 5.59 g FeF_3 per 100 g solution (0.525 mol·(kg H_2O)$^{-1}$). This work was described in considerable detail, and solutions with a wide range of HF(sln) concentrations also were used. However, the pH value of the equilibrium solution without added HF was not reported. A much lower total iron concentration value (0.0081 mol·kg^{-1} at 298.15 K) is calculated from the earlier work of Carter [1928CAR] for a solution with a pH value of 3. Several other groups have measured the solubility of β-$FeF_3 \cdot 3H_2O$ in aqueous HNO_3 and HNO_3-HF mixtures [1977KAN/KON], [1984TAK/KOS], [2006OST/RAS]. In the saturated solutions, both fluoride complexation and hydrolysis equilibria must be considered. In the present review, no values are selected for the thermodynamic quantities for $FeF_3 \cdot 3H_2O$.

VIII.3.2 Iron chloride compounds

VIII.3.2.1 Iron(II) chloride $FeCl_2$(cr)

VIII.3.2.1.1 Heat-capacity measurements for $FeCl_2$(cr)

There have been several sets of heat-capacity measurements for $FeCl_2$(cr) for temperatures above and below 300 K.

Drop-calorimetry measurements for $FeCl_2$(cr) have been reported by Krestovnikov and Karetnikov [1936KRE/KAR] (473 to 913 K) and by Moore [1943MOO] (386 to 1080 K). Low-temperature adiabatic calorimetry results were reported by Kelley and Moore [1943KEL/MOO]. Oetting [1960OET] (also [1961OET/GRE]) reported adiabatic calorimetry results at higher temperatures (~ 340 to 770 K) that are in good agreement with the results of Moore [1943MOO]. A function has been fitted to the appropriately weighted heat-capacity [1943KEL/MOO], [1960OET] and drop-calorimetry [1943MOO] values from 235 to 940 K:

$$[C^{\circ}_{p,\mathrm{m}}]^{950\,\mathrm{K}}_{240\,\mathrm{K}}\,(\mathrm{FeCl_2, cr}, T)/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = 78.796 + 9.212 \times 10^{-3}\,(T/\mathrm{K}) - 424935\,(T/\mathrm{K})^{-2}$$

and hence,

$$C^{\circ}_{p,\mathrm{m}}\,(\mathrm{FeCl_2, cr, 298.15\ K}) = (76.76 \pm 1.00)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

As discussed in Appendix A, the discordant results of Krestovnikov and Karetnikov [1936KRE/KAR] have not been used in this analysis.

Trapeznikowa and Schubnikow [1934TRA/SHU], [1935TRA/SCH] reported measurements done between 16 and 127 K, and identified a thermal anomaly near 23.5 K. The accuracy of their measurements was questioned by Kelley and Moore [1943KEL/MOO]. The latter authors carried out adiabatic calorimetry measurements from 53.2 to 295.0 K, and estimated $C^{\circ}_{p,\mathrm{m}}$ ($\mathrm{FeCl_2}$, cr, 298.15 K) to be (76.30 ± 0.20) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$. Lanusse *et al.* [1972LAN/CAR] showed a graph of their measurements (5 to 50 K); these measurements were done using single crystals.

Westrum also carried out a set of low-temperature adiabatic calorimetry measurements. Although the results apparently were never published as a paper or report, it seems that they were made available to several other research groups. Wilson and Gregory [1958WIL/GRE] reported that Westrum's study led to a value of S°_{m} ($\mathrm{FeCl_2}$, cr, 298.15 K) = 117.9 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$. Oetting [1960OET] reported that Westrum obtained a value of 76.8 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ for $C^{\circ}_{p,\mathrm{m}}$ ($\mathrm{FeCl_2}$, cr, 298.15 K). Stout [1961STO] even shows Westrum's data points (from two separate measurement sets) for temperatures between 19.1 and 28.8 K. These indicate that the anomaly is at 23.6 K, and that it makes approximately the same contribution to the entropy as suggested by the earlier study [1935TRA/SCH]. Unfortunately the published curve shows no data below 19.1 K, and thus information is unavailable for the low-temperature tail of the anomaly. The Westrum data were also used as part of the JANAF assessment [1998CHA] which proposed $C^{\circ}_{p,\mathrm{m}}$ ($\mathrm{FeCl_2}$, cr, 298.15 K) to be 76.66 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ and S°_{m} ($\mathrm{FeCl_2}$, cr, 298.15 K) = (117.947 ± 3.300) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$. Parker and Khodakovskii [1995PAR/KHO] selected S°_{m} ($\mathrm{FeCl_2}$, cr, 298.15 K) = (118.06 ± 0.20) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ without any particular discussion about the low uncertainty value.

The heat-capacity measuremenents of Lanusse *et al.* [1972LAN/CAR] suggested a slightly higher value, 24.8 K, for the Néel temperature [1960PAU], and there is good agreement with the limited available Westrum heat-capacity values [1961STO]. However, between 40 and 50 K the trend in heat capacities (and values of $C^{\circ}_{p,\mathrm{m}}/T$) is to slightly lower values than those reported both by Trapeznikowa and Schubnikow [1935TRA/SCH] and Kelley and Moore [1943KEL/MOO], by ~ 5% at 50 K).

Wong *et al.* [1982WON/MOL] reported thermal-relaxation measurements of the magnetic heat capacity for $FeCl_2$(cr) for temperatures between 16.9 and 26.9 K. The data are not suitable for resolving the differences between extrapolations from the earlier curves [1935TRA/SCH], [1961STO].

Kostryukova [1964KOS], [1969KOS] reported measurements of the specific heat of $FeCl_2$(cr) for temperatures between 1.8 and 4.0 K. Her plot of $C^{\circ}_{p,\mathrm{m}}(T)$ does not extrapolate smoothly to 0 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ at $T = 0$ K. The specific heats are small, and the contribution from 0 to 4 K to the value of S°_{m} ($FeCl_2$, cr, 298.15 K) is estimated here as (0.05 ± 0.02) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$. However, the results of Kostryukova do suggest that there may be an additional heat-capacity anomaly and entropy contribution below 1.8 K.

Figure VIII-13 illustrates the heat-capacity calorimetry results available for use in estimating the contributions to S°_{m} ($FeCl_2$, cr, 298.15 K) from 0 to 60 K. There is general agreement on the contributions for temperatures above 19 K. Integration of arbitrary functions fitted to the data of Lanusse *et al.* [1972LAN/CAR] indicate an entropy contribution of (6.1 ± 0.2) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ from 4 to 22 K. Several different extrapolation methods using only the Westrum data [1961STO] indicate an entropy contribution of (6.0 ± 0.2) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ from 4 to 22 K. If the Trapeznikowa and Schubnikow [1935TRA/SCH] data are also used, the contribution from 4 to 22 K is ~ 6.9 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$; less than 0.2 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ of the difference is from the integration between 19 and 22 K. The Lanusse *et al.* [1972LAN/CAR] and Westrum [1961STO] data are much less scattered than those of Trapeznikowa and Schubnikow [1935TRA/SCH]. In the present review we accept the entropy contribution derived from all three sets of data (2.28 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$) from 19 to 22 K, but use only the Lanusse *et al.* data for extrapolation to 4 K (~3.9 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ for the difference between S°_{m} ($FeCl_2$, 19 K) and S°_{m} ($FeCl_2$, 4 K)). Thus, in this review the overall entropy contribution from 4 to 22 K is estimated as (6.2 ± 0.7) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, and this leads to the assessed value

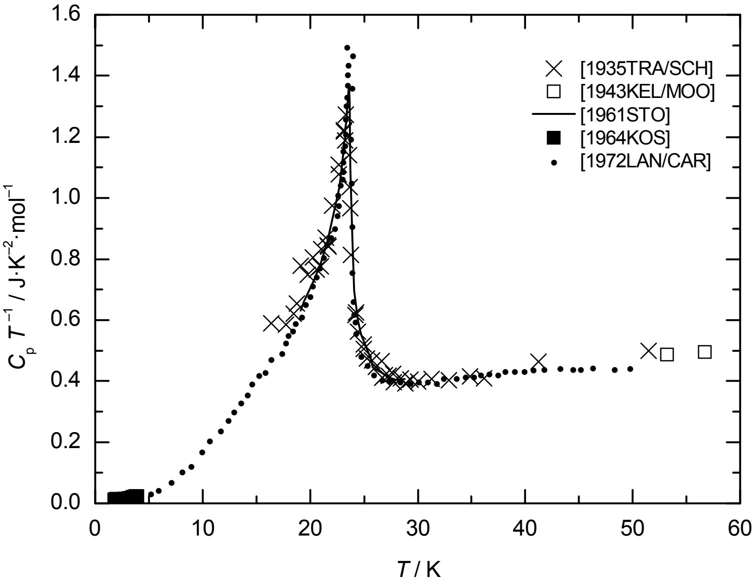
$$S^{\circ}_{\mathrm{m}}(\mathrm{FeCl_2, cr, 298.15\ K}) = (118.2 \pm 0.8)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

After evaluation of the available cycles for iron species and optimization to ensure consistency with other thermodynamic quantities for iron species (Chapter XI), this value is essentially unchanged.

The slightly adjusted value selected in the present review is:

$$S^{\circ}_{\mathrm{m}}(\mathrm{FeCl_2, cr, 298.15\ K}) = (118.2 \pm 0.5)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

Figure VIII-13: Experimental low-temperature heat-capacity results for $FeCl_2$(cr)



VIII.3.2.1.2 Enthalpy of formation of $FeCl_2$(cr)

The enthalpy of formation of $FeCl_2$(cr) was first determined calorimetrically by Thomsen [1908THO] from the heats of dissolution of the salt and Fe(cr) in aqueous hydrochloric acid. More precise measurements were done by Koehler and Coughlin [1959KOE/COU]. They determined the heat of dissolution of Fe(cr) in 4.360 m HCl(sln) and, by comparison with the experimentally determined heat of solution of $FeCl_2$(cr) in the acid medium at 303.15 K, a value of $-(341.84 \pm 0.48)$ kJ·mol^{-1} is calculated (Appendix A) for $\Delta_f H_m^\circ$ ($FeCl_2$, cr, 298.15 K). Evdokimova and Efimov [1989EVD/EFI2], [1989EFI/EVD] used a cycle in which Fe(cr) was oxidized by bromine and, with appropriate auxiliary data, a value of $\Delta_f H_m^\circ$ ($FeCl_2$, cr, 298.15 K) = $-(341.04 \pm 0.53)$ kJ·mol^{-1} is found. These values are in marginal agreement.

Another route to the value of the enthalpy of formation is provided by experiments to determine the equilibrium constant for the reaction:

$$FeCl_2(cr) + H_2(g) \rightleftharpoons Fe(cr) + 2\,HCl(g). \qquad (VIII.24)$$

Measurements have been reported by Sano [1938SAN], Kangro and Petersen [1950KAN/PET], and Novakov *et al.* [1952NOV/ORA], [1960NOV/MAK]. In the present review these have been subjected to a third-law reanalysis using the values of

S°_{m} at 298.15 K and $C^{\circ}_{p,m}(T)$ functions selected for Fe(α) and $FeCl_2$(cr) (Table VIII-12).

Table VIII-12: Thermodynamics of reduction of iron(II) chloride with hydrogen.

reference	T range	number of temperatures	$\Delta_r H^{\circ}_{m}$ ((VIII.24), 298.15 K)/kJ·mol^{-1}
[1938SAN]	769 to 868 K	9	154.4 ± 0.5
[1950KAN/PET]	757 to 935 K	18	159.5 ± 1.8
[1952NOV/ORA]	696 to 796 K	3	154.4 ± 2.3
[1960NOV/MAK]	673 to 823 K	4	157.6 ± 3.8

The uncertainties in $\Delta_r H^{\circ}_{m}$ ((VIII.24), 298.15 K) in Table VIII-12 are 2σ uncertainties based on the average values, and do not include an additional uncertainty of ~ ± 1 kJ·mol^{-1} based on the uncertainties in the entropy values (as that uncertainty is systematic, and common to all the values). The results are not in agreement within the statistical uncertainties. The simple (unweighted) average is 156.5 kJ·mol^{-1}, and an uncertainty of ± 4.6 kJ·mol^{-1} spans the values. If the uncertainty in the entropies is applied to the average value, this becomes (156.5 ± 4.7) kJ·mol^{-1}, and the value of $\Delta_f H^{\circ}_{m}$ ($FeCl_2$, cr, 298.15 K) is – (341.1 ± 4.7) kJ·mol^{-1}, in excellent agreement with the more accurate calorimetric results. As discussed in Appendix A, interpretation of measurements at temperatures above 950 K to generate thermodynamic quantities for 298.15 K is complicated by transitions in the condensed phases and by vaporization of $FeCl_2$ in the temperature range of the measurements (975 to 1278 K) [1927BAG], [1952SCH/KRE].

The uncertainties from the third-law analyses are relatively large. The weighted-average value for $\Delta_f H^{\circ}_{m}$ ($FeCl_2$, cr, 298.15 K) from the calorimetry studies of Koehler and Coughlin [1959KOE/COU] and Evdokimova and Efimov [1989EVD/EFI2] is – (341.48 ± 0.36) kJ·mol^{-1}.

However, in the preliminary optimization analysis of consistency between various thermodynamic quantities for iron species, the two calorimetric results for $\Delta_f H^{\circ}_{m}$ ($FeCl_2$, cr, 298.15 K), – (341.84 ± 0.48) and – (341.04 ± 0.53) kJ·mol^{-1}, are treated separately. After evaluation of the available cycles for iron species and optimization (Chapter XI), the value of $\Delta_f H^{\circ}_{m}$ ($FeCl_2$, cr, 298.15 K) becomes – (341.53 ± 0.50) kJ·mol^{-1}, in good agreement with the assessed values. This value is also consistent with the related experimentally determined and adjusted values for $\Delta_{sln} H^{\circ}_{m}$ ($FeCl_2$, cr, 298.15 K), (*cf.* Section VIII.3.5.1).

Therefore, the value selected in the present review is:

$$\Delta_f H^{\circ}_{m}(FeCl_2, cr, 298.15\ K), -(341.53 \pm 0.50)\ kJ\cdot mol^{-1}.$$

VIII.3.2.2 Hydrated iron(II) chlorides

The stable iron(II) chloride hydrate in equilibrium with the saturated aqueous solution at 298.15 K is the tetrahydrate [1881SAB], [1894LES]. Solubility measurements [1928SCH] indicate conversion to the hexahydrate at 285.5 K, and dehydration to the dihydrate at approximately 350 K. The dihydrate can also be prepared at lower temperatures in H_2O-HCl mixtures [1952SCH3]. Slightly lower solubilities were reported by Chou and Phan [1985CHO/PHA] (see Appendix A). There also is good evidence for the formation of the monohydrate [1949SCH]. There have been a number of thermogravimetric and differential scanning calorimetry experiments, [1960SHE/CHA], [1968LUM/JUN], [1971BOG/GOR], [1982ARG], [1988SHA/BAR]. Although several studies (*e.g.*, [1968LUM/JUN], [1971BOG/GOR]) suggest different dehydration sequences there is no consensus on other compounds formed at equilibrium in this system.

There are no low-temperature heat-capacity measurements for the hydrated solids that can be used to estimate entropies at 298.15 K, though there are papers on magnetic susceptibilities of the monohydrate [1998DEF/LEE] and dihydrate [1965NAR], [1988WEI/HIR] for temperatures below 80 K.

Osmotic-coefficient measurements for concentrated aqueous iron(II) chloride solutions have recently been reviewed [2004CHR], [2004MOO/HAG] and augmented [2004MOO/HAG]. From the equation for $\phi(m)$ from Moog *et al.* [2004MOO/HAG], [2004RUM/HAG], the calculated values of ϕ, $\gamma_{\pm}$, and a_{w} for the saturation molality, 5.087 $\mathrm{mol{\cdot}kg^{-1}}$, are 1.946, 2.540 and 0.586, respectively, and hence, a value of $-(17.16 \pm 0.40)\ \mathrm{kJ{\cdot}mol^{-1}}$ is determined for $\Delta_{\mathrm{r}}G^{\circ}_{\mathrm{m}}$ ((VIII.25), 298.15 K)

$$\mathrm{FeCl_2{\cdot}4H_2O(cr)} \rightleftharpoons \mathrm{Fe^{2+}} + 2\ \mathrm{Cl^-} + 4\ \mathrm{H_2O(l)}. \qquad \text{(VIII.25)}$$

The basis for the uncertainty estimate is discussed in Appendix A.

After evaluation of the available cycles for iron species and optimization to ensure the consistency with other thermodynamic quantities for iron species (Chapter XI), the value of $\Delta_{\mathrm{sln}}G^{\circ}_{\mathrm{m}}$ ($\mathrm{FeCl_2{\cdot}4H_2O}$, cr, 298.15 K) consistent with other quantities for iron species is $-(17.17 \pm 1.00)\ \mathrm{kJ{\cdot}mol^{-1}}$, essentially identical to the experimental result, but with a rather larger uncertainty.

Schäfer [1949SCH] reported a useful set of static and transpiration measurements of the vapour pressure of water above appropriate mixtures of $\mathrm{FeCl_2{\cdot}4H_2O(cr)}$, $\mathrm{FeCl_2{\cdot}2H_2O(cr)}$, $\mathrm{FeCl_2{\cdot}H_2O(cr)}$ and $\mathrm{FeCl_2(cr)}$ (see Table VIII-13). Reanalysis of the data is discussed in Appendix A.

$$\mathrm{FeCl_2{\cdot}4H_2O(cr)} \rightleftharpoons \mathrm{FeCl_2{\cdot}2H_2O(cr)} + 2\ \mathrm{H_2O(g)} \qquad \text{(VIII.26)}$$

$$\mathrm{FeCl_2{\cdot}2H_2O(cr)} \rightleftharpoons \mathrm{FeCl_2{\cdot}H_2O(cr)} + \mathrm{H_2O(g)} \qquad \text{(VIII.27)}$$

$$\mathrm{FeCl_2{\cdot}H_2O(cr)} \rightleftharpoons \mathrm{FeCl_2(cr)} + \mathrm{H_2O(g)} \qquad \text{(VIII.28)}$$

Table VIII-13: Thermodynamics of dehydration of iron(II) chloride hydrates based on the work of Schäfer [1949SCH].

Reaction	$\Delta_{\mathrm{dehyd}}G_{\mathrm{m}}$ (298.15 K)/kJ·mol^{-1}	$\Delta_{\mathrm{dehyd}}H_{\mathrm{m}}$ (298.15 K)/kJ·mol^{-1}
(VIII.26)	(23.58 ± 1.50)	(108.55 ± 2.00)
(VIII.27)	(18.97 ± 3.00)	(63.62 ± 4.00)
(VIII.28)	(25.00 ± 2.00)	(63.86 ± 3.00)

These lead to values of – (33.3 ± 3.9) kJ·mol^{-1} and – (60.0 ± 5.4) kJ·mol^{-1} for $\Delta_{\mathrm{r}}G^{\circ}_{\mathrm{m}}$ ((VIII.29), 298.15 K) and $\Delta_{\mathrm{r}}H^{\circ}_{\mathrm{m}}$ ((VIII.29), 298.15 K), respectively:

$$FeCl_2(cr) + 4\ H_2O(l) \rightleftharpoons FeCl_2{\cdot}4H_2O(cr). \quad \text{(VIII.29)}$$

After evaluation of the available cycles for iron species and optimization to ensure consistency with other thermodynamic quantities for iron species (Chapter XI), the calculated value of $\Delta_{\mathrm{dehyd}}G^{\circ}_{\mathrm{m}}$ ($FeCl_2{\cdot}4H_2O$, cr, 298.15 K) is (33.8 ± 1.0) kJ·mol^{-1}, essentially identical to the experimental result, but with a smaller uncertainty. The value consistent with this and the value of $\Delta_{\mathrm{sln}}G^{\circ}_{\mathrm{m}}$ ($FeCl_2{\cdot}4H_2O$, cr, 298.15 K) is:

$$\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}\ (FeCl_2{\cdot}4H_2O,\ \mathrm{cr},\ 298.15\ \mathrm{K}) = -\ (1284.55 \pm 0.71)\ \mathrm{kJ{\cdot}mol^{-1}}$$

and this value is selected.

The difference in the heats of solution of $FeCl_2$(cr) and $FeCl_2{\cdot}4H_2O$(cr) as determined by Thomsen [1908THO] (see Appendix A) leads to a value of – (64.4 ± 4.0) kJ·mol^{-1} for $\Delta_{\mathrm{r}}H^{\circ}_{\mathrm{m}}$ ((VIII.29), 298.15 K), which is consistent within the uncertainties. The weighted average of this and the value from the work of Schäfer [1949SCH] for $\Delta_{\mathrm{r}}H^{\circ}_{\mathrm{m}}$ ((VIII.29), 298.15 K), is – (62.8 ± 3.2) kJ·mol^{-1}. From this value of $\Delta_{\mathrm{r}}H^{\circ}_{\mathrm{m}}$ ((VIII.29), 298.15 K), the value

$$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}\ (FeCl_2{\cdot}4H_2O,\ \mathrm{cr},\ 298.15\ \mathrm{K}) = -\ (1547.65 \pm 3.24)\ \mathrm{kJ{\cdot}mol^{-1}}$$

is calculated. For the lower hydrates no values are selected for $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ (298.15 K); however, the values from Schäfer [1949SCH] are used to calculate

$$\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}\ (FeCl_2{\cdot}H_2O,\ \mathrm{cr},\ 298.15\ \mathrm{K}) = -\ (803.80 \pm 1.66)\ \mathrm{kJ{\cdot}mol^{-1}}$$

and

$$\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}\ (FeCl_2{\cdot}2H_2O,\ \mathrm{cr},\ 298.15\ \mathrm{K}) = -\ (505.77 \pm 1.07)\ \mathrm{kJ{\cdot}mol^{-1}}.$$

VIII.3.2.3 Iron(III) chloride $FeCl_3$(cr)

VIII.3.2.3.1 Heat capacity of $FeCl_3$(cr)

Todd and Coughlin [1951TOD/COU] reported heat-capacity measurements (adiabatic calorimetry) for temperatures from 52.9 to 296.8 K, and drop-calorimetry results from

339.6 to 536.2 K. The drop-calorimetry results are rather scattered, and do not mesh particularly well with the low-temperature results near 300 K. Stuve *et al.* [1980STU/FER], using an adiabatic calorimeter within a helium cryostat, obtained heat-capacity values for temperatures from 4.68 to 307.56 K. The heat-capacity curve for $FeCl_3$(cr) showed a sharp λ-type thermal anomaly, with a maximum at (8.34 ± 0.05) K. The heat capacity and entropy at 298.15 K were estimated by Stuve *et al.* [1980STU/FER] as 96.94 and (147.82 ± 0.29) $J\cdot K^{-1}\cdot mol^{-1}$, respectively. The two sets of low-temperature heat capacities are in good agreement except for temperatures above 220 K where the values from [1980STU/FER] are systematically greater.

A single function has been fitted to the heat capacities (σ estimated as 0.42 $J\cdot K^{-1}\cdot mol^{-1}$) and drop-calorimetry values (σ estimated as 1.05 $kJ\cdot mol^{-1}$) from 201 to 536.2 K. Values from drop-calorimetry experiments that showed premelting effects were eliminated. The selected values are

$$[C^{\circ}_{p,\mathrm{m}}]^{550\,\mathrm{K}}_{200\,\mathrm{K}}(\mathrm{FeCl_3, cr}, T)/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = 69.173 + 9.362 \times 10^{-2}\,(T/\mathrm{K}) - 43619\,(T/\mathrm{K})^{-2}$$

and

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{FeCl_3, cr, 298.15\,K}) = (96.59 \pm 1.00)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

A series of functions was fitted to the experimentally determined values of $C^{\circ}_{p,\mathrm{m}}(T)$ for temperatures from 4.7 to 220 K. The functions were integrated, and the sum of the entropy contributions over the temperature range 10 to 298.15 K was found to be 135.97 $J\cdot K^{-1}\cdot mol^{-1}$. Stuve *et al.* [1980STU/FER] reported a very similar value, 136.24 $J\cdot K^{-1}\cdot mol^{-1}$. As discussed in Appendix A, in the present review the entropy contribution from 0 to 10 K is estimated as (8.50 ± 0.70) $J\cdot K^{-1}\cdot mol^{-1}$. Therefore, the value

$$S^{\circ}_{\mathrm{m}}(\mathrm{FeCl_3, cr, 298.15\,K}) = (145.47 \pm 0.80)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

is chosen.

VIII.3.2.3.2 Enthalpy of formation of $FeCl_3$(cr)

There have been four calorimetric determinations of the enthalpy of formation of $FeCl_3$(cr). Roth and Wienert [1934ROT/WIE] measured the heat of dissolution of Fe(cr) in 17.3 m HCl(sln) at 293.8_5 K (20.7 °C), followed by oxidation of the iron(II) with peroxide to Fe(III). This can be used [1934ROT/WIE] with the experimentally determined heat of solution of $FeCl_3$(cr) at the same temperature and in the same acid medium [1935KAN/FLU] to calculate a value for $\Delta_f H^{\circ}_{\mathrm{m}}$ ($FeCl_3$, cr, 298.15 K); the value, as recalculated in the present review (Appendix A) is – (394.14 ± 2.19) $kJ\cdot mol^{-1}$. Koehler and Coughlin [1959KOE/COU] carried out similar measurements in 4.360 m HCl(sln) at 303.15 K, and from these a value of – (399.51 ± 0.56) $kJ\cdot mol^{-1}$ is calculated for 298.15 K (Appendix A). Evdokimova and Efimov [1989EVD/EFI2], [1989EFI/EVD] used a cycle in which KBr(cr), KCl(cr) and $FeCl_3$(cr) were dissolved in an aqueous solution of KBr, Br_2 and HBr, and then Fe(cr) was oxidized with bromine in a similar solution. Their results give a value of – (395.57 ± 0.74) kJ·mol^{-1} for $\Delta_f H^o_m$ ($FeCl_3$, cr, 298.15 K). Lavut *et al.* [1984LAV/TIM2] used combustion calorimetry, and their results from direct chlorination of Fe(cr) lead to a value of – (396.00 ± 0.14) kJ·mol^{-1} for $\Delta_f H^o_m$ ($FeCl_3$, cr, 298.15 K). Except for the value from Koehler and Coughlin [1959KOE/COU], these values are concordant.

There are large uncertainties in extrapolation of the heats of solution of 3:1 electrolytes to I = 0 (with additional problems from hydrolysis and complexation [1984NOV/BEL]), and heat of solution experiments from the dissolution of $FeCl_3$(cr) in water [1893LEM], [1935KAN/FLU], [1950BOB/LAR], [1985SOL/MON] cannot easily be used to confirm or refute the other calorimetry results.

As discussed in Appendix A and Section VIII.3.5.4, Parker and Khodakhovskii [1995PAR/KHO] supplied data from a more recent study of the heat of dissolution of $FeCl_3$(cr) in $HClO_4$(sln). An attempt was made to incorporate a recalculated value for $\Delta_{sln} H^o_m$ ($FeCl_3$, cr, 298.15 K) into the evaluation of the available cycles for iron species and optimization of thermodynamic quantities for iron species (Chapter XI).

Based on the optimization cycles, the inconsistent result from Koehler and Coughlin [1959KOE/COU] eventually was omitted from the analysis. The value for $\Delta_f H^o_m$ ($FeCl_3$, cr, 298.15 K) that is consistent with other thermodynamic quantities selected for iron species in this review is:

$$\Delta_f H^o_m (\text{FeCl}_3, \text{cr}, 298.15\ \text{K}) = -(395.98 \pm 0.09)\ \text{kJ·mol}^{-1}.$$

Ideally, any selected value for $\Delta_f H^o_m$ ($FeCl_3$, cr, 298.15 K) should also be rationalized with results from high-temperature equilibrium studies [1925MAI], [1925STI], [1943WAG/STE], [1949RIN], [1950KAN/PET], [1953SCH/OEH], [1983RUS/GRE] in conjunction with the selected value for $\Delta_f H^o_m$ ($FeCl_2$, cr, 298.15 K). However, no evaluation of the thermodynamic quantities for the gas-phase iron-halide species is done in the present review.

VIII.3.2.4 Hydrated iron(III) chlorides

The $FeCl_3$-H_2O and $FeCl_3$-HCl-H_2O solid-liquid systems are very complex, and have been the subject of excellent studies by Roozeboom and Schreinemakers [1892ROO], [1892ROO2], [1894ROO/SCH] and Linke [1956LIN]. $FeCl_3·10H_2O$ is formed only below 273.15 K, and $FeCl_3·6H_2O$, $FeCl_3·3.5H_2O$, $FeCl_3·2.5H_2O$ and $FeCl_3·2H_2O$ were found to melt congruently, at 310.15, 305.65, 329.15 and 350.65 K (37, 32.5, 56 and 73.5 °C), respectively. The stable iron(III) chloride hydrate in contact with saturated aqueous solutions at 298.15 K is $FeCl_3·6H_2O$.

Early measurements of the heat of solution of $FeCl_3·2.5H_2O$ and $FeCl_3·6.0H_2O$ were done by Sabatier [1881SAB], [1889SAB] but lack sufficient experimental details to be used. Novikov *et al.* [1984NOV/BEL] measured the heats of solution of $FeCl_3$(cr) and $FeCl_3·nH_2O$(cr) (n = 2.0, 2.5, 3.5, 6.0) in 0.67 m $HClO_4$(sln) to produce solutions with a final iron concentration of ~ 0.015 M. As discussed in Appendix A, using the enthalpies of dissolution and the partial molar enthalpy of formation of H_2O in this perchloric acid medium [1965PAR], [1989COX/WAG] (– (285.826 ± 0.041) kJ·mol^{-1}), the following enthalpy differences are calculated

$$\Delta_f H_m^\circ(\mathrm{FeCl_3}) - \Delta_f H_m^\circ(\mathrm{FeCl_3{\cdot}2.0H_2O}) = (615.47 \pm 1.50)\ \mathrm{kJ{\cdot}mol^{-1}}$$

$$\Delta_f H_m^\circ(\mathrm{FeCl_3}) - \Delta_f H_m^\circ(\mathrm{FeCl_3{\cdot}2.5H_2O}) = (766.41 \pm 1.50)\ \mathrm{kJ{\cdot}mol^{-1}}$$

$$\Delta_f H_m^\circ(\mathrm{FeCl_3}) - \Delta_f H_m^\circ(\mathrm{FeCl_3{\cdot}3.5H_2O}) = (1077.44 \pm 1.50)\ \mathrm{kJ{\cdot}mol^{-1}}$$

$$\Delta_f H_m^\circ(\mathrm{FeCl_3}) - \Delta_f H_m^\circ(\mathrm{FeCl_3{\cdot}6.0H_2O}) = (1825.95 \pm 1.50)\ \mathrm{kJ{\cdot}mol^{-1}},$$

From these and the selected value of $\Delta_f H_m^\circ$ ($FeCl_3$, cr, 298.15 K)

$$\Delta_f H_m^\circ(\mathrm{FeCl_3{\cdot}2.0H_2O}) = -(1011.45 \pm 1.50)\ \mathrm{kJ{\cdot}mol^{-1}}$$

$$\Delta_f H_m^\circ(\mathrm{FeCl_3{\cdot}2.5H_2O}) = -(1162.39 \pm 1.50)\ \mathrm{kJ{\cdot}mol^{-1}}$$

$$\Delta_f H_m^\circ(\mathrm{FeCl_3{\cdot}3.5H_2O}) = -(1473.42 \pm 1.50)\ \mathrm{kJ{\cdot}mol^{-1}}$$

$$\Delta_f H_m^\circ(\mathrm{FeCl_3{\cdot}6.0H_2O}) = -(2221.93 \pm 1.50)\ \mathrm{kJ{\cdot}mol^{-1}},$$

where the uncertainties are 95% confidence limits.

Rustad and Gregory [1988RUS/GRE] reported the formation of a condensed-phase iron(III) chloride hydrate (at 415 to 475 K) for which they proposed the formula $Fe_2(H_2O)_3Cl_6$(l). In the present review, no thermodynamic quantities are selected for this species.

Although there are no low-temperature heat-capacity measurements for the hydrated solids that can be used to estimate entropies at 298.15 K, Meisingset and Grønvold [1986MEI/GRO] carried out adiabatic-shield calorimetry to measure the heat capacities of a sample of $FeCl_3{\cdot}5.70H_2O$ (291.9 to 310.4 K). From their measurements,

$$C_{p,m}^\circ(\mathrm{FeCl_3{\cdot}6.00H_2O, cr, 298.15\ K}) = (342 \pm 4)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}},$$

and $\Delta_{fus} H_m^\circ$ ($FeCl_3{\cdot}6H_2O$, 310.0 K) = (54.5 ± 0.6) kJ·mol^{-1} was estimated.

VIII.3.2.4.1 FeOCl(cr)

VIII.3.2.4.1.1 Heat capacities and entropy

Based on the low-temperature adiabatic calorimetry and drop-calorimetry work of Stuve *et al.* [1980STU/FER] (see Appendix A)

$$C_{p,m}^\circ(\mathrm{FeOCl, cr}, T)/\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}} = 67.032 + 29.037 \times 10^{-3}\,(T/\mathrm{K}) - 4.619 \times 10^{5}\,(T/\mathrm{K})^{-2}$$

and hence,

$$C_{p,m}^\circ(\mathrm{FeOCl, cr, 298.15\ K}) = (70.49 \pm 0.20)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}.$$

The value

$$S^{\circ}_{m}\text{ (FeOCl, cr, 298.15 K)} = (82.70 \pm 0.20)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

is selected based on the same data.

VIII.3.2.4.1.2 Enthalpy of formation of FeOCl(cr)

Stuve *et al.* [1980STU/FER] carried out solution-calorimetry measurements that lead to a value of – (11.56 ± 0.24) $\text{kJ}\cdot\text{mol}^{-1}$ for $\Delta_{r}H^{\circ}_{m}$ (VIII.30).

$$FeCl_3(cr) + ½\ O_2(g) \rightleftharpoons FeOCl(cr) + Cl_2(g) \qquad \text{(VIII.30)}$$

Based on the work of Schäfer *et al.* [1956SCH/WIT] a value of – (8.25 ± 2.00) $\text{kJ}\cdot\text{mol}^{-1}$ is calculated for $\Delta_{r}H^{\circ}_{m}$ ((VIII.30), 298.15 K). There is no apparent reason to reject either value, and in the present review the average of these two results – (9.90 ± 3.00) $\text{kJ}\cdot\text{mol}^{-1}$ is used, and the uncertainty is an estimate.

From this, and the value selected above for $\Delta_{f}H^{\circ}_{m}$ ($FeCl_3$, cr, 298.15 K),

$$\Delta_{f}H^{\circ}_{m}\text{ (FeOCl, cr, 298.15 K)} = -\ (405.88 \pm 3.00)\ \text{kJ}\cdot\text{mol}^{-1}.$$

VIII.3.2.4.2 Mixed oxidation state iron chlorides

There have been several papers on the properties and thermodynamic quantities for the "green rust one" chloride compound [1993REF/GEN], [1998GEN/BOU], [2006GEN/RUB]. Thermodynamic quantities can be based on voltammetric measurements of the electrochemical potential at which suspensions of $Fe(OH)_2$ are oxidized in aqueous solutions [1993REF/GEN]. The chloride "green rust" has a more narrow range of stability than the carbonate-containing "green rust one" (Section X.1.2.2.2) or sulfate-containing "green rust two" (Section IX.1.2.2.6). The electrochemical studies [1993REF/GEN] (recalculated as described in Appendix A) indicate that for

$$4\ Fe(OH)_2(s) + Cl^{-} + H^{+} + n\ H_2O \rightarrow (Fe^{III})(Fe^{II})_3(OH)_8Cl\cdot nH_2O + ½\ H_2(g) \qquad \text{(VIII.31)}$$

$\Delta_{r}G^{\circ}_{m}$ (VIII.31) is $-(53.2 \pm 2.0)$ $\text{kJ}\cdot\text{mol}^{-1}$ at 298.15 K. However, in the present review no values are selected for the thermodynamic quantities of this chloridohydroxido complex.

VIII.3.2.4.3 Hydrated iron perchlorates

Lindstrand [1936LIN] carried out a series of experiments to characterize the hydrated perchlorate salts of Fe(II) and Fe(III). Solubilities (> 2 $\text{mol}\cdot\text{L}^{-1}$ in all cases) were reported for temperatures between 273.15 and 333.15 K. The stable solid in contact with a saturated aqueous solution of iron(II) perchlorate at 298.15 K is $Fe(ClO_4)_2\cdot 6H_2O$, and the stable solid in the iron(III) perchlorate system is $Fe(ClO_4)_3\cdot 10H_2O$. Above 315 K in contact with saturated aqueous solutions of iron(III), dehydration to $Fe(ClO_4)_3\cdot 9H_2O$ occurs, and the same lower hydrate is formed from the decahydrate at 293 K in concentrated (> 8.5 $\text{mol}\cdot\text{L}^{-1}$) aqueous solutions of perchloric acid. Equilibration of the iron(II) and iron(III) solids over highly concentrated aqueous solutions of H_2SO_4 at 291 K resulted in formation of less hydrated solids ($Fe(ClO_4)_2\cdot 5H_2O$, $Fe(ClO_4)_2\cdot 4H_2O$

and $Fe(ClO_4)_2\cdot 2H_2O$ (under vacuum), and $Fe(ClO_4)_3\cdot 6H_2O$). Equilibrium water-vapour pressures for transformation of $Fe(ClO_4)_2\cdot 6H_2O$ to $Fe(ClO_4)_2\cdot 5H_2O$ (20 Pa), $Fe(ClO_4)_3\cdot 10H_2O$ to $Fe(ClO_4)_3\cdot 9H_2O$ (410 Pa), and $Fe(ClO_4)_3\cdot 9H_2O$ to $Fe(ClO_4)_3\cdot 6H_2O$ (85 Pa) were also reported for 293 K. In the present review, no thermodynamic data are selected for any of these solids.

VIII.3.3 Iron bromide compounds

VIII.3.3.1 Iron(II) bromide $FeBr_2$(cr)

VIII.3.3.1.1 Heat capacity of $FeBr_2$(cr)

Miljutin and Nachimovitsch [1940MIL/NAC] measured the heat capacity of $FeBr_2$(cr) from 12 to 110 K. The authors reported two maxima, at 14.1 and 21.8 K. Lanusse *et al.* [1972LAN/CAR] measured the heat capacity of single crystals between 4 and 70 K, and also reported the sharp maximum at the Néel temperature (14.2 K). However, their results show no indication of a second maximum. Aruga Katori *et al.* [1997ARU/KAT] also reported measurements for temperatures below 20 K, and those show the sharp maximum at 14.2 K. According to Gregory and MacLaren [1955GRE/MAC], and Christian and Gregory [1967CHR/GRE], Westrum carried out a series of measurements for temperatures between 5 and 303 K. These appear never to have been published, though Gregory and O'Neal [1959GRE/NEA] reported a value of 79.75 $J\cdot K^{-1}\cdot mol^{-1}$ for $C^{o}_{p,m}$ ($FeBr_2$, cr, 298.15 K) based on Westrum's work.

O'Neal [1957NEA] carried out adiabatic calorimetry measurements from 330 to 720 K. Above 630 K, an apparent second-order λ-type transition was found. The magnitude of the transition heat obtained using different samples was inconsistent (0.2 to 0.6 $kJ\cdot mol^{-1}$). Despite extensive experiments, the author was unable to establish the cause of the anomaly, although it did appear to be related to structural ordering. Based on the measurements at lower temperatures, an equation for $C^{o}_{p,m}$ ($FeBr_2$, cr, T)/ $J\cdot K^{-1}\cdot mol^{-1}$:

$$[C^{o}_{p,m}]^{633\,K}_{323\,K}\,(FeBr_2,\,cr,\,T)/J\cdot K^{-1}\cdot mol^{-1} = 73.597 + 22.26\times 10^{-3}\,(T/K)$$

was proposed. This equation is accepted in the present review for the temperature range 298.15 to 630 K, though it leads to a value of

$$C^{o}_{p,m}\,(FeBr_2,\,cr,\,298.15\,K) = (80.23 \pm 1.20)\ J\cdot K^{-1}\cdot mol^{-1}\ ,$$

slightly greater than the value from Westrum's unpublished study.

VIII.3.3.1.2 Entropy and enthalpy of formation of $FeBr_2$(cr)

Christian and Gregory [1967CHR/GRE] reported 140.6 $J\cdot K^{-1}\cdot mol^{-1}$ (33.6 $cal\cdot K^{-1}\cdot mol^{-1}$) for S^{o}_{m} ($FeBr_2$, cr, 298.15 K) from the unpublished Westrum study. JANAF (1966) [1971STU/PRO], [1998CHA] reported 140.666 $J\cdot K^{-1}\cdot mol^{-1}$, apparently from the same source (33.62 $cal\cdot K^{-1}\cdot mol^{-1}$, as also cited by Gregory and MacLaren [1955GRE/MAC]).

There is no indication in these sources of the magnitude of the contribution to S°_{m} from the heat-capacity anomaly near 14 K. However, the work of Aruga Katori *et al.* [1997ARU/KAT] indicates that the contribution from the anomaly [1957BIZ/TER], [1972LAN/CAR] is of the order of 2 - 4 J·K^{-1}·mol^{-1}. Aside from the unpublished study or equivalent data from 50 to 300 K, any evaluation of S°_{m} from C_p data is only a rough estimate.

The enthalpy of formation for $FeBr_2$(cr) was determined by Hieber and Woerner [1934HIE/WOE] from the heats of dissolution of Fe(cr), Br_2(l) and $FeBr_2$(cr) in aqueous KBr at 273.15 K ($\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($FeBr_2$, cr, 298.15 K) = – (251.4 ± 3.3) kJ·mol^{-1}). This appears to be part of the basis for JANAF and US-NBS selections. Similarly, Evdokimova and Efimov [1989EVD/EFI2] carried out oxidation of Fe(cr) by bromine in aqueous HBr, KBr, and calculated $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($FeBr_2$, cr, 298.15 K) = – (244.73 ± 0.22) kJ·mol^{-1}.

Equilibria between $FeBr_2$(cr, l) and gas-phase species in the iron-bromine system are complex. The simple gas-phase species at temperatures well below the melting point of $FeBr_2$(cr), 964 K, include $FeBr_2$, $FeBr_3$ and Fe_2Br_6 [1955GRE/MAC], [1955MAC/GRE], but Fe_2Br_4(g) has been reported to form at higher temperatures [1959POR/SCH]. Spectroscopic and total equilibrium pressure studies of the reaction

$$\alpha\text{-}Fe_2O_3 + 6\ HBr(g) \rightleftharpoons 2\ FeBr_2(cr) + 3\ H_2O(g) + Br_2(g)$$

[1967CHR/GRE] are further complicated by formation of a volatile hydrate, identified as $Fe(H_2O)Br_3$(g) by Gregory [1988GRE]. The formation of this species would increase “the total concentration of iron(III) bromide molecules in the vapour, and hence the vapour-phase absorbance” [1988GRE]. Therefore, attempted measurements of such equilibria are of limited assistance in helping to resolve inconsistencies in the thermodynamic quantities for the condensed phases. Novikov *et al.* [1952NOV/ORA] reported equilibrium constants for

$$FeBr_2(cr) + H_2(g) \rightleftharpoons Fe(cr) + 2\ HBr(g)$$

from 726 to 896 K. If their results are used in third-law calculations assuming no vapour-phase iron-containing species are present (see Appendix A), they suggest that the $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($FeBr_2$, cr, 298.15 K) value of Evdokimova and Efimov [1989EVD/EFI2] is statistically compatible with the “Westrum” entropy value ((137 ± 5) J·K^{-1}·mol^{-1} from the third-law calculation as compared to the “Westrum” value of 140.6 J·K^{-1}·mol^{-1} *fide* [1967CHR/GRE]). However, combining the Novikov *et al.* results with those of Hieber and Woerner [1934HIE/WOE] leads to a much lower (and probably inaccurate) estimate of S°_{m} ($FeBr_2$, cr, 298.15 K), (~ 129 ± 4) J·K^{-1}·mol^{-1}.

On the basis of the marginal compatibility of the results from the studies of Evdokimova and Efimov [1989EVD/EFI2], Novikov *et al.* [1952NOV/ORA] and Westrum *fide* [1967CHR/GRE], the value

$$S^{\circ}_{\mathrm{m}}\,(\mathrm{FeBr_2, cr, 298.15\ K}) = (140 \pm 3)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

is selected, and $-(245 \pm 4)$ kJ·mol^{-1} is used as the preliminary assessed value for $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($FeBr_2$, cr, 298.15 K). Uncertainties are estimated in the present review.

After evaluation of the available thermodynamic cycles for iron species and optimization of the thermodynamic quantities for iron species (Chapter XI), this value is adjusted to

$$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}\,(\mathrm{FeBr_2, cr, 298.15\ K}) = -(247.50 \pm 0.99)\ \mathrm{kJ{\cdot}mol^{-1}},$$

in agreement with the assessed value within the uncertainty limits.

VIII.3.3.2 Hydrated iron(II) bromides

The $FeBr_2$-H_2O system was the subject of a study by Schimmel [1929SCH] who identified a series of hydrates. Transition temperatures between $FeBr_2{\cdot}9H_2O$, $FeBr_2{\cdot}6H_2O$, $FeBr_2{\cdot}4H_2O$, and $FeBr_2{\cdot}2H_2O$ in saturated solutions were reported, but no other thermodynamic information appears to be available. The stable iron(II) bromide hydrate in contact with saturated aqueous solutions for temperatures between 244 and 322 K is $FeBr_2{\cdot}6H_2O$.

VIII.3.3.3 Iron(III) bromide $FeBr_3$(cr)

At 298.15 K, anhydrous $FeBr_3$(cr) is reported to be unstable with respect to decomposition to $FeBr_2$(cr) and Br_2(g) unless "the bromine pressure in the system is greater than 0.5 mm" (*i.e.*, ~ 70 Pa) [1950GRE/THA]. Gregory and Thackrey measured the extent of the decomposition reaction at equilibrium as a function of temperature from 340 to 411 K. Based on the values selected above for $FeBr_2$(cr), this leads to $-(263.4 \pm 5.0)$ kJ·mol^{-1} for $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($FeBr_3$, cr, 298.15 K) and (180.2 ± 10.0) J·K^{-1}·mol^{-1} for S°_{m} ($FeBr_3$, cr, 298.15 K) (see Appendix A). From solution calorimetry Efimov and Evdokimova [1989EFI/EVD] determined $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($FeBr_3$, cr, 298.15 K) = $-(262.63 \pm 0.20)$ kJ·mol^{-1}. The values are in good agreement.

In the present review the value of $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($FeBr_3$, cr, 298.15 K) from Efimov and Evdokimova [1989EFI/EVD] is chosen as a preliminary value, but with an increased uncertainty, $-(262.63 \pm 1.00)$ kJ·mol^{-1}.

After evaluation of the available cycles for iron species and optimization to ensure consistency with other thermodynamic quantities for iron species (Chapter XI), this value is adjusted to

$$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}\,(\mathrm{FeBr_3, cr, 298.15\ K}) = -(262.59 \pm 0.63)\ \mathrm{kJ{\cdot}mol^{-1}}$$

in excellent agreement with the assessed value.

When this value is used as a constraint,

$$S^{\circ}_{\mathrm{m}}\,(\mathrm{FeBr_3, cr, 298.15\ K}) = (182.2 \pm 8.0)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}},$$

based on the work of Gregory and Thackrey [1950GRE/THA], is calculated and selected. The uncertainty is an estimate.

VIII.3.3.4 Hydrated iron(III) bromides

Gregory [1988GRE] reported the formation of a condensed-phase iron(III) hydrate for which he proposed the formula $Fe_2(H_2O)_3Br_6$ (or $Fe(H_2O)_6(FeBr_4)_3$). Although there is a discussion of the temperature dependence of the equilibrium constant for the formation of this phase with $FeBr_2$(cr), Br_2(g) and H_2O(g) near 600 K, no thermodynamic quantities are selected in the present review.

VIII.3.4 Iron iodide compounds

VIII.3.4.1 Iron(II) iodide FeI_2(cr)

VIII.3.4.1.1 Heat capacity of FeI_2(cr)

Miljutin and Parfenova [1940MIL/PAR] measured the heat capacity of FeI_2(cr) from 11.5 to 129.2 K. Their results show a broad, shallow peak in $C^{\circ}_{p,\mathrm{m}}(T)$ near 90 K. A magnetic transition has been reported at 10 K [1957BIZ/TER], but there do not appear to have been any corresponding heat-capacity measurements. Oetting and Gregory [1961OET/GRE2] carried out adiabatic-calorimetry measurements between 340 and 770 K. A thermal anomaly, possibly related to a structural change, was found near 650 K, though the magnitude of the anomaly appeared to be related to impurities in the solid [1966ZAU/GRE]. The results also indicate that $C^{\circ}_{p,\mathrm{m}}$ (FeI_2, cr) increases more rapidly with increasing temperature above 650 K.

Oetting and Gregory proposed an equation for $C^{\circ}_{p,\mathrm{m}}$ (FeI_2, cr, T) over the temperature range 323 to 633 K. In the present review this equation is accepted over a slightly expanded temperature range:

$$[C^{\circ}_{p,\mathrm{m}}]^{633\,\mathrm{K}}_{298\,\mathrm{K}}(\mathrm{FeI_2, cr}, T)/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = 82.969 + 2.427 \times 10^{-3}\,(T/\mathrm{K})$$

and hence,

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{FeI_2, cr, 298.15\ K}) = (83.69 \pm 5.00)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

The authors [1961OET/GRE2] indicated that the increase in $C^{\circ}_{p,\mathrm{m}}$ with temperature was more rapid “than normally expected”. Therefore, extrapolation of $C^{\circ}_{p,\mathrm{m}}$ to temperatures beyond those of the measurements (*i.e.*, $T \geq 770$ K) is inadvisable. An expression for the heat capacity suitable only for temperatures between 700 and 765 K is $[C^{\circ}_{p,\mathrm{m}}]^{765\,\mathrm{K}}_{700\,\mathrm{K}} = (12.50 + 0.153\,(T/\mathrm{K}))\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$. Because of variations in the thermal anomaly near 650 K, noted above, no heat-capacity expression can be recommended for temperatures between 633 and 700 K.

VIII.3.4.1.2 Enthalpy of formation of FeI_2(cr)

Values of $\Delta_f H_m^o$ (FeI_2, cr, 298.15 K) and S_m^o (FeI_2, cr, 298.15 K) from several standard compilations are in poor agreement. The values from the JANAF tables [1998CHA] (as compiled in 1966, and later also used by Barin and Knacke [1973BAR/KNA]) are – (104.6 ± 8.4) kJ·mol^{-1}, and (167.4 ± 8.4) J·K^{-1}·mol^{-1}. The JANAF values are based primarily on a re-evaluation of the high-temperature study of Zaugg and Gregory [1966ZAU/GRE], [1966ZAU/GRE2], who reported – 100.4 kJ·mol^{-1} and 171 J·K^{-1}·mol^{-1}. The 1979 compilation of Kubaschewski and Alcock [1979KUB/ALC] lists – (116.3 ± 8.4) kJ·mol^{-1} and (169.9 ± 3.3) J·K^{-1}·mol^{-1}, values based primarily on [1966ZAU/GRE] and measurements of heats of reaction in aqueous solution by Hieber and Woerner [1934HIE/WOE] (– 125.9 kJ·mol^{-1}, see Appendix A). The US-NBS [1982WAG/EVA] selected – 113 kJ·mol^{-1} for $\Delta_f H_m^o$ (FeI_2, cr, 298.15 K) (and no entropy value), based on the same data sets. Later, Efimov and Evdokimova [1990EFI/EVD], using a heat of reaction cycle, reported – (118.1 ± 0.3) kJ·mol^{-1} for $\Delta_f H_m^o$ (FeI_2, cr, 298.15 K). This formed the basis for – (118.7 ± 0.8) kJ·mol^{-1} as selected for $\Delta_f H_m^o$ (FeI_2, cr, 298.15 K) by Parker and Khodakovskii [1995PAR/KHO], but these authors also did not select a value for S_m^o (FeI_2, cr, 298.15 K).

In general, values reported for $\Delta_f H_m^o$ (FeI_2, cr, 298.15 K) based on high-temperature equilibrium studies (transpiration, [1956SCH/HON], [1966ZAU/GRE], [1966ZAU/GRE2], torsion-effusion and Knudsen cell mass spectrometry [1959SCH/FRI], [1960SIM/GRE], [1984GRA/ROS], [1985HIL/VIS], [1996SCA/PIA], and high-temperature flow [1968BAR/BAR] measurements) are between – 90 and – 110 kJ·mol^{-1}, considerably less negative than those found from the solution-calorimetric studies [1934HIE/WOE], [1990EFI/EVD]. Moreover, it is often difficult to disentangle the values assumed for the gas-phase species, not just I_2(g), I_2(g) and FeI_2(g), but also Fe_2I_4(g), FeI_3(g) and Fe_2I_6(g). Second-law calculations using data obtained over small temperature ranges are suspect, and reported values of $\Delta_f H_m^o$ and S_m^o for 298.15 K are strongly correlated ([1966ZAU/GRE] gives examples). Heat-capacity values for FeI_2(cr) are available to above 750 K, and therefore enthalpy and entropy differences between these temperatures and 298.15 K can be calculated, whereas values for FeI_2(l) all seem to be estimates. This introduces extra uncertainties in the interpretation of measurements [1956SCH/HON], [1956SHC/ORA], [1968BAR/BAR] made at temperatures above the melting point of FeI_2(cr).

The potentiometric work of Khandkar *et al.* [1983KHA/TAR] suggests the values – (114.4 ± 1.5) kJ·mol^{-1} and (181.6 ± 3.0) J·K^{-1}·mol^{-1} for $\Delta_f H_m^o$ (FeI_2, cr, 298.15 K) and S_m^o (FeI_2, cr, 298.15 K), respectively. The second-law analysis leads to entropy values that are systematically larger (by approximately 30 J·K^{-1}·mol^{-1}) than those from the gas-phase equilibrium studies for the same assumed value for $\Delta_f H_m^o$. The key papers are discussed in more detail in Appendix A.

The sole useful measurement of the heat of solution of FeI_2(cr) in dilute aqueous solution appears to be that of Paoletti *et al.* [1965PAO/SAB]. Even though estimated heats of dilution are likely to introduce uncertainties of 1-2 $kJ\cdot mol^{-1}$, the uncertainties in the enthalpies of formation of $FeCl_2$(cr) and $FeBr_2$(cr) are unlikely to be nearly as discrepant as those listed for FeI_2(cr), Based on the intercomparison of the values for the iron(II) halides, a value between – 117 and – 122 $kJ\cdot mol^{-1}$ can be estimated for $\Delta_f H_m^o$ (FeI_2, cr, 298.15 K). If consistency were to be maintained with the gas-phase equilibrium values, an error of approximately 15 $kJ\cdot mol^{-1}$ in the heat of solution from [1965PAO/SAB] would need to be accommodated (*i.e.*, an enthalpy of solution of ~ – 100 $kJ\cdot mol^{-1}$ rather than the experimental value of between – 80 and – 85 $kJ\cdot mol^{-1}$). This is unlikely.

One reason for some of the apparent discrepancies could lie in the composition of "FeI_2(cr)". Oetting [1960OET], Shcukarev *et al.* [1956SHC/ORA], and Efimov and Evodokima [1990EFI/EVD] gave analyses for carefully prepared samples suggesting I:Fe ratios of 1.924 to 1.974, 1.94 and 1.98, respectively. The iron analysis reported for the material used by Miljutin and Parfenova [1940MIL/PAR] for their heat-capacity measurements is consistent with an I:Fe ratio of 1.91.

In the present review a value is selected for $\Delta_f H_m^o$ (FeI_2, cr, 298.15 K) using the unweighted average of the values from the heat of solution study of Paoletti *et al.* [1965PAO/SAB], the calorimetric cycle of Efimov and Evdokimova [1990EFI/EVD], and the potentiometric work of Khandkar *et al.* [1983KHA/TAR] (– 121.1, – 118.1 and – 114.4 $kJ\cdot mol^{-1}$)

$$\Delta_f H_m^o (FeI_2, cr, 298.15 K) = -(117.9 \pm 5.0)\ kJ\cdot mol^{-1}.$$

When this value is used as a fixed value in the analysis of the work of Khandkar *et al.* [1983KHA/TAR], 174.0 $J\cdot K^{-1}\cdot mol^{-1}$ is obtained for S_m^o (FeI_2, cr, 298.15 K). This is a reasonable value [1966ZAU/GRE], though perhaps a bit larger than might be expected by comparison with the value for $FeCl_2$(cr). It is selected, but with a large uncertainty:

$$S_m^o (FeI_2, cr, 298.15 K) = (174 \pm 20)\ J\cdot K^{-1}\cdot mol^{-1}.$$

VIII.3.5 Enthalpy cycles based on heats of solution of simple iron(II) and iron(III) halide salts

There have been many reported measurements of the heat of solution of $FeCl_2$(cr) in water (*e.g.*, [1908THO], [1952LI/GRE], [1977CER/HEP]), aqueous HCl (*e.g.*, [1934HIE/APP], [1970ASH], [1976COR/OUW]), or aqueous $HClO_4$ [1982COB/MUR] but only a few for $FeBr_2$(cr) and FeI_2(cr). If such measurements are corrected to infinite dilution, then the enthalpies of formation should form a consistent set, linked through the CODATA values for the aqueous halide ions.

VIII.3.5.1 Heats of solution of $FeCl_2$(cr)

Probably the most careful measurements of the heat of solution of $FeCl_2$(cr) at low molalities were those of Cerutti and Hepler [1977CER/HEP] in 0.0001 m HCl(sln), and of Cobble and Murray [1982COB/MUR] in 0.005 m $HClO_4$(sln). Recalculations and extrapolation to infinite dilution (see Appendix A) give $-(83.00 \pm 0.40)$ and $-(82.76 \pm 0.50)$ $kJ \cdot mol^{-1}$, respectively. These results are comparable to values from the work of Li and Gregory [1952LI/GRE] (-82.4 $kJ \cdot mol^{-1}$) and from Efimov *et al.* in the late 1980s or early 1990s. The latter measurements (in 0.001 m $HClO_4$(sln)) apparently remain unpublished, though Parker and Khodakovskii [1995PAR/KHO] supplied some details in their review. Using the same procedure that is described in Appendix A for treating the data of Cobble and Murray [1982COB/MUR], a value of -83.2 $kJ \cdot mol^{-1}$ is calculated for $\Delta_{sln}H^{o}_{m}$ in the present review, based on the data of Efimov *et al.* [1995PAR/KHO].

A value of $-(82.91 \pm 0.31)$ $kJ \cdot mol^{-1}$ is calculated for $\Delta_{sln}H^{o}_{m}$ from the weighted results from the studies of Cerutti and Hepler [1977CER/HEP], and of Cobble and Murray [1982COB/MUR].

After evaluation of the available cycles for iron species and optimization to ensure consistency with other thermodynamic quantities for iron species (Chapter XI), the value of $\Delta_{sln}H^{o}_{m}$ ($FeCl_2$, cr, 298.15 K), consistent with other quantities for iron species is $-(82.92 \pm 0.86)$ $kJ \cdot mol^{-1}$, essentially identical to the experimental result, but with a rather larger uncertainty.

VIII.3.5.2 Heats of solution of $FeBr_2$(cr)

For $FeBr_2$(cr), there are values from Li and Gregory [1952LI/GRE] (0.00247 to 0.00828 m, at 298.15 K), Paoletti [1965PAO], [1966PAO] (0.03 m, probably at 298.15 K) and Hieber *et al.* [1934HIE/APP] (0.033 m, at 293.15 K). Despite the temperature and concentration differences, all experimental values were between -82.4 and -85.7 $kJ \cdot mol^{-1}$[1]

As the measurements by Hieber *et al.* [1934HIE/WOE] were obtained at a lower temperature, they are not used here in the estimation of the heat of solution at

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[1] In the late 1980s or early 1990s Efimov *et al.* also carried out measurements of the heat of solution of $FeBr_2$(cr) in 0.001, 0.0105, 0.1085 and 1.085 $mol \cdot kg^{-1}$ $HClO_4$(sln). The results apparently remain unpublished, though Parker and Khodakovskii [1995PAR/KHO] supplied some details in their review. The measured values in 0.001 $mol \cdot kg^{-1}$ $HClO_4$(sln) were between -86.8 and -86.1 $kJ \cdot mol^{-1}$ for solutions with final iron molalities of 0.0043 to 0.0076 $mol \cdot kg^{-1}$. However, there appear to be inconsistencies, typographical errors and insufficient detail in the discussion in Parker and Khodakovskii. Using the same procedure that is described in Appendix A for treating the data of Cobble and Murray [1982COB/MUR], an approximate value of -87 $kJ \cdot mol^{-1}$ is calculated for $\Delta_{sln}H^{o}_{m}$ in the present review, based on the data of Efimov *et al.* *fide* [1995PAR/KHO].

298.15 K. The single average value of Paoletti is more negative than those of Li and Gregory, even though it was obtained in a higher molality solution. Application of a limiting-law correction leads to $-(85.7 \pm 2.0)$ kJ·mol^{-1}. The Li and Gregory results, after application of a limiting-law correction, show a concentration dependence not seen in any of the corresponding sets of data for $FeCl_2$. The result from Li and Gregory [1952LI/GRE], corrected to $I = 0$, is $-(85.0 \pm 1.5)$ kJ·mol^{-1}. The weighted average is $-(85.3 \pm 1.4)$ kJ·mol^{-1}. The unpublished results of Efimov *et al.* (described by Parker and Khodakovskii [1995PAR/KHO], see Appendix A) suggest a slightly more negative value than this average, but still a consistent value within these uncertainty limits. The $-(85.3 \pm 1.4)$ kJ·mol^{-1} value was used in the evaluation of the available cycles for iron species and optimization to ensure consistency with other thermodynamic quantities for iron species (Chapter XI).

From the evaluation of the available cycles for iron species (Chapter XI), the consistent value of $\Delta_{\text{sln}}H^{\circ}_{\text{m}}$ ($FeBr_2$, cr, 298.15 K) is calculated to be $-(85.6 \pm 1.2)$ kJ·mol^{-1}. This is in good agreement with the assessed value.

VIII.3.5.3 Heat of solution of FeI_2(cr)

Paoletti *et al.* [1965PAO/SAB] measured the heat of solution of FeI_2(cr) to form a dilute aqueous solution near 298 K. Correction to $I = 0$ leads to a value of $-(82.5 \pm 3.0)$ kJ·mol^{-1}. As discussed above, in the present review this heat of solution of FeI_2(cr) is used as part of the determination of a value for $\Delta_{\text{f}}H^{\circ}_{\text{m}}$ (FeI_2, cr, 298.15 K), rather than in the determination of a value for $\Delta_{\text{f}}H^{\circ}_{\text{m}}$ (Fe^{2+}, 298.15 K).

VIII.3.5.4 Heats of solution of $FeCl_3$(cr)

There also have been many reported measurements of the heat of solution of $FeCl_3$(cr) in water ([1893LEM], [1908THO], [1952LI/GRE], [1985SOL/MON]), aqueous HCl ([1935KAN/FLU], [1958SHC/VAS2], [1959KOE/COU], [1976COR/OUW], [1980STU/FER]), and $HClO_4$ [1984NOV/BEL], [1995PAR/KHO]. In general, the measurements done to form solutions with similar iron, acid, and chloride concentrations are in reasonably good agreement (*e.g.*, [1935KAN/FLU], [1958SHC/VAS2]). Most experiments have been done in a manner that resulted in solutions with high final iron molalities (> 0.01 m). Also, the reported values are affected by both hydrolysis and chloride complexation of Fe^{3+}. Only Li and Gregory [1952LI/GRE] reported an attempt to correct their heat of solution values (final iron molalities of 0.0008 to 0.003 m) both for formation of $FeCl^{2+}$ and for hydrolysis. Their reported heat of solution at infinite dilution was $-(159.2 \pm 1.2)$ kJ·mol^{-1}. The heats of solution measured by Solozheako *et al.* [1985SOL/MON] are consistent within 1.5 kJ·mol^{-1} with those determined by Li and Gregory under similar conditions.

In principle, the results from dissolution into perchloric acid solutions should be somewhat simpler to interpret. However, in the Parker and Khodakovskii review [1995PAR/KHO] considerable emphasis is placed on measurements made by Efimov *et* *al.* in the late 1980s or early 1990s, and which do not appear to have been published elsewhere. The assessed heat of solution at infinite dilution from these measurements was – (156.8 ± 1.2) kJ·mol^{-1} [1995PAR/KHO] although these reported heats of solution are inconsistent with those published earlier by Novikov *et al.* [1984NOV/BEL]. The difference of 7% is difficult to rationalize. Furthermore, estimation of the required enthalpies of dilution for the 3:1 electrolyte from 0.7 to 4.6 m $HClO_4$(sln) to infinite dilution is not straightforward [1959LAN], [1995PAR/KHO], [1997GRE/PLY2]. Estimates differ by 2 kJ·mol^{-1} for the extended Debye-Hückel terms alone, and that still rests on the assumption that the Debye-Hückel limiting slope is followed at low $FeCl_3$ molalities. The work of Lange's group [1959LAN] suggests that even the sign of the correction for the heat of dilution from a mixed-electrolyte solution 1 m in ionic strength is in doubt without electrolyte-specific information.

In the present review, a value of – (158.3 ± 3.0) kJ·mol^{-1} for $\Delta_{\text{sln}}H^{\circ}_{\text{m}}$ ($FeCl_3$, cr, 298.15 K), recalculated from the study of Efimov *et al.* (*fide* Parker and Khodakovskii [1995PAR/KHO]), was used in the evaluation of the available cycles for iron species (Chapter XI). In the consistency calculation it was necessary to increase the estimated uncertainty to ± 3.6 kJ·mol^{-1}. The consistent value of $\Delta_{\text{sln}}H^{\circ}_{\text{m}}$ ($FeCl_3$, cr, 298.15 K) was calculated to be – (155.3 ± 1.0) kJ·mol^{-1}. This is only in marginal agreement with the experimental result, probably, as noted above, because of difficulties in calculating heats of dilution.

VIII.3.5.5 Heats of solution of $FeBr_3$(cr)

Measurements have been reported for the heat of solution of $FeBr_3$(cr) in water by Li and Gregory [1952LI/GRE] and in aqueous $HClO_4$ by Parker and Khodakovskii (based on unpublished results of Efimov *et al.*) [1995PAR/KHO]. Li and Gregory attempted to correct their heat of solution values (final iron molalities of 0.001 to 0.007 m) for both formation of $FeBr^+$ and hydrolysis and, based on their seven measurements, the average value for the heat of solution at infinite dilution is – (146.7 ± 4.2) kJ·mol^{-1}. The heat of solution at infinite dilution from the data of the $HClO_4$ solution measurements was reported [1995PAR/KHO] as – (150.4 ± 1.3) kJ·mol^{-1}. In the present review, a value of – (152.2 ± 3.0) kJ·mol^{-1} for $\Delta_{\text{sln}}H^{\circ}_{\text{m}}$ ($FeBr_3$, cr, 298.15 K) was recalculated from the study of Efimov *et al.* (*fide* Parker and Khodakovskii [1995PAR/KHO]).

This value of – (152.2 ± 3.0) kJ·mol^{-1} for $\Delta_{\text{sln}}H^{\circ}_{\text{m}}$ ($FeBr_3$, cr, 298.15 K) was used in the evaluation of the available cycles for iron species (Chapter XI). The optimized consistent value for $\Delta_{\text{sln}}H^{\circ}_{\text{m}}$ ($FeBr_3$, cr, 298.15 K) was calculated to be – (151.7 ± 1.2) kJ·mol^{-1}. This is in fair agreement with the experimental result, despite problems in obtaining a satisfactory value for the enthalpy of solution at infinite dilution, similar to those discussed above for $FeCl_3$(cr).

Chapter IX

Group 16 compounds and complexes

IX.1 Sulfur compounds and complexes

IX.1.1 Iron sulfides

IX.1.1.1 Aqueous iron(II)-sulfide complexes

When a solution containing iron(II) is mixed with a sulfide solution at room temperature, a black precipitate is observed immediately. It has been suggested that the black material is iron sulfide, which is X-ray amorphous and has a chemical composition close to FeS ([1967BER2], [1987MOR/MIL], [1991DAV], [2005RIC/MOR]). The precipitate formed immediately after mixing may be considered to be a highly disordered gel approaching the composition of $Fe(HS)_2$ on a water-free basis, but it will transform into X-ray amorphous FeS in less than 1 s ([1989RIC], [1995WEI/OSS]). This product has been shown to be the nanoparticulate mackinawite (tetragonal FeS) by a number of investigators ([1967BER2], [1997THE/LUT], [2000BEN/WIL], [2005WOL/CHA], [2006OHF/RIC], [2006RIC]). As shown in Figure IX-1 ([1999DAV/PHI], [2006RIC]), the solubility of Fe(II) in the presence of a constant concentration of H_2S(aq) decreases with pH and approaches a nearly constant value.

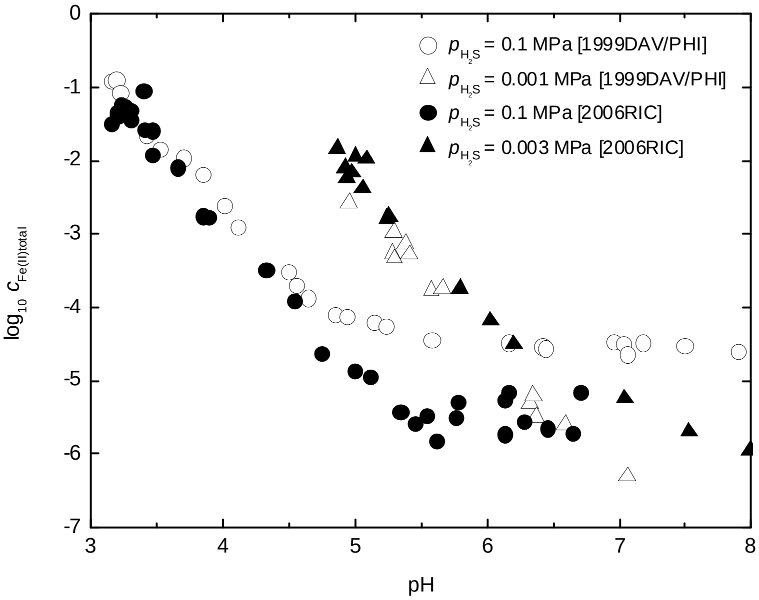
The solubilities of iron sulfides were shown to be in the order: mackinawite > troilite (hexagonal FeS) > pyrrhotite (hexagonal FeS) > pyrrhotite (monoclinic FeS) > pyrite (cubic FeS_2) ([1978TEW/WAL], [1987MOR/MIL]). The mackinawite has been shown to be stable for up to 4 months in reduced sulfur solutions at a low temperature, and changes into pyrite *via* greigite (cubic Fe_3S_4) in slightly oxidizing conditions, presumably using zerovalent sulfur ([2000BEN/WIL], [2007HUN/BEN]). Since the solubility of FeS is sensitive to the characterization of the solid (phase, ageing and surface conditions), there is still considerable disagreement as to the aqueous iron sulfide complexes formed and the values of their thermodynamic constants.

The literature data for equilibrium constants relevant to the solubility of FeS are given in Table IX-2. For FeS other than mackinawite, attainment of a state of equilibrium (precipitation from oversaturation and dissolution from undersaturation) is considered questionable. For mackinawite, the values of $\log_{10} K^{\circ}$ (IX.1) were obtained by assuming the reaction

$$\text{FeS(mackinawite)} + 2\,\text{H}^+ \rightleftharpoons \text{Fe}^{2+} + \text{H}_2\text{S(aq)} \qquad \text{(IX.1)}$$

and by using the Davies equation to estimate activity coefficients. If the values were reported for other reactions such as FeS(mackinawite) + $H^+ \rightleftharpoons Fe^{2+} + HS^-$ or FeS(mackinawite) $\rightleftharpoons Fe^{2+} + S^{2-}$, they were converted into values for the above reaction using the dissociation constant values for H_2S(aq) from the original papers. Some of the papers claimed the solid phases to be amorphous FeS, but they can be considered to be nanoparticulate mackinawite. As shown in Figure IX-1, the experimental results from measurements of the solubility of nanoparticulate mackinawite at higher pH values disagree with each other, presumably due to the effect of ageing or surface condition of the precipitate. Also, even very small amounts of oxidizing materials introduced in the preparation of the precipitate may affect the surface speciation of the precipitate (the formation of greigite or pyrite) [2000BEN/WIL], which in turn affects its solubility. On the other hand, the values of $\log_{10} K^\circ$ (IX.1) obtained at lower pH values reported in the accepted papers roughly agree with each other as shown in Table IX-3.

Figure IX-1: The dependence of the solubility of mackinawite (FeS) on pH reported by Davison *et al.* [1999DAV/PHI] and Rickard [2006RIC].



Although there are many values for complexation constants of iron sulfides reported in the literature as shown in Table IX-1, most of them have been calculated based on the solubility data of nanoparticulate mackinawite at higher pH values and different models for the sulfide complexes. Examination of the original papers as shown in the Appendix revealed that no good evidence was given for the aqueous complexes in these papers. This review does not accept the speciation given in these papers or for the species proposed by Chadwell *et al*. [2001CHA/RIC].

Table IX-1: Literature data on the formation constants of Fe(II) sulfide complexes.

Method	I /M, Medium	t/°C	$\log_{10} \beta^{o}_{n,m}$ (a)	Reference
$\mathrm{Fe^{2+} + HS^- \rightleftharpoons FeHS^+}$				
analogy (b)		25	1.4	[1988DYR]
voltammetry		25	5.50 ± 0.24	[1993LUT/FER]
voltammetry	0.7, NaCl	25	5.07 ± 0.09	[1996LUT/RIC]
	0.35, NaCl	25	5.07 ± 0.16	
	0.07, NaCl	25	5.17 ± 0.01	
voltammetry	salinity 35	25	6.07 ± 0.06	[1999FAR/BER]
	salinity 21	25	5.97 ± 0.04	
	salinity 10.5	25	5.86 ± 0.02	
$\mathrm{Fe^{2+} + S^{2-} \rightleftharpoons FeS(aq)}$				
analogy b		25	13.3	[1988DYR]
$\mathrm{Fe^{2+} + 2\,H_2S(aq) \rightleftharpoons Fe(HS)_2(aq) + 2\,H^+}$				
analogy b		25	−4.63	[1985DYR]
$\mathrm{Fe^{2+} + 2\,HS^- \rightleftharpoons Fe(HS)_2(aq)}$				
analogy b		25	8.9	[1988DYR]
solubility	0.1, $\mathrm{NaClO_4}$	20	6.45 ± 0.12	[1999DAV/PHI]
$\mathrm{Fe^{2+} + 2\,H_2S(aq) \rightleftharpoons FeHS_2^- + 3\,H^+}$				
analogy b		25	10.91	[1985DYR]
$\mathrm{2\,Fe^{2+} + HS^- \rightleftharpoons Fe_2(HS)^{3+}}$				
voltammetry	seawater	25	11.08 ± 0.25	[1993LUT/FER]
voltammetry	0.7, NaCl	25	10.07 ± 0.04	[1996LUT/RIC]
	0.35, NaCl	25	9.71 ± 0.35	
	0.07, NaCl	25	10.17 ± 0.15	
$\mathrm{3\,Fe^{2+} + HS^- \rightleftharpoons Fe_3(HS)^{5+}}$				
voltammetry	0.7, NaCl	25	16.15 ± 0.06	[1996LUT/RIC]
	0.35, NaCl	25	16.03 ± 0.11	
	0.07, NaCl	25	16.82 ± 0.21	

(a) The values of $\log_{10} \beta^{o}_{n,m}$, for the reactions as defined by the equations in the Table, were calculated in the original papers using activity coefficients estimated with the Davies equation [1962DAV] (also *cf*. Appendix B, pg. 848). The uncertainties are as given in the original paper.

(b) Linear free energy relationship with dithizone ((1E)-3-anilino-1-phenylimino-thiourea) as a model ligand and stability constants for silver/cadmium and mercury sulfides as reference.

Table IX-2: Literature data on the equilibrium constants relevant to the solubility of FeS. In Appendix A reasons for not accepting values proposed in two other studies [1994BAG/CAR] and [1998MOU/SEW] are discussed.

Form of solid FeS	I/M, medium	t /°C	pH	$\log_{10} K^{\mathrm{o}}$ (a)	Reference
$FeS(s) + 2 H^+ \rightleftharpoons Fe^{2+} + H_2S(aq)$					
mackinawite	water	25	2.5 ~ 4.1	3.44	[1967BER2]
amorphous	water	25	3 ~ 4	4.04	
troilite	water	25		1.73 ± 0.07	[1976TEW/CAM]
unspecified		25		2.8 (b)	[1985DYR]
unspecified		25		3.03 (b)	[1988DYR]
mackinawite	water	25		4.05 ± 0.10	[1997THE/LUT]
amorphous	0.1, $NaClO_4$	20	3.1 ~ 7.9	4.01 ± 0.12	[1999DAV/PHI]
mackinawite	~ 0.3	25	4.5	3.21	[2000BEN/WIL]
		50	4.3 ~ 4.9	2.47	
		75	4.5	1.84	
		80	7.4 ~ 8.2	1.72	
		90	3.9	1.50	
		100	3.6	1.29	
mackinawite	0.1 ~ 0.65, NaCl	23	3 ~ 10	3.5 ± 0.25	[2006RIC]
$Fe^{2+} + 2 HS^- \rightleftharpoons Fe(HS)_2(aq)$ (c)					
amorphous	0.1, $NaClO_4$	20	3.1 ~ 7.9	6.45 ± 0.12	[1999DAV/PHI]
$FeS(makinawite) \rightleftharpoons FeS(aq)$ (c)					
mackinawite	0.1 ~ 0.65, NaCl	23	3 ~ 10	–5.7 ± 0.27	[2006RIC]

(a) The values of $\log_{10} K^{\mathrm{o}}$, for the reactions as defined by the equations in the Table, were calculated in the original papers by using the activity coefficients estimated by the Davies equation. The uncertainties are as given in the original paper. The constants reported in the original paper were converted into the constants for the reaction indicated in this table.

(b) The values reported by Dyrssen [1985DYR], [1988DYR] were obtained using chemical analogy.

(c) The constants for the reactions listed below in the table were proposed to explain the solubility of FeS in regions of higher pH.

Table IX-3: Accepted data for the equilibrium constant of the dissolution of mackinawite at 298.15 K and I = 0 with their assigned uncertainty.

$\log_{10} K^{\mathrm{o}}$(IX.1)	Reference
3.7 ± 0.5	[1967BER2]
4.1 ± 0.3	[1997THE/LUT]
4.0 ± 0.3	[1999DAV/PHI]
3.2 ± 0.5	[2000BEN/WIL]
3.5 ± 0.3	[2006RIC]

In this review, fairly large uncertainties are given to the accepted values because of the experimental uncertainties. Although the data may consist of two sets of solubilities which correspond to fresh and aged precipitates (the fresh ones may give higher solubilities due to the larger surface area), they cannot be separated because of the large uncertainties. Thus, this review takes all data, a procedure that leads to the recommended value of $\log_{10} K^{\circ}$ (IX.1) = (3.79 ± 0.16). However, as the original data may contain two separate series of constants, this review assigns a larger uncertainty of ±0.4. Thus, the recommended constant for Reaction (IX.1) is

$$\log_{10} K^{\circ}\,(\text{IX.1}) = (3.8 \pm 0.4).$$

To explain the solubilities at higher pH values, Davison *et al.* [1999DAV/PHI] assumed the reaction $Fe^{2+} + 2\,HS^{-} \rightleftharpoons Fe(HS)_2(aq)$, as their data seemed to indicate that the concentration of Fe(II) depends on the partial pressure of $H_2S(g)$. On the other hand, Rickard [2006RIC] considered that the concentration of Fe(II) does not depend on the partial pressure of $H_2S(g)$, and assumed the reaction of FeS(mackinawite) $\rightleftharpoons$ FeS(cluster) where FeS(cluster) is a quantum-sized iron sulfide cluster or complex, which contains a discrete number of atoms in a molecule or ion that is small enough to behave as a dissolved species. The existence of this cluster has been discussed and claimed in several recent papers ([1997THE/LUT], [1998DAV/BUF], [2005LUT/RIC]) but the reviewer considers that the evidence or substantiation is insufficient. As shown in Figure IX-1, two seemingly very reliable papers report quite different solubility behaviour at higher pH values, and the reviewer cannot discern a reason for the difference. The difference in the crystallinity or in the surface condition, formation of a very small amount of surface FeS solid other than mackinawite, or differences in the rates of precipitation and dissolution at higher pH values may affect the solubility. The speciation of the soluble iron sulfide can be discussed only after reproducible and reliable solubility data in this pH region are obtained. So far this review cannot recommend any speciation or formation constant in this pH region.

IX.1.2 Iron sulfates

IX.1.2.1 Aqueous iron - sulfato complexes

IX.1.2.1.1 Sulfate as ligand

The SO_4^{2-} ion is a rather highly-charged tetrahedral anion having four S = O bonds with an interatomic distance of 0.148 nm. In aqueous solutions the ion interacts preferentially with hard acceptor cations of the Hard-Soft Acid-Base (HSAB) classification. So it is expected that it will form rather stable complexes with Fe^{3+}.

X-ray diffraction of solids has shown many modes of coordination for the sulfate ion [1987HAT]. In most of them the SO_4^{2-} anion is shared by several metallic cations. For example in $CuSO_4$ it is linked to six Cu(II) ions.

This tendency to bridge metallic ions disappears in highly polar solvents such as water in which no or very few polynuclear sulfate complexes are encountered. Hydrogen sulfato (HSO_4^-) complexes of metallic ions exist, and in those the sulfate anion bridges two cations, one of them being H^+.

As the SO_4^{2-} ion is rather rigid, bidentate coordination is not common. As the charge of the anion is high, the order of the complexes is limited.

Sulfate-ion interactions with univalent alkali- and divalent alkaline-earth-cations have sometimes been described in terms of ion pairs of non-negligible stability. This complicates the determination of values for thermodynamic complexation constants because it is often difficult to separate real association with metallic ions from medium effects due to the interaction of sulfate with cations of salts added to maintain a constant ionic strength.

IX.1.2.1.2 Aqueous iron(II) sulfato complexes

In principle, one would expect that "simple" systems like Fe(II) sulfate as an aqueous electrolyte have been thoroughly investigated. Unfortunately, the contrary is true. The present review only found approximately a half-dozen papers dealing with the quantitative aspects of the formation of $Fe(SO_4)_q^{2-2q}$ and $Fe(HSO_4)_r^{2-r}$ complexes. Various experimental methods have been used to investigate the reactions

$$Fe^{2+} + SO_4^{2-} \rightleftharpoons FeSO_4(aq) \qquad (IX.2)$$

and

$$Fe^{2+} + HSO_4^{-} \rightleftharpoons FeHSO_4^{+}. \qquad (IX.3)$$

In Table IX-4 and all Sections IX.1.2.1.2 through IX.1.2.1.2.4 the equilibrium constant K(IX.2) is often represented by the symbol β_1 and K(IX.3) by the symbol β_{H1}.

Huffmann and Davidson [1956HUF/DAV] photometrically studied the oxidation of Fe(II) by O_2 at various sulfate concentrations. The stability determination then was based on the variation of the kinetic parameters. A similar method was used by Wells and Salam [1968WEL/SAL]. The difference is that these authors used H_2O_2(aq) as an oxidant, and thus had better control of reactant concentrations. The calculated complex stability is sensitive to the evaluation of auxiliary kinetic constants. Wells and Salam [1968WEL/SAL] reached the important conclusion that even high concentrations of ClO_4^- do not affect the reaction rates. This, in turn, is a strong argument that no Fe(II) perchlorate complexes are formed. Beukenkamp and Herrington [1960BEU/HER] developed ion-exchange elution techniques in sulfuric and perchloric acid to study the iron sulfate system. They postulated the existence of the hydrogen sulfate complex ($FeHSO_4^+$) and provided an upper limit for a possible $FeClO_4^+$ complex. Unfortunately, the quality of their data is highly questionable.

Table IX-4: Summary of experimental conditions and experimental and re-evaluated formation constants for the iron sulfate and hydrogen sulfate complexes. For discussion of the re-evaluations, see the corresponding Appendix A entries.

Method	Ionic medium	t/°C	β_i or $\log_{10}\beta_i$	Reference	Re-evaluation
$Fe^{2+} + SO_4^{2-} \rightleftharpoons FeSO_4(aq)$					
con	2×10^{-4}–2 M $FeSO_4$	25		[1941DEM/FED]	not accepted
sp, kin	1 M $NaClO_4$ + H_2SO_4/Na_2SO_4 mixtures from 0.07 to 0.58 M	30.5	(1.1 ± 0.2) $dm^3\cdot mol^{-1}$	[1956HUF/DAV]	$\beta_1 = (1.04 \pm 0.19)\ kg\cdot mol^{-1}$ (I_m = 1.05 to 1.66 $mol\cdot kg^{-1}$; $[ClO_4^-] = 1.054\ mol\cdot kg^{-1}$)
cix	< 2.2 M H_2SO_4,	?	1.7 $dm^3\cdot mol^{-1}$	[1960BEU/HER]	not accepted
sp, kin	1 M $NaClO_4$, Na_2SO_4 = 0.15 M, $HClO_4$ = 0.004 M	25	10 $dm^3\cdot mol^{-1}$	[1968WEL/SAL]	$\beta_1 = 9.5\ kg\cdot mol^{-1}$ ($I_m = 1.53\ mol\cdot kg^{-1}$; $[ClO_4^-] = 1.054\ mol\cdot kg^{-1}$)
	1 M $NaClO_4$, Na_2SO_4 = 0.2 M, $HClO_4$ = 0.004	0	55 $dm^3\cdot mol^{-1}$		$\beta_1 = 52\ kg\cdot mol^{-1}$ ($I_m = 1.68\ mol\cdot kg^{-1}$)
	4 M $NaClO_4$, Na_2SO_4 = 0.3 M $HClO_4$ = 0.004	35	5.8 $dm^3\cdot mol^{-1}$		$\beta_1 = 4.6\ kg\cdot mol^{-1}$ ($I_m = 6.2\ mol\cdot kg^{-1}$; $[ClO_4^-] = 5.02\ mol\cdot kg^{-1}$)
	4 M $NaClO_4$, Na_2SO_4 = 1.25 M $HClO_4$ = 0.004	45	2.5 $dm^3\cdot mol^{-1}$		$\beta_1 = 1.9\ kg\cdot mol^{-1}$ ($I_m = 10.15\ mol\cdot kg^{-1}$; $[ClO_4^-] = 5.24\ mol\cdot kg^{-1}$)
cal	I = 0.02 m $Fe(ClO_4)_2$ + 0.02? m $(Me_4N)_2SO_4$	25	$\log_{10}\beta_1^{\circ}$ = (2.20 ± 0.06)	[1969IZA/EAT2]	$\log_{10}\beta_1^{\circ} = (2.56 \pm 0.15)$
isop	0.1 to 1.964 $mol\cdot kg^{-1}$ $FeSO_4$	25		[1974OYK/BAL]	Most simple chemical model produces $\beta_1^{\circ} = (154 \pm 3)\ kg\cdot mol^{-1}$ (value not used in the present review, see Appendix A**)**
con	$I = 0.5–5\times10^{-3}$ M $FeSO_4$	var	$\beta_1^{\circ} = 247$ $dm^3\cdot mol^{-1}$	[1988KUB/MOC]	$\log_{10}\beta_1^{\circ}$ (25 °C, I = 0) = (2.44 ± 0.03) $\Delta_r H_m^{\circ} = (8.4 \pm 6.2)\ kJ\cdot mol^{-1}$.

(Continued on next page)

Table IX-4 (continued)

Method	Ionic medium	t/°C	β_i or $\log_{10}\beta_i$	Reference	Re-evaluation
E_{cell}	I = 3 M $NaClO_4$ $FeSO_4$ = 0.01 to 0.125 Na_2SO_4 = 0.01 to 0.25	25	$\log_{10}\beta_1$ = (0.60 ± 0.05)	[2002CIA/TOM]	recalc. to kg·mol^{-1}–units $\log_{10}\beta_1$ = (0.53 ± 0.05) (I_m = (3.72 ± 0.22) mol·kg^{-1}); [ClO_4^-] = (3.20 ± 0.29) mol·kg^{-1} possible formation of $NaSO_4^-$ not considered
	I = 3 M $NaClO_4$	25	$\log_{10}\beta_2$ = (0.87 ± 0.05)		recalc. to kg^2·mol^{-2} – units $\log_{10}\beta_2$ = (0.74 ± 0.05)
$Fe^{2+} + HSO_4^- \rightleftharpoons FeHSO_4^+$					
cix	< 2.2 M H_2SO_4,	?	β = 0.61 dm^3·mol^{-1}	[1960BEU/HER]	
sp, kin	4 M $NaClO_4$, $NaHSO_4$ = 0.7 M	25		[1968WEL/SAL]	β_{H1} = 1.5 kg·mol^{-1} (I_m = 6.0 mol·kg^{-1})
	4 M $NaClO_4$, $NaHSO_4$ = 0.22 M	0			β_{H1} = 3.7 kg·mol^{-1} (I_m = 5.1 mol·kg^{-1})
	4 M $NaClO_4$, $NaHSO_4$ = 0.3 M	5			β_{H1} = 3.0 kg·mol^{-1} (I_m = 5.3 mol·kg^{-1})
	4 M $NaClO_4$, $NaHSO_4$ = 0.7 M	10			β_{H1} = 2.4 kg·mol^{-1} (I_m = 5.9 mol·kg^{-1})

Izatt *et al.* [1969IZA/EAT2] performed calorimetric measurements in metal perchlorate solutions titrated with sulfate solutions and interpreted their results in terms of a simple model where only 1:1 complexes are formed. They also performed similar experiments with a series of trivalent metals. As expected, in this case the analysis required a more complicated model including both, 1:1 and 2:1 complexes. Oykova and Balarew [1974OYK/BAL] and Nikolaev *et al.* [1989NIK/DIK] investigated $FeSO_4$ solutions with isopiestic methods over a wide range of solute concentrations. The interpretation of those discrepant results is not straightforward; an attempt to derive thermodynamic quantities from one of the sets of measurements is outlined and discussed below.

Kubota *et al.* [1988KUB/MOC] performed conductivity measurements in dilute $FeSO_4$(aq) solutions in the temperature range 283.15 to 308.15 K. The procedure used in the treatment of activity corrections was incompatible with the TDB procedures outlined in Appendix B and a re-evaluation of the [1988KUB/MOC] conductivity data was necessary. Conductivity measurements were also carried out earlier by Demassieux and Fedoroff [1941DEM/FED].

Ciavatta *et al.* [2002CIA/TOM] studied equilibria between iron(II) and sulfate ions with a glass electrode in 3 M $NaClO_4$. This paper provides one of the most careful discussions about the impact of changing media on cell-potential measurements in this electrochemical cell. Based on the detailed discussion, the authors also provided evidence for formation of the complex $Fe(SO_4)_2^{2-}$. Unfortunately, the evaluation of the [2002CIA/TOM] data is biased by the ("not well known") formation constants of $NaSO_4^-$ ion pairs and their impact in high ionic strength systems. A summary of available experimental information is given in Table IX-4.

IX.1.2.1.2.1 Complexes of Fe^{2+} with SO_4^{2-}

Many methods of studying weak aqueous iron(II) sulfato complexes require a substantial amount of sulfate ion to be present and varied in solution. This interferes with the need to keep the ionic medium constant, and causes difficulties particularly when the contribution of the inert medium to the ionic strength of the solution is not "very much" greater than the contribution of the sulfate salt(s) (an old problem). Weak complexes are characterized by low formation constants. At a high ionic strength the magnitude of the necessary Debye-Hückel correction term thus may exceed the magnitude of the formation constant itself (note that for formation of a complex between a doubly-charged cation and a doubly-charged anion, the magnitudes of the contributions to ($\log_{10} \beta^{\circ} - \log_{10} \beta_m$) from the Debye-Hückel terms (*i.e.*, $\Delta z^2 D$) are 0.35, 0.87 and 1.63 for solutions with ionic strengths I = 0.01, 0.1, and 1 m at 298.15 K).

Hence, reliable studies at low to very low ionic strengths, or studies without inert electrolytes, are especially valuable because correction terms are low and/or no additional ionic interactions need to be considered.

Kubota *et al.* [1988KUB/MOC] studied the formation of the complex $FeSO_4(aq)$ in dilute, aqueous iron(II) sulfate solutions, free of other electrolytes, by conductivity measurements. Re-evaluation of their data for 283.15 to 308.15 K (see Appendix A) leads to the selected value of

$$\log_{10} \beta_1^{\circ}\,((\text{IX.2}),\ 298.15\ \text{K}) = (2.44 \pm 0.03).$$

Conductance data obtained half a century earlier by Demassieux and Fedoroff [1941DEM/FED] lead to $\log_{10} \beta_1^{\circ}$ = (2.2 ± 0.3) (when re-evaluated with the same approach as for the data of [1988KUB/MOC]). However, comparison of the Demassieux and Fedoroff nickel-sulfate data with literature values [2005GAM/BUG] leads to the conclusion that the results of these earlier experiments [1941DEM/FED] are likely biased by systematic errors.

Izatt *et al.* [1969IZA/EAT] studied Reaction (IX.2) calorimetrically by titrating $(Me_4N)_2SO_4$-solutions into 0.02 M metal perchlorate solutions. Unfortunately, the final solution composition was not given and additional iterative calculations using estimated ionic strengths are needed because the final ionic strength may be as high as

0.2 mol·kg^{-1} (details are provided in Appendix A). However, recalculation of the results from the study produces $\log_{10}\beta_1^{\circ}$ ((IX.2), 298.15 K) = (2.56 ± 0.15), in fair agreement with the value from [1988KUB/MOC].

Huffman and Davidson [1956HUF/DAV], Wells and Salam [1968WEL/SAL] and Ciavatta *et al.* [2002CIA/TOM] studied iron(II) sulfato complexes by spectroscopic, kinetic and electrochemical potential-difference methods in perchlorate solutions at various temperatures. In the SIT formalism the formation constant can be described with Eq. (IX.4).

$$\begin{aligned}\log_{10}\beta_1^{\circ} + \varepsilon(\mathrm{Fe}^{2+},\mathrm{ClO}_4^-)\,m_{\mathrm{ClO}_4^-} = {} & \log_{10}\beta_1\ (\mathrm{FeSO_4}, \mathrm{aq}, 298.15\text{-}318.15\ \mathrm{K}; I_m\ (\mathrm{NaClO_4}))\\ & + 8\,D - \varepsilon(\mathrm{Na}^+,\mathrm{SO}_4^{2-})\,m_{\mathrm{Na}^+} + [-\,\varepsilon(\mathrm{H}^+,\mathrm{SO}_4^{2-})\,m_{\mathrm{H}^+}\\ & - \varepsilon(\mathrm{Fe}^{2+},\mathrm{SO}_4^{2-})(\,m_{\mathrm{Fe}^{2+}} + m_{\mathrm{SO}_4^{2-}}\,)\\ & - \varepsilon(\mathrm{Fe}^{2+},\mathrm{HSO}_4^-)\,m_{\mathrm{HSO}_4^-}\,] \qquad \text{(IX.4)}\end{aligned}$$

The last three terms on the right side of Eq. (IX.4) [in square brackets] do not significantly contribute to the sum because $m_{\mathrm{Fe}^{2+}}$, $m_{\mathrm{SO}_4^{2-}}$, $m_{\mathrm{HSO}_4^-}$ and m_{H^+} are usually much smaller than m_{Na^+}. Thus, if we assume $\varepsilon(\mathrm{H}^+,\mathrm{SO}_4^{2-}) \approx \varepsilon(\mathrm{Na}^+,\mathrm{SO}_4^{2-}) = -0.12$ kg·mol^{-1}, the first of thses three terms is less than +0.01 for solutions with a pH greater than 1. From osmotic data a small, positive value for $\varepsilon(\mathrm{Fe}^{2+},\mathrm{SO}_4^{2-}) \sim 0$ might be inferred as outlined below. Hence, the second of the three terms is less than −0.01 when Fe^{2+} and SO_4^{2-} concentrations specified in the experiments are considered. Nothing is known about the value of $\varepsilon(\mathrm{Fe}^{2+},\mathrm{HSO}_4^-)$, but by analogy that value may be assumed to lie between $\varepsilon(\mathrm{Na}^+,\mathrm{SO}_4^{2-})$ and $\varepsilon(\mathrm{Fe}^{2+},\mathrm{SO}_4^{2-})$, *i.e.*, $\varepsilon(\mathrm{Fe}^{2+},\mathrm{HSO}_4^-) \sim -0.05$ kg·mol^{-1}. It is noted that an estimate based on analogy with interaction coefficients for transition metal ions with nitrate would lead to a value of about (0.15 ± 0.05) kg·mol^{-1}, similar to an empirical estimate proposed in a recent, commercially available ionic-strength-correction computer programme[1] [2003PET]. From a calculation based on experimental SO_4^{2-} concentrations, it follows that the third term has a value between −0.09 and 0.03, which in turn justifies the hypothesis that the "square-brackets-terms" in Eq. (IX.4) do not significantly contribute to the sum.

Temperature corrections to 298.15 K (T_0) were made using

$$\log_{10}\beta_1\,(T_0) = \log_{10}\beta_1\,(T) - \Delta_{\mathrm{r}}H_{\mathrm{m}}^{\circ}\,(\mathrm{IX.2}) \times (1/T_0 - 1/T)/R\,\ln(10)$$

with the enthalpy of reaction value selected in Section IX.1.2.1.2.2. All the necessary corrections are given in Table IX-4. In theory, the right hand side of Eq. (IX.4) *vs.* the molality of perchlorate should produce $\log_{10}\beta_1^{\circ}$ and $\varepsilon(\mathrm{Fe}^{2+},\mathrm{ClO}_4^-)$ values, but Figure IX-2 shows that the available data points are not suited to producing an unambiguous value because the scatter of the data, particularly around ~1 m ClO_4^-, is

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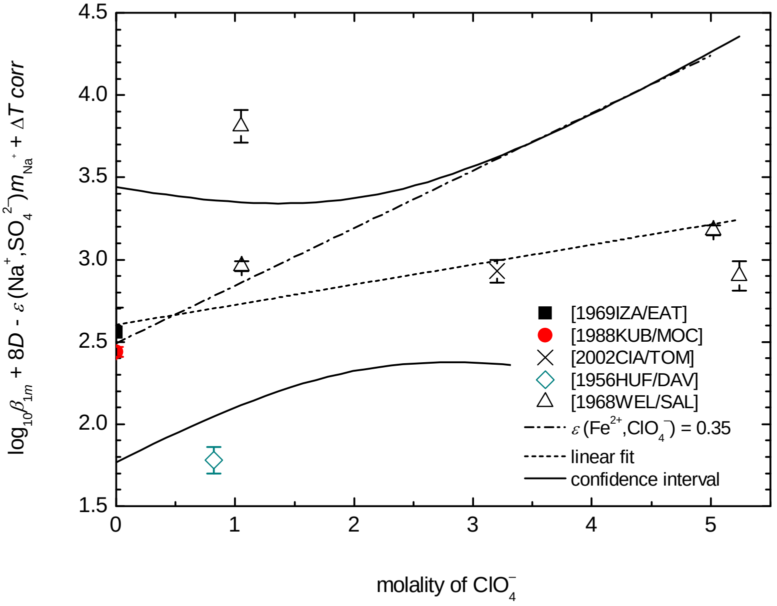
[1] Petitt L.D., Ionic Strength Corrections for Stability Constants using Specific Interaction Theory (SIT), Academic Software, UK, © IUPAC 2003.

much greater than predicted based on the experimental uncertainties and the uncertainties of the correction terms.

Figure IX-2: Linear regression (dashed line) of corrected (temperature, $NaSO_4^-$ formation) $FeSO_4(aq)$ formation constants *vs.* the molality of ClO_4^-, producing $\log_{10}\beta_1^{\circ} = (2.60 \pm 0.06)$ and $\varepsilon(Fe^{2+}, ClO_4^-) = (0.12 \pm 0.02)\ kg\cdot mol^{-1}$ at 298.15 K. A much more realistic $\varepsilon(Fe^{2+}, ClO_4^-)$ of 0.35 $kg\cdot mol^{-1}$ (represented by the dashed-dotted line originating from the selected $\log_{10}\beta_1^{\circ} = 2.44$; see text) is still compatible with the given scatter of individual data points (*i.e.*, within the confidence bands).



It also is not clear what realistic adjustments to the uncertainties might be made to the results from the different studies to improve this situation. There is a substantial danger that in "adjusting" individual uncertainties the best value might be discarded. Only further experimental work will resolve the problem. It is very clear that at present the available experiments in perchlorate solutions do not lead to a meaningful SIT-plot. The available data are clustered at perchlorate molalities of ~1 m, ~3.5 m, ~ 5 m as well as at I ~ 0. Formation constants from experiments in ~1 m ClO_4^- media [1956HUF/DAV], [1968WEL/SAL] differ significantly from each other. Treating the values as discrepant data according to the guidelines would lead to an uncertainty of ± 1.15 in $\log_{10}\beta(1\,m\,ClO_4^-)$. The smallest uncertainty (±0.09 in $\log_{10}\beta$) is certainly associated with the formation constant from Ciavatta *et al.* [2002CIA/TOM]. Based on the careful analysis of the various contributions to the potential-difference measurements, the low uncertainty of ± 0.05 as given in the original paper seems realistic. This original uncertainty is nearly doubled by considering the ionic strength uncertainty of ±0.22 mol·kg^{-1} in the calculation of 8*D*. Wells and Salam [1968WEL/SAL] did not provide uncertainties for their experimental results (~5 m ClO_4^-), the ranges given in Table IX-5 originate from the correction terms. Treating these formation constants as discrepant data would lead to an uncertainty of ~ ±0.23 in $\log_{10}\beta(5\,\mathrm{m}\,ClO_4^-)$ according to the guidelines.

Table IX-5: Selected experiments for the first complexation constant of Fe^{2+} with sulfate in perchlorate solutions, including experiments at $I = 0$. Necessary corrections according to Eq. (IX.4) as well as temperature corrections are given. For $\varepsilon(Na^+, SO_4^{2-})$ the extended form of $-(0.184 \pm 0.002) + (0.139 \pm 0.006)\log_{10} I_m$ was applied.

Ref.	t / °C	I_m	$m_{ClO_4^-}$	m_{Na^+}	$\log_{10}\beta_{1m}$	8*D*	$-m_{Na^+} \times \varepsilon(Na^+, SO_4^{2-})$	Δt correction to 25 ° for $\log_{10}\beta_1$	$\log_{10}\beta_1 + 8D - m_{Na^+} \times \varepsilon(Na^+, SO_4^{2-})$
a	25	0	0	0	2.47/2.64	0	0	0	2.56±0.15
b	30.5	1.04	0.822	0.822	0.02±0.08	1.642	0.149±0.016	−0.027±0.020	1.78±0.08
c	0	1.68	1.05	1.47	1.72	1.73	0.22±0.03	0.135±0.100	3.81±0.10
c	25	1.53	1.053	1.37	0.98	1.764	0.217±0.027	0	2.96±0.03
c	35	6.2	5.02	5.78	0.66	2.14	0.43±0.03	−0.048±0.035	3.18±0.05
c	45	10.15	5.24	8.51	0.28	2.33	0.383±0.054	−0.092±0.069	2.90±0.09
d	25	3.72±0.22	3.20±0.29	3.49	0.53±0.05	2.018 ± 0.074	0.37±0.02	0	2.92±0.09
e	25	0	0	0	2.44±0.03†	0	0	0	2.44±0.03
f	25	0	0	0	2.19±0.01‡	0	0	0	2.19±0.01

Refs: a: [1969IZA/EAT]; b: [1956HUF/DAV]; c: [1968WEL/SAL]; d: [2002CIA/TOM];
e: [1988KUB/MOC] and f: [1974OYK/BAL].

† This is based on analysis of data for 10, 15, 20, 25, 30 and 35 °C (*cf.* Appendix A)

‡ This is based on analysis of osmotic data of pure $FeSO_4$ solutions (*cf.* Appendix A)

Interaction coefficients for $\varepsilon(Ni^{2+}, ClO_4^-)$, $\varepsilon(Co^{2+}, ClO_4^-)$ and $\varepsilon(Cu^{2+}, ClO_4^-)$ have values of (0.370 ± 0.032) kg·mol^{-1}, (0.34 ± 0.03) kg·mol^{-1} and (0.32 ± 0.02) kg·mol^{-1}, respectively [2005GAM/BUG]. Based on well-established analogy principles for the first transition metal series there is no reason that $\varepsilon(Fe^{2+}, ClO_4^-)$ should deviate very much from these values. A straight line defined by $\log_{10}\beta_1^{\circ}$ = 2.44 and $\varepsilon(Fe^{2+}, ClO_4^-)$ = 0.35 kg·mol^{-1} (Figure IX-2) demonstrates that estimates made with $\varepsilon(Fe^{2+}, ClO_4^-)$ = 0.35 kg·mol^{-1} are within the confidence band up to 5 m.

The only credible quantitative study reporting a value for the formation constant of $Fe(SO_4)_2^{2-}$ is that of Ciavatta *et al.* [2002CIA/TOM]. From their measurements of $\log_{10}\beta_2$ = (0.87 ± 0.05) in 3 M aqueous $NaClO_4$, the formation constant at zero molality can be calculated using ρ = 1.224 kg·dm^{-3} at 298.15 K, $\varepsilon(\mathrm{Fe^{2+}, ClO_4^-})$ = (0.35 ± 0.04) kg·mol^{-1}, $\varepsilon(\mathrm{Na^+, SO_4^{2-}})$ = − (0.184 ± 0.002) + (0.139 ± 0.006) $\log_{10} I_m$, $\varepsilon(\mathrm{H^+, SO_4^{2-}}) \approx \varepsilon(\mathrm{Na^+, SO_4^{2-}})$, $\varepsilon(\mathrm{Fe^{2+}, SO_4^{2-}}) \approx$ – (0.09 ± ~ 0.03) kg·mol^{-1} (*cf.* the analysis of osmotic data below), $\varepsilon(\mathrm{Fe^{2+}, Fe(SO_4)_2^{2-}}) \approx \varepsilon(\mathrm{Na^+, Fe(SO_4)_2^{2-}}) \approx$ −(0.1 ± 0.1) kg·mol^{-1} and by assuming $\varepsilon(\mathrm{Fe^{2+}, HSO_4^-})$ = 0.5($\varepsilon(\mathrm{Fe^{2+}, SO_4^{2-}})$ + $\varepsilon(\mathrm{Na^+, SO_4^{2-}})$) ≈ −(0.10 ± 0.02) kg·mol^{-1}. Ciavatta *et al.* [2002CIA/TOM] used a solution with $m_{\mathrm{Na^+}}$ = 3.49 mol·kg^{-1}, $m_{\mathrm{ClO_4^-}}$ = (3.20 ± 0.29) mol·kg^{-1}, $m_{\mathrm{SO_4^{2-}}}$ < 0.25 mol·kg^{-1}, $m_{\mathrm{Fe^{2+}}}$ < 0.125 mol·kg^{-1}, $m_{\mathrm{HSO_4^-}}$ < ~0.12 mol·kg^{-1}, $m_{\mathrm{H^+}}$ < 0.03 mol·kg^{-1} with I_m = (3.72 ± 0.22) mol·kg^{-1}. Hence, the individual terms and their numerical values are given by:

$$\begin{aligned}
\log_{10} \beta_2^{\circ} = \ & \log_{10} \beta_2 && (= (0.73 \pm 0.05)) \\
& + 8D && (= (2.018 \pm 0.074)) \\
& + \varepsilon(\mathrm{Na^+, Fe(SO_4)_2^{2-}})\, m_{\mathrm{Na^+}} && (= -(0.35 \pm 0.35)) \\
& - \varepsilon(\mathrm{Fe^{2+}, ClO_4^-})\, m_{\mathrm{ClO_4^-}} && (= -(1.12 \pm 0.16)) \\
& - 2\varepsilon(\mathrm{Na^+, SO_4^{2-}})\, m_{\mathrm{Na^+}} && (= (0.73 \pm 0.04)) \\
& - \varepsilon(\mathrm{Fe^{2+}, Fe(SO_4)_2^{2-}})\,(m_{\mathrm{Fe^{2+}}} - m_{\mathrm{Fe(SO_4)_2^{2-}}}) && (\sim -(\mathit{0.01} \pm \mathit{0.01})) \\
& - \varepsilon(\mathrm{Fe^{2+}, SO_4^{2-}})\,(2\, m_{\mathrm{Fe^{2+}}} + m_{\mathrm{SO_4^{2-}}}) && (\sim (\mathit{0.045} \pm \mathit{0.015})) \\
& - \varepsilon(\mathrm{Fe^{2+}, HSO_4^-})\, m_{\mathrm{HSO_4^-}} && (\sim (\mathit{0.02} \pm \mathit{0.02})) \\
& - 2\varepsilon(\mathrm{H^+, SO_4^{2-}})\, m_{\mathrm{H^+}} && (\sim (\mathit{0.006} \pm \mathit{0.001})),
\end{aligned}$$

or

$$\log_{10} \beta_2^{\circ}(\mathrm{Fe(SO_4)_2^{2-}}, 298.15\ \mathrm{K}) = (2.0 \pm 0.4).$$

Too many corrections with too many assumptions and estimates are involved in this correction to zero ionic strength, and therefore no value is selected in the present review for the formation constant of the 2:1 complex.

IX.1.2.1.2.2 Heat of complexation of $\mathrm{Fe^{2+}}$ with $\mathrm{SO_4^{2-}}$

Wells and Salam [1968WEL/SAL] reported temperature-independent (~ 298 K) values of − (12.0 ± 0.4) kcal·mol^{-1} (−(50.2 ± 1.7) kJ·mol^{-1}) for $\Delta_r H_m^{\circ}$ ((IX.2), I = 1 M) and −(36 ± 1) cal·K^{-1}·mol^{-1} (−(151 ± 4) J·K^{-1}·mol^{-1}) for $\Delta_r S_m^{\circ}$ ((IX.2), I = 1 M). However, the method used by the authors to calculate values from the experimental data cannot be traced.

Izatt *et al.* [1969IZA/EAT2] simultaneously determined $\log_{10} \beta_1^{\circ}$ (FeSO$_4$, aq) = (2.20 ± 0.06) and $\Delta_r H_m^{\circ}$ (IX.2) = (0.56 ± 0.02) kcal·mol^{-1} ((2.34 ± 0.08) kJ·mol^{-1}) and calculated $\Delta_r S_m^{\circ}$ (IX.2) = (12.0 ± 0.2) cal·K^{-1}·mol^{-1} ((50 ± 1) J·K^{-1}·mol^{-1}) with the Gibbs-Helmholtz equation. The method applied by Izatt *et al.* (*i.e.*, [1966CHR/IZA]) leads to $\Delta_r H_m$ (IX.2) values that are (or should be) independent of the activity correction model (but the determination of β is not). Later on, the method used by [1966CHR/IZA] and [1969IZA/EAT2], was criticized by Cabani and Gianni [1972CAB/GIA], who said that the method may lead to “spurious” values when the concentration ranges involved are not carefully selected.

Hedwig and Powell [1973HED/POW] reinvestigated $\Delta_r H$ values of a series of bivalent transition metal sulfates (Zn^{2+}, Mn^{2+}, Mg^{2+}, Cu^{2+}, Co^{2+}). In all cases $\Delta_r H^\circ_m$ was found to be in the range 6.2 to 10.2 $kJ\cdot mol^{-1}$, about 4 to 7 $kJ\cdot mol^{-1}$ higher than the [1969IZA/EAT2] values for the same systems. Unfortunately, [1973HED/POW] did not investigate the iron(II) system, but an educated guess would favour a value for $\Delta_r H^\circ_m$ (IX.2) in the same range. Most likely, $\Delta_r H^\circ_m$ (IX.2) as given by Izatt *et al.* [1969IZA/EAT2] is too low.

From the conductivity data of Kubota *et al.* [1988KUB/MOC] at low ionic strength and 283.15 to 308.15 K, the enthalpy of reaction of

$$\Delta_r H^\circ_m ((\text{IX.2}), 298.15\ \text{K}) = (8.4 \pm 6.2)\ \text{kJ}\cdot\text{mol}^{-1}$$

is selected, compatible with the range of values from [1973HED/POW]. With $\log_{10} \beta^\circ_1$ ($FeSO_4$, aq) = (2.44 ± 0.03) the entropy of reaction is then calculated as

$$\Delta_r S^\circ_m (\text{IX.2}) = (74.81 \pm 20.80)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

IX.1.2.1.2.3 Evaluation of osmotic data

A study by Oykova and Balarew [1974OYK/BAL] provided values for the osmotic coefficients for $FeSO_4$(sln) from 0.1 m to saturation (1.9641 m) at 298.15 K. Recalculation of the “rounded” values of molality and adjustment of the value of the molar mass of H_2O to a more precise value, (18.0153 $g\cdot mol^{-1}$ instead of 18.0 $g\cdot mol^{-1}$ as given in the paper) is discussed in Appendix A. The results from a similar study reported by Nikolaev *et al.* [1989NIK/DIK] appear to be somewhat less reliable, and were not reanalysed in the same detail.

The osmotic coefficient is a function of the number of dissolved ions/complexes in solution:

$$\log_{10} a_{H_2O} = \frac{-\phi_1 \sum_k m_k}{\ln(10)\, M^{-1}_{H_2O}} \qquad (\text{IX.5})$$

Even if the iron(II)-sulfate complexes that may form are weak, significant amounts of these species may be present at equilibrium at higher molalities. Thus, strictly speaking, such complexes contribute to the sum Σm_k of molalities in Eq. (IX.5), and the molalities of Fe^{2+} and SO_4^{2-} are lower than the stoichiometric molality of $FeSO_4$(sln). Therefore, if evaluating complexation constants from the osmotic data, this needs to be considered (*cf.* the discussion of [1974OYK/BAL] in Appendix A).

When the osmotic data [1974OYK/BAL] were considered, no combination of $\varepsilon(\mathrm{Fe}^{2+}, \mathrm{SO}_4^{2-})$ and ε(neutral) could provide a satisfactory fit when using the value (275.4 ± 19.0) for $\beta_1^{\circ}(\mathrm{FeSO_4, aq})$ selected in Section IX.1.2.1.2.1 of this review ($\log_{10} \beta_1^{\circ} = (2.44 \pm 0.03)$). However, the osmotic data also do not support the suggestion of Ciavatta *et al.* [2002CIA/TOM] that a significantly strong 1:2 complex exists. The best representation of the data (*cf.* Appendix A) is achieved with the "most simple" model including just the 1:1 complex with a formation constant of $\beta_1^{\circ}(\mathrm{FeSO_4, aq}) = (154 \pm 3)$, and $\varepsilon(\mathrm{Fe}^{2+}, \mathrm{SO}_4^{2-}) = -(0.09 \pm {\sim}0.03)\ \mathrm{kg \cdot mol^{-1}}$. The value derived for this interaction coefficient is not zero, as might have been expected when a complex formation constant is used to express the interaction between Fe^{2+} and SO_4^{2-}. Because of the danger of over-interpretation of the somewhat scattered data, no value is recommended for $\varepsilon(\mathrm{Fe}^{2+}, \mathrm{SO}_4^{2-})$.

In the solutions used for the osmotic coefficient measurements, about 50 to 60% of the iron and sulfate are present in the form of the complex $\mathrm{FeSO_4(aq)}$. It is interesting to note that when a calculation is done specifically considering the amount of $\mathrm{FeSO_4(aq)}$ formed, the measured osmotic $\mathrm{FeSO_4}$ data cannot be represented without assuming a specific interaction coefficient for this neutral complex with the remaining charged species in solution ($\varepsilon(\mathrm{FeSO_4, Fe^{2+} + SO_4^{2-}}) = (0.32 \pm 0.03)\ \mathrm{kg \cdot mol^{-1}}$ is suggested by the analyses in Appendix A).

This situation has arisen in previous TDB assessments. Gamsjäger *et al.* [2005GAM/BUG] defined a "neutral" SIT coefficient $\varepsilon(\mathrm{Ni(SCN)_2(aq), Na^+ + ClO_4^-}) = (0.38 \pm 0.06)\ \mathrm{kg \cdot mol^{-1}}$, and Hummel *et al.* [2005HUM/AND] defined a series of "neutral" coefficients for the undissociated organic acids $\mathrm{H_2ox}$, $\mathrm{H_3cit}$ and $\mathrm{H_4edta}$ with electro-neutral combinations of inert electrolytes. Usually, the magnitude of such interaction coefficients is close to zero. The size of the above-mentioned $\mathrm{Ni(SCN)_2(aq)}$ interaction coefficient is an exception. Hence, the "neutral" SIT coefficient evaluated for $\varepsilon(\mathrm{FeSO_4, Fe^{2+} + SO_4^{2-}})$ from the osmotic data of $\mathrm{FeSO_4}$, seems high, but not unreasonable. However, it is not an "accepted value in the present review". Another study of osmotic coefficients for $\mathrm{FeSO_4}$ aqueous solutions was reported by Nikolaev *et al.* [1989NIK/DIK], and appears to be somewhat less reliable. There are some concerns about the consistency of both sets of measurements for $\mathrm{FeSO_4}$ solutions when they are compared to measurements for other transition metal surfaces (Appendix A).

IX.1.2.1.2.4 Formation of $\mathrm{FeHSO_4^+}$

For Reaction (IX.3), Beukenkamp and Herrington [1960BEU/HER] gave $\beta_{\mathrm{H1}} = 0.61\ \mathrm{kg \cdot mol^{-1}}$ ($\log_{10} \beta_{\mathrm{H1}} = -0.21$, $I_m < 2.2$ m). Wells and Salam [1968WEL/SAL] provided four experimental points at four different temperatures. Although the authors entitled their sub-table 1 with "$\mu = 4$", the ionic strength is not $I_m = 4\ \mathrm{mol \cdot kg^{-1}}$ due to the medium change. Correction of I_m and β_{H1} is outlined in Table IX-4 and Appendix A, and a summary is given in Table IX-6.

Table IX-6: The temperature dependence of the formation constant of $\mathrm{FeHSO_4^+}$ at high ionic strength [1968WEL/SAL].

temperature/°C	I_m	$\beta_{\mathrm{H1}}(\mathrm{FeHSO_4^+})/\mathrm{kg{\cdot}mol^{-1}}$
0	5.1	3.7
5	5.3	3.0
10	5.9	2.4
25	6.0	1.5

From the regression of $\log_{10}\beta_{\mathrm{H1}}(\mathrm{FeHSO_4^+}, I_m)$ *vs.* $(1/T_0 - 1/T)$ one finds $\Delta_r H(\mathrm{FeHSO_4^+}, I_m \approx 5.5) = -(24 \pm 6)\ \mathrm{kJ{\cdot}mol^{-1}}$ and $\log_{10}\beta_{\mathrm{H1}}(\mathrm{FeHSO_4^+}, I_m \approx 5.5) = (0.17 \pm 0.07)$. These results are not suitable for calculation of a formation constant value at $I = 0$, and no chemical thermodynamic quantities are selected for $\mathrm{FeHSO_4^+}$ in the present review. Note that at $I_m \approx 5.5$ the necessary correction terms, as well as their cumulative uncertainties, are (much) larger than the formation constant itself.

IX.1.2.1.3 Aqueous iron(III) - sulfato complexes

Early observations of colour changes of Fe(III) solutions upon addition of reagents showed that iron(III) ions form complexes. With sulfate, the fading of the strong yellow colour of chlorido complexes showed that sulfato complexes were stronger and less coloured than the chlorido complexes. The addition of phosphate to Fe(III) sulfato complexes gave a new discoloration showing that sulfate is a weaker ligand than phosphate.

It has been concluded that, for iron(III) in natural waters, sulfato complexes are important only at low and moderate pH [1995MIL/YAO]. Reviews of Fe(III) sulfato complexes in acidic aqueous solutions [2005CAS/CRI], [1990STI], have indicated that the main species to be considered are: $\mathrm{FeSO_4^+}$, $\mathrm{Fe(SO_4)_2^-}$, $\mathrm{Fe(SO_4)(HSO_4)(aq)}$, $\mathrm{FeHSO_4^{2+}}$.

There have been three substantial isopiestic studies of $\mathrm{H_2O}$-$\mathrm{H_2SO_4}$-$\mathrm{Fe_2(SO_4)_3}$ solutions [1985MAJ/AWA], [2004RUM/HAG], [2006VEL/PAL]. The result from the latter two studies, in which some of the solutions had high ratios of acid to iron, appear to be in reasonably good agreement. Tosca *et al.* [2007TOS/SMI] used these results to generate sets of Pitzer ion-interaction parameters; however, no attempt seems to have been made to use the osmotic data to determine formation constants for iron(III) sulfato complexes, and these isopiestic data are not analyzed further in the present review.

Experimentally determined values of formation constants for the sulfato complexes of iron(III) are presented in Table IX-7. They confirm that sulfate is only a moderately strong ligand, which cannot compete with $\mathrm{OH^-}$ at neutral and high pH.

IX.1.2.1.3.1 $FeSO_4^+$

The 1:1 aqueous sulfate complex of iron(III) is formulated without inner-sphere water because there are few investigations of the coordination mode of sulfate, which could be mono-, di- or tri-dentate in its association with iron (III). In a recent study by Majzlan and Myneni [2005MAJ/MYN] the monodentate character of the SO_4^{2-}/Fe^{3+} bond has been deduced from X-ray absorption data near the S absorption edge (XANES); but due to the nature of the ligand the number of water molecules in the first coordination sphere remains uncertain. $FeSO_4^+$ coexists with $Fe(H_2O)_6^{3+}$ and (probably) $FeHSO_4^{2+}$, in moderately acidic solutions of Fe(III), rather dilute in SO_4^{2-}. In spectra of Fe^{3+} solutions, upon addition of sulfate, there is a new UV-visible absorption band with a maximum absorption at 310 nm. This band is blue-shifted from the band of $FeCl^{2+}$ as expected for a charge-transfer band.

IX.1.2.1.3.2 $Fe(SO_4)_2^-$

This species is observed in more concentrated sulfate solutions. Its UV-visible spectrum is very similar to the spectrum of $FeSO_4^+$ except that its molar absorption coefficient is higher.

IX.1.2.1.3.3 $Fe(SO_4)_3^{3-}$

The potentiometric data of Mattoo [1959MAT] indicated that with an increase in SO_4^{2-} concentration in aqueous solutions, complex species in addition to $FeSO_4^+$ and $Fe(SO_4)_2^-$ are formed. This raises the question of the existence and stability of the $Fe(SO_4)_3^{3-}$ complex. However as this increase in sulfate concentration was not independent of the pH increase, it also could have been due to the formation of mixed $Fe(OH)_y(SO_4)_x^{(2x+y-3)-}$ species. Very few solid compounds with a SO_4^{2-}/Fe^{3+} ratio greater than two have been described in the literature (but see Section IX.1.2.2.3). A well-characterised polymeric mixed hydroxidosulfato complex has been found in the solid known as Maus's salt, $K_5Fe_3(SO_4)_6(OH)_2{\cdot}nH_2O$ [1975GIA/SCO]. Therefore a complete investigation of the iron (III) sulfate complexes in aqueous solution must add the iron concentration to the parameters which influence the speciation.

IX.1.2.1.3.4 $FeHSO_4^{2+}$

$FeHSO_4^{2+}$ has been reportedly observed in acidic sulfate solutions. In such solutions the concentrations of SO_4^{2-} become low because of the formation of HSO_4^-. So in acidic media a good interpretation of the data for the determination of the formation constant of the $FeHSO_4^{2+}$ complex requires precise knowledge of the protonation constant of SO_4^{2-}.

The nature of the cation present in the salt used for the ionic strength adjustment also plays a role. In some references the interaction between sulfate ions and sodium or potassium ions is described using a formation constant (sometimes with a value greater than 1) for the species MSO_4^- in which M is the alkali metal ion. Such interactions must be taken into account for the $FeHSO_4^{2+}$ formation-constant calculations. However the TDB practice is that these types of interactions are incorporated in activity coefficients using interaction coefficients, and MSO_4^- complexation constants were not used explicitly in the present review.

IX.1.2.1.3.5 $Fe(SO_4)(HSO_4)(aq)$

The existence of this species in acidic, concentrated sulfate solutions has been claimed in two papers (see Table IX-7). Its existence seems confirmed. It can be considered as the protonated form of the species $Fe(SO_4)_2^-$.

IX.1.2.1.3.6 Mixed hydroxidosulfato Fe(III) complexes

The existence of Fe(III) solid compounds containing both hydroxide and sulfate raises the question of the formation of mixed hydroxidosulfato complexes in aqueous solution as precursors of these insoluble species. Comparison with other trivalent cations suggests that the $\log_{10} K^\circ$ for dissociation of $Fe(OH)SO_4(aq)$ and $Fe(OH)_2SO_4^-$ expressed as: $\left(a_{FeOH^{2+}} a_{SO_4^{2-}}\right) / a_{Fe(OH)SO_4(aq)}$ and $\left(a_{Fe(OH)_2^+} a_{SO_4^{2-}}\right) / a_{Fe(OH)_2SO_4^-}$ are of the order of -2.3 and -0.8 [1990STI]. Several papers dealing with research on these mixed hydroxidosulfato complexes [1969ZVY/LYA], [1977SAP/PAT], [1978YAK/KUL], [1988KHO/ROB], [2002CIA/TOM2], [2002CIA/TOM3], [2003LIU/PAP] have been analyzed in the course of this review (*cf.* Appendix A).

Zvyagintsev and Lyakhamanov [1969ZVY/LYA] used potentiometry at a platinum electrode and pH measurements to show the presence of mixed complexes between pH 2 and 2.5 in 3 M $NaClO_4$ They claimed that $Fe_2(OH)_2(SO_4)_2(aq)$ and $Fe_2(OH)_2(SO_4)^{2+}$ coexist with the well-established binary complexes $FeSO_4^+$ and $Fe(SO_4)_2^-$. They varied the iron(III) concentration between 0.01 and 0.1 M and provided results at several temperatures. Their formation constant values for the binary complexes, as well as the value for the protonation constant for SO_4^{2-}, are in moderate agreement with other literature values, but no detailed data were provided that would have allowed a re-evaluation using the SIT model.

Sapiesko *et al.* [1977SAP/PAT] in their extended investigation of binary sulfato and hydroxido complexes of Fe^{3+} did not observe ternary mixed complexes in solutions in equilibrium with solid $Fe_3(OH)_5(SO_4)_2{\cdot}2H_2O$ at pH 1.7. Their solutions were concentrated in iron(III); the initial solution, before precipitation was 0.18 M in iron(III), and 0.53 M in Na_2SO_4.

Khoe and Robins [1988KHO/ROB] also investigated complexes of Fe(III) in solutions with compositions favourable to the possible formation of mixed hydroxidosulfato complexes. By addition of $NaHCO_3$, they varied the pH of solutions that were 1 M in $NaNO_3$, 2×10^{-4} to 2×10^{-2} M in sulfate and 2×10^{-4} to 1.977×10^{-2} M in iron(III). The best fit to their data was obtained with a model that included the species $FeSO_4^+$, $FeOH^{2+}$, $Fe_2(OH)_4^{2+}$, $Fe_3(OH)_4^{5+}$, and $Fe_3(OH)_4(SO_4)^{3+}$.

More recently Ciavatta *et al.* [2002CIA/TOM2], [2002CIA/TOM3], using pH measurements, again investigated speciation in solutions of Fe(III) in 3 M $NaClO_4$.

Their experiments covered a wide range of pH and of sulfate and metal concentrations. In their models the authors used values for formation constants for the binary complexes, as determined previously in similar media (*cf.* Appendix A). The best fit to their experimental data was obtained with a model containing only one ternary species, $Fe(OH)(SO_4)(aq)$.

Over the period 1969 to 2002 there has been a continuous improvement in computational methods, an increasing number of data points in each successive study, and more careful determination of values of auxiliary constants, such as those for formation of the binary iron(III) sulfato- and hydroxido- species. Also, it has become clearer that it is important to establish the changes that occur in the predominant iron(III) species formed in solution as the pH is varied. No agreement is found between the investigations that have used a pH-variation technique. Therefore, in the present review we do not recommend formation-constant values or stoichiometry for any hydroxidosulfato species. As discussed in Appendix A, more direct methods of speciation might improve the situation.

IX.1.2.1.3.7 Mixed sulfatothiocyanato Fe(III) complexes

The ability of Fe(III) sulfates to form mixed complexes in aqueous solution has been demonstrated by use of sulfatothiocyanato competition as a method of investigation [1955LIS/RIV], [1955LIS/RIV2]. Mixed species such as $Fe(SO_4)(SCN)(aq)$ and (probably) $Fe(SO_4)_2(SCN)^{2-}$ were claimed, as SO_4^{2-} ions do not simply replace SCN^- ions in the iron(III) thiocyanate complexes.

IX.1.2.1.3.8 Literature dealing with the iron(III) sulfato complexes

A review of the main papers dealing with the iron(III) sulfato complexes is presented in Table IX-7. Experimental conditions and experimental and re-evaluated formation constants for iron(III) sulfato complexes are summarized. A more complete discussion of the re-evaluations is given in the corresponding Appendix A entries.

The contents of Table IX-7 indicate that there are difficulties in obtaining standard thermodynamic values even for the well-established sulfato complexes of Fe(III), such as $FeSO_4^+$, $Fe(SO_4)_2^-$ and $FeHSO_4^{2+}$, because of the interference of side reactions such as the formation of hydrogen sulfate, and of sulfate interaction with alkali metal ions of the medium (in some cases described in the literature as ion-pair formation). There have been many different determinations of the acid dissociation constant for HSO_4^-, and of the ion-pair association constants with the alkali cations. Spectrophotometry, which has been the key method for the investigation of chlorido complexes, is less decisive in sulfate studies because the charge-transfer bands of Fe(III) sulfato complexes are blue-shifted and partially mixed with bands for $Fe(H_2O)_6^{3+}$. Mixed species such as $Fe(SO_4)(HSO_4)(aq)$ and soluble hydroxidosulfato complexes are not as well established because of the interference between species. Raman spectroscopy in the low-energy zone seems to be a good tool to characterize such species. Casas *et al.* [2005CAS/CRI] claimed that they distinguished the

$Fe\text{-}OSO_3H^{2+}$ stretching band from the $Fe\text{-}OSO_3^+$ band in the Raman spectrum of concentrated acidic Fe(III) sulfate solutions. Further research into the $Fe\text{-}OH^{2+}$ Raman emission bands seems worthwhile; they could be used to characterize mixed hydroxidosulfato complexes if they can be distinguished from the $Fe\text{-}OSO_3^+$ band.

Table IX-7: Summary of the main publications dealing with the aqueous sulfate complexes of iron(III).

Reference	Method	Ionic medium	t /°C	reported value $^{(a)}$	Re-evaluation $^{(b)}$
[1952SYK]	kin	$I_c = 0.066$ (HNO_3 + $NaClO_4$)	18	$\beta_1 = 1040$	$\beta_{1m} = (1330 \pm 300)$
[1953WHI/DAV]	ix	$I_c = 1$ ($HClO_4$, H_2SO_4)	28	$\beta_1 = (95 \pm 4)$	$\beta_{1m} = (114 \pm 21)$
				$\beta_2 =(898 \pm 159)$	$K_{2m} = (12.1 \pm 4.1)$
	sp		27	$\beta_1 = (101 \pm 2)$	$\beta_{1m} = (126 \pm 25)$
				$\beta_1 = (121 \pm 2)$	$K_{2m} = (151 \pm 30)$
[1954SYK]	sp	$I_c = 0.15$ (ClO_4)	19	$\beta_1 = 228$	———
				$K = 60$ for $HSO_4^- + Fe^{3+} \rightleftharpoons FeHSO_4^{2+}$	
[1955LIS/RIV]	sp	$I_c = 1.2$	25	$\beta_1 = (165 \pm 10)$	(89 ± 10)
[1955LIS/RIV2]				$\beta_2 =16600$	———
				$K = (6 \pm 1)$ for $HSO_4^- + Fe^{3+} \rightleftharpoons FeHSO_4^{2+}$	(6.6 ± 3.6)
				$K = (380 \pm 5)$ for $HSO_4^- + SO_4^{2-} + Fe^{3+} \rightleftharpoons Fe(SO_4)(HSO_4)(aq)$	Not optimized
				$K_{11} = 1.15 \times 10^4$ ($Fe(SO_4)(SCN)(aq)$)	Not optmized
				$K_{21} = 4.9 \times 10^5$ ($Fe(SO_4)_2SCN^{2-}$)	Not optimized
[1959BAB/MAR]	sp	0.1 M HNO_3	20	$\beta_1 = (455 \pm 60)$	———
[1959MAT]	pot	var	25		
		$HClO_4/NaClO_4$		$\beta_{1c} = 263$	$\beta_{1m} = (263 \pm 50)$
		$I_m = 0.253$		$K_{2c} = 7.9$	$K_{2m} = (31.4 \pm 5.0)$
				$\beta_{1c} = 162$	$\beta_{1m} = (184 \pm 30)$
		$I_m = 0.776$		$K_{2c} = 3.5$	$K_{2m} = (7.6 \pm 3.0)$
				$\beta_{1c} = 117$	$\beta_{1m} = (132 \pm 20)$
		$I_m = 1.65$		$K_{2c} = 3.0$	$K_{2m} = (11.5 \pm 4.0)$
				$\beta_{1c} = 105$	$\beta_{1m} = (95 \pm 15)$

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Table IX-7 (continued)

Reference	Method	Ionic medium	t /°C	reported value $^{(a)}$	Re-evaluation $^{(b)}$
		$I_m = 3.5$		$\log_{10} \beta_1^\circ = 4.04$	$\log_{10} \beta_1^\circ = (4.3 \pm 0.2)$
					$-\Delta\varepsilon = (0.24 \pm 0.04)$
		$I = 0$ (extrap)		$\log_{10} K_2^\circ = 1.34$	$\log_{10} K_2^\circ = (2.0 \pm 0.6)$
[1960KUM]	sp	$HClO_4/H_2SO_4$			
		$I_c = 0.10$	20	$\beta_1 = (417 \pm 8)$	$\beta_{1m} = (533 \pm 80)$
		$I_c = 0.20$	20	$\beta_1 = (243 \pm 4)$	$\beta_{1m} = (330 \pm 40)$
		$I_c = 0.40$	20	$\beta_1 = (131 \pm 2)$	$\beta_{1m} = (188 \pm 24)$
		$I_c = 0.69$	20	$\beta_1 = (94.5 \pm 2.0)$	$\beta_{1m} = (133 \pm 20)$
		$I_c = 1.0$	20	$\beta_1 = (67.7 \pm 1.0)$	$\beta_{1m} = (87 \pm 16)$ at 20 °C
		$I_c = 1.0$	30	$\beta_1 = (85.6 \pm 1.0)$	$\beta_{1m} = (104 \pm 20)$ at 25 °C
					$\beta_{1m} = (122 \pm 20)$ at 30 °C
					$\log_{10} \beta_1^\circ = (4.05 \pm 0.10)$
					extrap.
		$I = 0$	25		$\Delta_r H_{1m} = (25 \pm 18)$
		$I_c = 1.0$	20-30	$\Delta_r H_1 = 17.6$	
[1962BRO/MIN]	sp	$I_c = 0.15$ (H_2SO_4)	21.5	$\beta_1 = (114 \pm 9)$	———
[1962DAV/SMI]	sp	$HClO_4/H_2SO_4$			
		$I_c = 0.5$	1.4	$\beta_1 = (95 \pm 6)$	$\beta_{1m} = (70 \pm 7)$
		$I_c = 0.5$	15.0	$\beta_1 = (149 \pm 10)$	$\beta_{1m} = (119 \pm 12)$
		$I_c = 0.5$	25.0	$\beta_1 = (205 \pm 18)$	$\beta_{1m} = (180 \pm 30)$
		$I_c = 0.5$	35.0	$\beta_1 = (280 \pm 22)$	$\beta_{1m} = (258 \pm 30)$
		$I_c = 0.5$	1.4-35	$\Delta_r H_1 = 23.0$	$\Delta_r H_{1m} = (28 \pm 18)$
[1963BAC/LIE]	sp	$I_c = 1.0$	25	$\beta_1 = 173$	———
				$K_2 = 8.8$	
			0-25 ?	$\Delta_r H_1 = 21.5$[1]	
				$\Delta_r H_2 = -60.2$	
[1963WIL]	pot	$I_c = 0.5$	0	$\beta_1 = 75$	
		($HClO_4 + NaClO_4$)	25	$\beta_1 = 211$	———
	kin		0	$\beta_1 = 68$	
			25	$\beta_1 = 198$	$\beta_{1m} = (173 \pm 30)$
	sp		1.0	$\beta_1 = 86$	$\beta_{1m} = (76 \pm 17)$
			11.0	$\beta_1 = 129$	$\beta_{1m} = (113 \pm 10)$
			22.0	$\beta_1 = 199$	$\beta_{1m} = (175 \pm 20)$

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[1] The original paper appears to have had the signs of these enthalpies of reaction reversed (*cf.* Appendix A)

Table IX-7 (continued)

Reference	Method	Ionic medium	t /°C	reported value [(a)]	Re-evaluation [(b)]
		$I = 0$ (extrap.)	25	$\Delta_r H_1 = (25.9 \pm 1.3)$	$\Delta_r H_{1m} = (26.7 \pm 2.0)$
[1967MAS]	sp	$I_c = 1.2$ ($HClO_4$ (0.2 M) + $NaClO_4$)	20	$\beta_1 = (115 \pm 3)$	———
[1969SID/GOR]	amper	$I_c = 0.058$ ($HClO_4$)	25	$\beta_1 = 870$	———
[1969ZVY/LYA]	pot	3.0 M $NaClO_4$	25	$\beta_1 = 170$	———
				$\beta_2 = 1800$	$K_{2m} = (9.1 \pm 1.0)$
				$K_{2,1} = 320$ $(Fe_2(OH)_2^{4+} + SO_4^{2-} \rightleftharpoons Fe_2(OH)_2SO_4^{2+})$	———
				$K_{2,2} = 1100$ $(Fe_2(OH)_2^{4+} + 2SO_4^{2-} \rightleftharpoons Fe_2(OH)_2(SO_4)_2^{0})$	———
			35	$\beta_1 = 250$	———
				$\beta_2 = 2050$	$K_{2m} = (7.0 \pm 1.0)$
				$K_{2,1} = 500$	———
				$K_{2,2} = 6700$	———
			45	$\beta_1 = 310$	———
				$\beta_2 = 2200$	$K_{2m} = (6.1 \pm 1.0)$
				$K_{2,1} = 650$	———
				$K_{2,2} = 9600$	———
				$\Delta_r H_1 = -24.3$	
				$\Delta_r H_2 = -(15.5 \pm 1.3)$	$\Delta_r H_{2m} = -(15.8 \pm 2.0)$
[1973NIK/PAL]	pot	$I_c = 3.0$ (Na_2SO_4/$NaClO_4$)	25	$\beta_1 = (85 \pm 8)$	$\beta_{1m} = (103 \pm 11)$
				$\beta_2 = (130 \pm 30)$	$K_{2m} = (19 \pm 4)$
				$K = (1.0 \pm 0.5)$ (for $HSO_4^- + Fe^{3+} \rightleftharpoons FeHSO_4^{2+}$)	$K_{1FeHSO_4^{2+}} = (4.8 \pm 2.4)$
[1975NIK/TSV]		$I = 0$ authors' extrap. and eqn.	25	$\log_{10} \beta_1 = 4.43$	———
			50	$\log_{10} \beta_1 = 4.87$	
			70	$\log_{10} \beta_1 = 5.26$	
			90	$\log_{10} \beta_1 = 5.68$	
			100	$\log_{10} \beta_1 = 5.89$	
			125	$\log_{10} \beta_1 = 6.41$	
			150	$\log_{10} \beta_1 = 6.92$	

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Table IX-7 (continued)

Reference	Method	Ionic medium	t /°C	reported value (a)	Re-evaluation (b)
[1977ASH/HAN2]	sp	$I_c = 5.0$	25	$\beta_1 = (210 \pm 3)$	———
		($HClO_4$ (1.0 M)	34	$\beta_1 = (265 \pm 4)$	
		+ $NaClO_4$)	47	$\beta_1 = (324 \pm 3)$	
			60	$\beta_1 = (432 \pm 6)$	
			25-60	$\Delta H_1 = 21.5$	
[1977SAP/PAT]		$I_c = 2.67$	25	$\beta_1 = (84 \pm 7)$	$\beta_{1m} = (73.7 \pm 6.0)$
		$HClO_4 + NaClO_4$	55	$\beta_1 = (245 \pm 20)$	
			80	$\beta_1 = (1020 \pm 110)$	
			25-80	$K = (4 \pm 1)$ (for HSO_4^-	$K_{1FeHSO_4^{2+}} = (2.7 \pm 0.8)$
				$+ Fe^{3+} \rightleftharpoons FeHSO_4^{2+}$)	
[1988FEN/WAK]	sp	$I_c = 0.4$	20	$\beta_1 = 196$	———
		($HClO_4 + H_2SO_4$)			
[1988KHO/ROB]	pot	1.0 M $NaNO_3$	25	$\log_{10} {}^*\beta_{110} = -3.01$(c)	———
				$\log_{10} {}^*\beta_{220} = -3.09$	
				$\log_{10} {}^*\beta_{430} = -6.92$	
				$\log_{10} {}^*\beta_{011} = 1.51$	
				$\log_{10} {}^*\beta_{431} = -4.34$	
[1990STI]				*Review*	
[2002CIA/TOM2]	pot	3 M $NaClO_4$	25	$\log_{10} \beta_{1c} = (1.65 \pm 0.02)$	$\log_{10} \beta_{1m}$ average
	sp	3 M $NaClO_4$	25	$\log_{10} \beta_{1c} = (1.55 \pm 0.12)$	(pot, sp) =
					(1.61 ± 0.14)
	pot	3 M $NaClO_4$	25	$\log_{10} \beta_{2c} = (2.68 \pm 0.02)$	$\log_{10} K_{2m}$ average
	sp	3 M $NaClO_4$	25	$\log_{10} \beta_{2c} = (2.77 \pm 0.20)$	(pot, sp) =
					(1.13 ± 0.14)
	pot	3 M $NaClO_4$	25	$\log_{10} K_c = (2.36 \pm 0.20)$	$\log_{10} K_m$ average
				(for $Fe^{3+} + H^+ + SO_4^{2-} \rightleftharpoons$	(pot, sp) =
				$FeHSO_4^{2+}$)	(2.33 ± 0.14)
	sp	3 M $NaClO_4$	25	$\log_{10} K_c = (2.39 \pm 0.26)$	
				(for $Fe^{3+} + H^+ + SO_4^{2-} \rightleftharpoons$	
				$FeHSO_4^{2+}$)	
[2002CIA/TOM3]	pot	3 M $NaClO_4$	25	$\log_{10} {}^*\beta_{111c} =$	
				$-(0.49 \pm 0.03)$ (c)	

(Continued on next page)

Table IX-7 (continued)

Reference	Method	Ionic medium	t /°C	reported value [(a)]	Re-evaluation [(b)]
[2005CAS/CRI]	sol, modelling	$I = 0$ authors' model		$\log_{10} K^\circ = (8.1 \pm 0.3)$ (for $Fe^{3+} + 2SO_4^{2-} + H^+ \rightleftharpoons$ $Fe(SO_4)(HSO_4)(aq)$)	———

(a) Molar constants; values of $\Delta_r H$ in kJ·mol^{-1}; values of $\Delta_r S$ in J·K^{-1}·mol^{-1}.

(b) Molal constants; when necessary, molar values were converted to molal values using the conversion factors in Table II-5.

(c) $^*\beta_{qmr}$ is the equilibrium constant for $m\,Fe^{3+} + q\,H_2O(l) + r SO_4^{2-} = Fe_m(OH)_q(SO_4)_r^{3m-q-2r} + q\,H^+$.

IX.1.2.1.4 Application of the SIT formalism for the Fe(III) sulfato complexes

There are fewer publications dealing with the formation constants of the sulfato iron(III) complexes as a function of the ionic strength than there are for the chlorido complexes. Most investigations were carried out at only a single ionic strength. Also, there are difficulties in applying the SIT because of the more limited availability of interaction coefficients involving SO_4^{2-} or HSO_4^- ions. Attempts to apply the SIT formalism to the values in the literature are described below.

IX.1.2.1.4.1 $FeSO_4^+$

The reaction investigated is:

$$Fe^{3+} + SO_4^{2-} \rightleftharpoons FeSO_4^+. \qquad \text{(IX.6)}$$

The equilibrium constant K(IX.6) is reprensented by the symbol β_1 in Table IX-7 and all Sections IX.1.2.1.4 through IX.1.2.1.6.

For extrapolation to zero ionic strength, the formula (IX.7) might be used.

$$\log_{10} \beta_{1m} + 12D = \log_{10} \beta_1^\circ - \Delta\varepsilon\, I_m \qquad \text{(IX.7)}$$

In this equation, D is the Debye-Hückel term

$$D = 0.509\, I_m^{½} / (1 + 1.5\, I_m^{½}). \qquad \text{(IX.8)}$$

The value of $-\Sigma z_i^2$ for Reaction (IX.6), where z_i is the charge number for each species involved, is + 12 in Eq. (IX.7).

The value of $\Delta\varepsilon$ in Eq. (IX.7) is the difference between the interaction coefficients of the products and the reactants. However, the equation can be applied only if for each ε the approximation holds that the ionic strength is approximately equal to the concentration of the main interacting ion. This is the case for the solutions in which the main interacting ions are the cation and the anion of the salt added to maintain a constant ionic strength. Five studies are examined here in detail.

The work of Mattoo [1959MAT] can be considered to be one case in which the ionic strength is approximately equal to the concentration of the main interacting ion because $m_{\mathrm{Na}^+} >> m_{\mathrm{H}^+}$. If the ligand and the metal are much less concentrated than the added salt, then for Reaction (IX.6), Eq. (IX.7) becomes:

$$\log_{10}\beta_{1m} + 12D = \log_{10}\beta_1^{\circ} - (\varepsilon(\mathrm{FeSO}_4^+, \mathrm{ClO}_4^-) - \varepsilon(\mathrm{Fe}^{3+}, \mathrm{ClO}_4^-) - \varepsilon(\mathrm{Na}^+, \mathrm{SO}_4^{2-}))I_m \quad \text{(IX.9)}$$

The data of Mattoo have been reinterpreted, taking into account the nature of iron(II)-sulfate interactions as discussed in Section IX.1.2.1.2 of this review. Because the iron(II) interactions with sulfate are not negligible, it is found here that the 1:1 and 2:1 Fe(III)–SO_4^{2-} associates are generally more stable than described in the literature. The introduction of a third species $\mathrm{Fe(SO_4)}_3^{3-}$ provides the best fit to the potentiometric data (see Appendix A). The results of the reinterpretation of Mattoo's data are the following. The total uncertainty in $\log_{10}\beta_1^{\circ}$ has been increased to ±0.20 to take into account the probable systematic errors.

$$\log_{10}\beta_1^{\circ} = (4.30 \pm 0.20);\ -\Delta\varepsilon = (0.24 \pm 0.08)\ \mathrm{kg \cdot mol^{-1}} \qquad R^2 = 0.97$$

Taking into account the values (0.73 ± 0.05) kg·mol^{-1} for $\varepsilon(\mathrm{Fe}^{3+}, \mathrm{ClO}_4^-)$ (SIT$_1$, Section VI.1.2.1.1.1) and $-(0.12 \pm 0.06)$ kg·mol^{-1} for $\varepsilon(\mathrm{Na}^+, \mathrm{SO}_4^{2-})$, one gets:

$$\varepsilon(\mathrm{FeSO}_4^+, \mathrm{ClO}_4^-) = (0.34 \pm 0.10)\ \mathrm{kg \cdot mol^{-1}}$$

The SIT$_2$ formulation with $\varepsilon(\mathrm{Fe}^{3+}, \mathrm{ClO}_4^-)$ = {(0.78 ± 0.05) – (0.41 ± 0.05) $\log_{10} I_m$} (see Section VI.1.2.1.1.1) was not applied in the analysis of data for the Fe^{3+} sulfato complexes because, as discussed for the chlorido complexes, it yields different (though probably better) results only at very low and high ionic strengths. Moreover, other simplifications are necessary to treat the literature data with the SIT, and in view of those, the complexity introduced by using the SIT$_2$ formulation is not justified.

Equation (IX.7) is not useful for extrapolation of constants β_{1m} obtained in constant ionic strength mixtures such as ($\mathrm{NaClO_4}$, $\mathrm{HClO_4}$) or ($\mathrm{H_2SO_4}$, $\mathrm{HClO_4}$) to zero ionic strength. However, the value of $\varepsilon(\mathrm{FeSO}_4^+, \mathrm{ClO}_4^-)$ derived above can be used to calculate β_1°. The second study, the work of Whiteker and Davidson [1953WHI/DAV] was carried out in acidic medium 1 M ($\mathrm{H_2SO_4}$ + $\mathrm{HClO_4}$, no other salts were present as part of the supporting electrolyte) at 300.15 or 301.15 K. Therefore, $\log_{10}\beta_{1m}$ for the chemical composition of the solutions used is recalculated using the value of $\log_{10} K_{m1,1(\mathrm{HSO}_4^-)}$ recalculated in this review

$$\mathrm{H}^+ + \mathrm{SO}_4^{2-} \rightleftharpoons \mathrm{HSO}_4^- \qquad \text{(IX.10)}$$

$$K_{1,1(\mathrm{HSO}_4^-)} \equiv K(\text{IX.10})$$

(from the TDB recommended value of $\log_{10} K^{\circ}_{1,1(\mathrm{HSO}_4^-)}$ = (1.98 ± 0.05) and the SIT formalism). Temperature corrections have been carried out (see Appendix A for the details). For the ion-exchange data a complete recalculation was possible, but for the spectrophotometric investigations it proved possible only to correct the authors' β_1 values for the differences in temperature and $K_{1,1(\mathrm{HSO}_4^-)}$ values. These corrected constants have been used for the overall optimization.

For the application of the SIT formalism to systems involving $\mathrm{SO_4^{2-}}$ and $\mathrm{HSO_4^-}$ ions, many interaction coefficients are unavailable in Tables B-4 and B-5 of earlier TDB volumes [2005GAM/BUG]. In such cases estimates were made, as described below, taking the formation of $\mathrm{FeSO_4^+}$ as an example.

One has:

$$\begin{aligned}\log_{10}\beta_1^\circ &= \log_{10}\beta_{1m} + 12D + \varepsilon(\mathrm{FeSO_4^+},\mathrm{ClO_4^-})\,m_{\mathrm{ClO_4^-}} + \varepsilon(\mathrm{FeSO_4^+},\mathrm{HSO_4^-})\,m_{\mathrm{HSO_4^-}}\\ &+ \varepsilon(\mathrm{FeSO_4^+},\mathrm{SO_4^{2-}})\,m_{\mathrm{SO_4^{2-}}} - \varepsilon(\mathrm{Fe^{3+}},\mathrm{ClO_4^-})\,m_{\mathrm{ClO_4^-}} - \varepsilon(\mathrm{Fe^{3+}},\mathrm{HSO_4^-})\,m_{\mathrm{HSO_4^-}} -\\ &\varepsilon(\mathrm{Fe^{3+}},\mathrm{SO_4^{2-}})\,m_{\mathrm{SO_4^{2-}}} - \varepsilon(\mathrm{H^+},\mathrm{SO_4^{2-}})\,m_{\mathrm{H^+}}\end{aligned} \qquad \text{(IX.11)}$$

In Eq. (IX.11): $\varepsilon(\mathrm{FeSO_4^+},\mathrm{HSO_4^-})$, $\varepsilon(\mathrm{FeSO_4^+},\mathrm{SO_4^{2-}})$, $\varepsilon(\mathrm{Fe^{3+}},\mathrm{HSO_4^-})$, $\varepsilon(\mathrm{Fe^{3+}},\mathrm{SO_4^{2-}})$, $\varepsilon(\mathrm{H^+},\mathrm{SO_4^{2-}})$ are unknown and some assumptions are necessary to estimate β_1°. The assumptions used are:

$\varepsilon(\mathrm{FeSO_4^+},\mathrm{HSO_4^-}) \approx \varepsilon(\mathrm{FeSO_4^+},\mathrm{ClO_4^-}) = (0.34 \pm 0.10)\ \mathrm{kg\cdot mol^{-1}}$ determined from the SIT treatment of the Mattoo work;

$\varepsilon(\mathrm{Fe^{3+}},\mathrm{HSO_4^-}) \approx \varepsilon(\mathrm{Fe^{3+}},\mathrm{ClO_4^-}) = (0.73 \pm 0.05)\ \mathrm{kg\cdot mol^{-1}}$ (SIT$_1$ of Chapter VI of this review);

$\varepsilon(\mathrm{H^+},\mathrm{SO_4^{2-}}) \approx \varepsilon(\mathrm{Li^+},\mathrm{SO_4^{2-}}) = -(0.03 \pm 0.04)\ \mathrm{kg\cdot mol^{-1}}$ (Table B-5);

$\varepsilon(\mathrm{Fe^{3+}},\mathrm{SO_4^{2-}})\,m_{\mathrm{SO_4^{2-}}} < \varepsilon(\mathrm{FeSO_4^+},\mathrm{HSO_4^-})\,m_{\mathrm{HSO_4^-}}$ and in our recalculations is arbitrarily fixed at 10% of the latter. Although the value of $\varepsilon(\mathrm{Fe^{3+}},\mathrm{SO_4^{2-}})$ is probably > $\varepsilon(\mathrm{FeSO_4^+},\mathrm{HSO_4^-})$, at least in the work of Whiteker and Davidson [1953WHI/DAV], $m_{\mathrm{HSO_4^-}} >> m_{\mathrm{SO_4^{2-}}}$.

Finally we used Eq. (IX.12) to calculate β_1° from the six values from the ion exchange data of Whiteker and Davidson [1953WHI/DAV]. The values of β_{1m} were those obtained from the β_{1c} of the original paper converted to molal constants and corrected for the value of the $K^{-1}_{1,1(\mathrm{HSO_4^-})}$ acidity constant of $\mathrm{HSO_4^-}$; 0.059 $\mathrm{mol\cdot kg^{-1}}$ instead of 0.075 $\mathrm{mol\cdot dm^{-3}}$.

$$\log_{10}\beta_1^\circ = \log_{10}\beta_{1m} + 12D - 0.389\,m_{\mathrm{ClO_4^-}} - 0.428\,m_{\mathrm{HSO_4^-}} + 0.03\,m_{\mathrm{H^+}} \qquad \text{(IX.12)}$$

Average $\log_{10}\beta_1^\circ$ (301.15 K) = (4.27 ± 0.10).

For the spectrophotometric part the calculation yields:

$$\log_{10}\beta_1^\circ\ (300.15\ \mathrm{K}) = (4.29 \pm 0.10).$$

After corrections for the temperature taking the value of $\Delta_r H_{1m}$ = (26.0 ± 6.3) $\mathrm{kJ\cdot mol^{-1}}$, which can be deduced from the temperature influence upon K_1' (see Section IX.1.2.1.4.2), and averaging the spectrophotometric and ion-exchange data one gets:

$$\log_{10}\beta_1^\circ\ (298.15\ \mathrm{K}) = (4.24 \pm 0.14).$$

So this value is reasonably consistent with the value found in an aqueous medium in which Na^+ was the main cation [1959MAT], and does not invalidate the assumptions made for its determination.

Other values of β_1 are those of Sapieszko *et al.* [1977SAP/PAT] and Lister and Rivington [1955LIS/RIV2] obtained by spectrophotometry in mixed $HClO_4$-$NaClO_4$ media and Nikol'skii *et al.* [1973NIK/PAL], also from experiments in a mixed medium, but obtained from potentiometric data.

The paper of Sapieszko *et al.* [1977SAP/PAT] does not contain raw numerical experimental values to allow complete recalculation of the stability constant β_{1m} at 298.15 K. Its value, (73.7 ± 6.0) $kg\cdot mol^{-1}$, was used for extrapolation to the standard conditions according to the SIT method using Eq. (IX.13).

As no details of solution composition were given in the original paper, Eq. (IX.12) has been applied to the composition: $I_c = 2.67$ M, $c_{NaClO_4} = 1.67$ M, $c_{HClO_4} = 1.0$ M, and the concentrations of Fe(III), HSO_4^-, and SO_4^{2-} are negligible compared to those of Na^+, H^+, and ClO_4^-. In this case, the value of the conversion factor from the molar to the molal scale, $\xi = 1.14$, was obtained by using the values of $NaClO_4$ and $HClO_4$ (see Appendix A).

The SIT Eq. (IX.13) is used to calculate a $\log_{10} \beta_1^o$ value which is comparable with the other values given above.

$$\begin{aligned}\log_{10} \beta_1^o = {} & \log_{10} \beta_{1m} + 12D + [\varepsilon(\mathrm{FeSO_4^+}, \mathrm{ClO_4^-}) - \varepsilon(\mathrm{Fe^{3+}}, \mathrm{ClO_4^-})]\, m_{\mathrm{ClO_4^-}} \\ & - [\varepsilon(\mathrm{H^+}, \mathrm{SO_4^{2-}})\, m_{\mathrm{H^+}}] - [\varepsilon(\mathrm{Na^+}, \mathrm{SO_4^{2-}})\, m_{\mathrm{Na^+}}]\end{aligned} \quad \text{(IX.13)}$$

$$\begin{aligned}\log_{10} \beta_1^o = {} & \log_{10} (73.7 \pm 6.0) + 12\,(0.2455) - (0.39 \pm 0.11)\,3.043 \\ & + (0.03 \pm 0.04)\,1.14 + (0.12 \pm 0.06)\,1.904\end{aligned} \quad \text{(IX.14)}$$

which yields: $\log_{10} \beta_1^o = (3.89 \pm 0.42)$.

The value of β_{1m} at 298.15 K given by [1955LIS/RIV2], (165 ± 10) $kg\cdot mol^{-1}$ at $I_m = 1.27$, is higher than the other values found in the literature. One obvious reason is the value of 0.035 $mol\cdot kg^{-1}$ selected for the averaged HSO_4^- dissociation constant, which yields an average $\log_{10} K_{m1,1(\mathrm{HSO_4^-})}$ value of 1.456. The TDB selected value, $\log_{10} K^o_{1,1(\mathrm{HSO_4^-})} = (1.98 \pm 0.05)$ and the application of the SIT formalism with the assumptions proposed in the Appendix A leads to $\log_{10} K_{m1,1(\mathrm{HSO_4^-})} = (1.13 \pm 0.09)$ for $m_{\mathrm{H^+}} = 0.53$ and $\log_{10} K_{m1,1(\mathrm{HSO_4^-})} = (1.16 \pm 0.09)$ for $m_{\mathrm{H^+}} = 0.053$, the two extreme acidities used by the authors. Averaging these values of $\log_{10} K_{m1,1(\mathrm{HSO_4^-})}$ yields 0.072 $mol^{-1}\cdot kg$ instead of 0.037 $mol^{-1}\cdot kg$ for the dissociation constant $K^{-1}_{m1,1(\mathrm{HSO_4^-})}$. That increases the values of SO_4^{2-} and lowers the calculated β_m values.

Another reason for this discrepancy could be some hydrolysis in the less acidic solutions.

The charge-transfer band of $\mathrm{FeOH^{2+}}$ is very similar to that of $\mathrm{FeSO_4^+}$. We have recalculated the formation constants for all the acidities and find values consistent with the rest of the literature (see Appendix A). The results of the lowest-acidity experiment (0.05 M acid) have been discarded.

The paper of Nikol'skii *et al.* [1973NIK/PAL] is another report that dealt with a potentiometric investigation of iron(III) sulfato complexes. The medium was a mixture of $\mathrm{NaClO_4}$ and $\mathrm{H_2SO_4}$ at various pH values, and at a constant ionic strength, $I_m = 3.5$. The value of β_{1m}, (72.8 ± 6.9), is surely underestimated because the authors assumed that $\mathrm{Fe^{2+}}$ does not form sulfato complexes. In contrast to Mattoo's publication [1959MAT], which provides detailed information, in the paper of Nikol'skii *et al.* [1973NIK/PAL] there are no tables of numerical values which would have allowed a reviewer to account properly for formation of sulfato complexes by $\mathrm{Fe^{2+}}$. A reanalysis of the work of Nikol'skii *et al.* is decribed in detail in Appendix A. The reported formation constants of $\mathrm{FeSO_4^+}$, $\mathrm{Fe(SO_4)_2^-}$ and $\mathrm{FeHSO_4^{2+}}$ were used to generate a list of electrode potentials E and these were fitted by the Nernst equation (Eq. (IX.15)):

$$\begin{aligned} E = E^{\circ} &+ (RT(\ln(10))/F)\log_{10}\{m_{\mathrm{Fe(III)total}}[1+\beta_{1m\mathrm{FeSO_4}}m_{\mathrm{SO_4^{2-}}}]\} \\ &-(RT(\ln(10))/F)\log_{10}\{m_{\mathrm{Fe(II)total}}[1+(\beta_{1m}m_{\mathrm{SO_4^{2-}}})+(\beta_{1m}K_{2m}(m_{\mathrm{SO_4^{2-}}})^2) \\ &+(K_{m1,1(\mathrm{HSO_4^-})}K_{m\mathrm{FeHSO_4^+}}m_{\mathrm{SO_4^{2-}}}m_{\mathrm{H^+}})]\} \end{aligned} \qquad \text{(IX.15)}$$

In Eq. (IX.15) $\mathrm{Fe(III)_{tot}}$ and $\mathrm{Fe(II)_{tot}}$ stand for the total molalities of the iron(III) and iron(II) aqueous species and $\beta_{1m\mathrm{FeSO_4}}$ (which refers to Eq. (IX.2)) is a known parameter. The values of β_{1m}, K_{2m}, the equilibrium constants for Reactions (IX.6) and (IX.17) respectively, and $K_{m\mathrm{HFeSO_4^{2+}}}$ (the formation constant for $\mathrm{FeHSO_4^{2+}}$ from $\mathrm{Fe^{3+}}$ and $\mathrm{HSO_4^-}$ (Reaction (IX.16))) were treated as unknowns.

$$\mathrm{Fe^{3+}} + \mathrm{HSO_4^-} \rightleftharpoons \mathrm{FeHSO_4^{2+}} \qquad \text{(IX.16)}$$

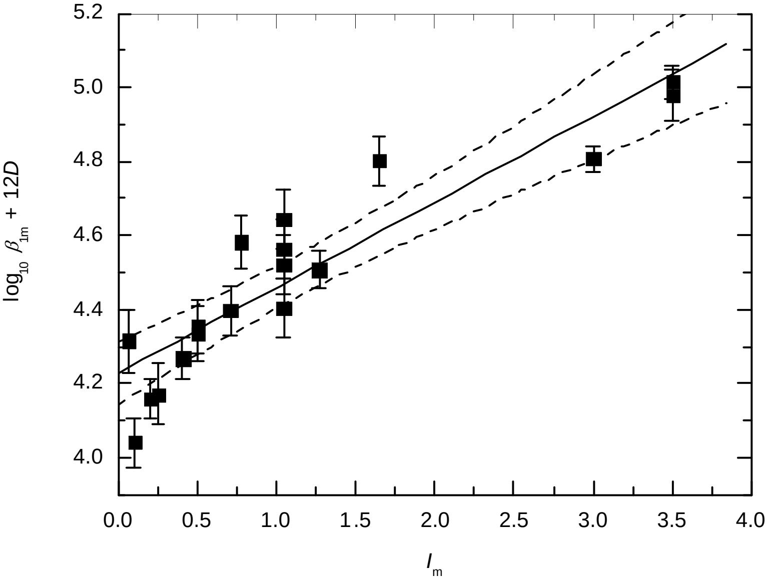
The fit yielded:

$$\beta_{1m} = (102.5 \pm 7.5)\ \mathrm{kg{\cdot}mol^{-1}} \text{ instead of } (72.8 \pm 6.9)\ \mathrm{kg{\cdot}mol^{-1}}.$$

Several other papers listed in Table IX-7 have been retained and reviewed for the overall optimization of β_1° and $\Delta\varepsilon$ for Reaction (IX.6) (see Figure IX-3).

These include the papers of Sykes [1952SYK] (a kinetic study of particular interest because of the low ionic strength at which the data were obtained), Kumai [1960KUM] (a spectrophotometric investigation at several ionic strengths and two temperatures), Davis and Smith [1962DAV/SMI] (spectrophotometric measurements at 0.5 M ionic strength at several temperatures), and Willix [1963WIL] (both the spectrophotometric and kinetic investigations at 0.5 M ionic strength). As described in Appendix A, in each case the reported values were converted to the molal scale and corrections applied for the differences between $K_{c1,1(\mathrm{HSO_4^-})}$ and $K_{m1,1(\mathrm{HSO_4^-})}$.

Figure IX-3: Extrapolation to $I = 0$ of the function $\log_{10} \beta_{1m} + 12D$ for the complex $FeSO_4^+$ without taking into account differences in the major cations (H^+ or Na^+) in the solutions.



The results are (4.23 ± 0.08) for $\log_{10} \beta_1^o$ and − (0.23 ± 0.05) kg·mol^{-1} for $\Delta\varepsilon$ (R^2 = 0.837). They are quite comparable to those based on the results of Mattoo [1959MAT] treated alone ((4.30 ± 0.16) for $\log_{10} \beta_1^o$; and − (0.24 ± 0.08) kg·mol^{-1} for $\Delta\varepsilon$) and in moderate agreement with the much more scattered results of Kumai [1960KUM] ((4.06 ± 0.11) for $\log_{10} \beta_1^o$ and − (0.37 ± 0.18) kg·mol^{-1} for $\Delta\varepsilon$). The values of many authors who worked at only one ionic strength extrapolated to zero ionic strength are also in fair agreement. This is the case for values calculated from the results of Whiteker and Davidson [1953WHI/DAV] (4.24 ± 0.14) and Sapieszko *et al.* [1977SAP/PAT] (3.99 ± 0.20).

More recently, Ciavatta *et al.* [2002CIA/TOM2] redetermined the stability of the 1:1 sulfato complex of Fe^{3+} by potentiometry and spectrophotometry in 2.9 M $NaClO_4$, 0.1 M H^+ (see Appendix A). The value that they found was smaller than reported by others for solutions of similar ionic strength [1959MAT], [1973NIK/PAL]. This recent value has been included in the literature data for the overall evaluation of $\log_{10} \beta_1^o$ (see Figure IX-3).

Although falling outside the limits of the 95% confidence bands, the value of Ciavatta *et al.* [2002CIA/TOM2] does not change the value of $\log_{10} \beta_1^o$ significantly. It is shifted from (4.22 ± 0.10) to (4.25 ± 0.10). The slope of the straight line is more affected and the value of $\Delta\varepsilon$ shifts from – (0.23 ± 0.06) to – (0.19 ± 0.06) kg·mol^{-1}.

The value of (4.25 ± 0.10) for $\log_{10} \beta_1^{\circ}$ is also in rather good agreement with that given in the review of Stipp [1990STI], obtained for zero ionic strength using extrapolation methods different from the SIT and is therefore recommended:

$$\log_{10} \beta_1^{\circ} = (4.25 \pm 0.10).$$

The slope of the straight line of Figure IX-3 represents $-\Delta\varepsilon$, and $\Delta\varepsilon = \{\varepsilon(\mathrm{FeSO}_4^+, \mathrm{ClO}_4^-) - \varepsilon(\mathrm{Fe}^{3+}, \mathrm{ClO}_4^-) - \varepsilon(\mathrm{Na}^+ \text{ or } \mathrm{H}^+, \mathrm{SO}_4^{2-})\}$.

With a value of $\Delta\varepsilon$ equal to – (0.19 ± 0.06) kg·mol^{-1}, and the interaction coefficients (0.73 ± 0.05) kg·mol^{-1} (SIT$_1$) for $\varepsilon(\mathrm{Fe}^{3+}, \mathrm{ClO}_4^-)$, – (0.12 ± 0.06) kg·mol^{-1} for $\varepsilon(\mathrm{Na}^+, \mathrm{SO}_4^{2-})$, a value of (0.42 ± 0.10) kg·mol^{-1} is obtained for $\varepsilon(\mathrm{FeSO}_4^+, \mathrm{ClO}_4^-)$.

If one uses $\varepsilon(\mathrm{H}^+, \mathrm{SO}_4^{2-}) = \varepsilon(\mathrm{Li}^+, \mathrm{SO}_4^{2-}) = -$ (0.03 ± 0.04) kg·mol^{-1} one finds (0.51 ± 0.10) kg·mol^{-1} for $\varepsilon(\mathrm{FeSO}_4^+, \mathrm{ClO}_4^-)$.

The value (0.42 ± 0.10) kg·mol^{-1} based on media with Na$^+$ as the major cation overlaps with (0.34 ± 0.10) kg·mol^{-1} found from the more elaborate SIT treatment described above (pg. 332) for the work of Mattoo [1959MAT], which was carried out mainly in $\mathrm{NaClO_4}$ medium.

There is a rather large discrepancy if one uses $\varepsilon(\mathrm{H}^+, \mathrm{SO}_4^{2-}) = \varepsilon(\mathrm{Li}^+, \mathrm{SO}_4^{2-}) = -$ (0.03 ± 0.04) kg·mol^{-1}. Probably this is not the best choice, but as the scatter of the formation constant values is high, no definitive conclusion can be drawn.

All these treatments used approximations. If the unweighted average of the three results is used as the selected value, then considering the spread and approximations an uncertainty of 0.1 kg·mol^{-1} is recommended.

Thus:

$$\varepsilon(\mathrm{FeSO}_4^+, \mathrm{ClO}_4^-) = (0.4 \pm 0.1)\ \mathrm{kg\cdot mol^{-1}}.$$

IX.1.2.1.4.2 $\Delta_{\mathrm{r}} H_{\mathrm{m}}^{\circ}$ for the reaction $\mathrm{Fe}^{3+} + \mathrm{SO}_4^{2-} \rightleftharpoons \mathrm{FeSO}_4^+$

No experimental calorimetric measurements have been reported of $\Delta_{\mathrm{r}}H$ for the formation of FeSO_4^+ from Fe^{3+} and SO_4^{2-}, but several papers did report measurements of $\log_{10} \beta_{1c}$ as a function of the temperature between 273.15 and 308.15 K [1960KUM], [1962DAV/SMI], [1963WIL]. The results of Sapiezsko *et al.* [1977SAP/PAT] for higher temperatures have not been used because of the poor agreement between the calculated value of $\Delta_{\mathrm{r}}H$ and values reported from measurements at lower temperatures. This indicates that $\Delta_{\mathrm{r}}H$ is not constant over the temperature range 293.15 to 353.15 K, even though plots of $\log_{10} \beta_{1m}$ *vs.* f(1/T) are linear at lower temperatures. Results from other papers [1969ZVY/LYA], [1977ASH/HAN2], [1975NIK/TSV] have been rejected for reasons discussed in Appendix A. The formation constants from the three papers mentioned above have been recalculated after conversion to the molal scale and using TDB-consistent values for $K_{m1,1(\mathrm{HSO}_4^-)}$. The calculated values of $\Delta_r H_m$ are (27.5 ± 2.0) kJ·mol^{-1} [1962DAV/SMI] and (26.7 ± 2.0) kJ·mol^{-1} [1963WIL], both for an ionic strength of 0.51 mol·kg^{-1}, and (25 ± 18) kJ·mol^{-1} at I_m = 1.05 mol·kg^{-1} [1960KUM]. As discussed in Appendix A, the only results used from the study of Willix [1963WIL] are the spectrophotometric values. The high uncertainty for the Kumai [1960KUM] value is also discussed in Appendix A.

The unweighted average of these three values of $\Delta_r H_m$ is (26.0 ± 6.3) kJ·mol^{-1}, where the uncertainty has been increased to try to take into account the limited number of data points and the various methods of investigation. This value cannot be a selected TDB value because of the lack of data at several ionic strengths and the uncertainties introduced in the SIT calculations by several unverified assumptions. The data of Sapieszko *et al.* [1977SAP/PAT] for temperatures from 328.15 to 353.15 K seem to show a strong change in the value of $\Delta_r H_c$, which is then close to 55.0 kJ·mol^{-1}. If confirmed, this change could be due to a change in the mode of coordination of the sulfate anion. At room temperature the $\Delta_r H_c$ value for the association of a sulfate to Fe^{3+} is roughly the same as that of association with the monodentate chloride (see Chapter VIII). Transition from mono- to bidentate coordination of the SO_4^{2-} might also be accompanied by an increase in the value of $\Delta_r S$ by about a factor of two, as it involves a double dehydration of the reactants [1977ASH/HAN]. From the work of Sapieszko *et al.* [1977SAP/PAT] the value of $\Delta_r S$ is calculated to be 124 J·K^{-1}·mol^{-1} at 298.15 K and 213 J·K^{-1}·mol^{-1} at 353.15 K, values which support the assumption of a coordination change. Monodentate bonding of SO_4^{2-} to Fe^{3+} in FeSO_4^+, at room temperature, has been found experimentally by XANES spectroscopy [2005MAJ/MYN].

The strong increase of the formation constant of FeSO_4^+ at temperatures higher than 323.15 K has also been observed by Nikolaeva and Tsvelodub [1975NIK/TSV] (*cf.* Appendix A). The $\Delta_r H^\circ$ value based on data from 298.15 to 323.15 K, is less than the value at higher temperatures (323.15 to 398.15 K) by approximately a factor of two.

IX.1.2.1.4.3 $\mathrm{Fe(SO_4)_2^-}$ and $\mathrm{Fe(SO_4)(HSO_4)}$ (aq)

The number of papers dealing with the formation constant of $\mathrm{Fe(SO_4)_2^-}$ or $\mathrm{Fe(SO_4)(HSO_4)}$(aq) as a function of the ionic strength are even more limited than for FeSO_4^+. Below we have analyzed the work of [1959MAT] with the SIT formalism, and the isolated values found elsewhere in the literature [1953WHI/DAV], [1959MAT], [1969ZVY/LYA], [1973NIK/PAL], [2002CIA/TOM2] are indicated on the same graph (Figure IX-4).

The reaction investigated was:

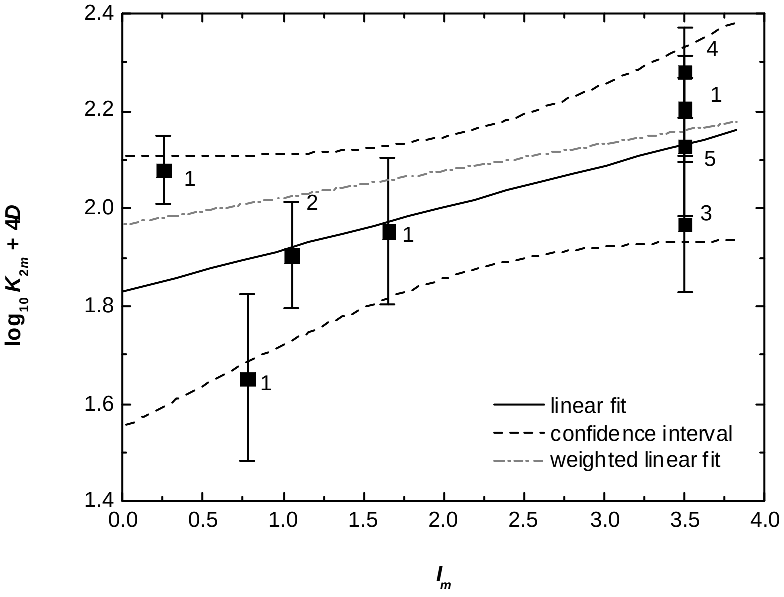
$$\mathrm{FeSO}_4^+ + \mathrm{SO}_4^{2-} \rightleftharpoons \mathrm{Fe(SO_4)_2^-} \qquad \text{(IX.17)}$$

We applied the formula

$$\log_{10} K_{2m} + 4D = \log_{10} K_2^\circ - \Delta\varepsilon I_m \qquad \text{(IX.18)}$$

Again, in this equation, D is the Debye-Hückel term, see Eq. (IX.8), and the value of $-\Delta z^2$ for the complex-formation Reaction (IX.17) is $+4$.

Figure IX-4: SIT treatment of the literature data for the formation constant of the complex $Fe(SO_4)_2^-$ (1 [1959MAT], 2 [1953WHI/DAV], 3 [1969ZVY/LYA], 4 [1973NIK/PAL], 5 [2002CIA/TOM2]).



The unweighted and weighted linear fits of Eq. (IX.18) to the experimental values of $\log_{10} K_{2m} + 4D$ are shown in Figure IX-4. It can be seen that the data are limited and the results are widely scattered. The linearity of the function is poor (r = 0.52). The weighted fit produces $\log_{10} K_2^{\circ} = (1.97 \pm 0.13)$, and $\Delta\varepsilon = -(0.057 \pm 0.055)$ kg·mol^{-1}. The unweighted fit yields: $\log_{10} K_2^{\circ} = (1.83 \pm 0.23)$ and $\Delta\varepsilon = -(0.087 \pm 0.100)$ kg·mol^{-1} with r = 0.62.

The values from the weighted fit are recommended here.

The value of $\log_{10} K_2^{\circ}$ is in agreement with that reported in the review of Stipp [1990STI] (1.34 ± 1.00), but only because of her large estimated uncertainty.

The value of K_2° found here multiplied by the value of K_1° leads to $\log_{10} \beta_2^{\circ} = (6.22 \pm 0.16)$, in moderate agreement with the value (5.38 ± 1.00) as assessed by Stipp [1990STI].

The $\Delta\varepsilon$ value is rather low, as would be expected because of the relatively small change of charge. Thus, $\varepsilon(\mathrm{Na^+}, \mathrm{Fe(SO_4)_2^-}) - \varepsilon(\mathrm{FeSO_4^+}, \mathrm{ClO_4^-}) - \varepsilon(\mathrm{Na^+}, \mathrm{SO_4^{2-}}) = (0.057 \pm 0.055)\ \mathrm{kg{\cdot}mol^{-1}}$.

Taking the value of $\varepsilon(\mathrm{FeSO_4^+}, \mathrm{ClO_4^-}) = (0.42 \pm 0.12)\ \mathrm{kg{\cdot}mol^{-1}}$ in this paper and $\varepsilon(\mathrm{Na^+}, \mathrm{SO_4^{2-}}) = -(0.12 \pm 0.06)\ \mathrm{kg{\cdot}mol^{-1}}$ in the NEA-TDB table one gets:

$$\varepsilon(\mathrm{Na^+}, \mathrm{Fe(SO_4)_2^-}) = (0.24 \pm 0.14)\ \mathrm{kg{\cdot}mol^{-1}}.$$

The existence of the acid form of this complex, $\mathrm{Fe(SO_4)(HSO_4)(aq)}$, has been claimed by Lister and Rivington [1955LIS/RIV2]. The claim was based on deviation of the UV-visible spectrum from that of $\mathrm{Fe(SO_4)_2^-}$. The existence of $\mathrm{Fe(SO_4)(HSO_4)(aq)}$ in aqueous solution has been confirmed recently by Raman spectroscopy [2005CAS/CRI]— in the low-energy region there is a band attributable to the Fe−O stretch of the $\mathrm{Fe{-}HSO_4}$ moiety.

The equilibrium constant for the reaction: $\mathrm{Fe^{3+}} + \mathrm{SO_4^{2-}} + \mathrm{HSO_4^-} \rightleftharpoons \mathrm{FeSO_4(HSO_4)(aq)}$ was estimated [1955LIS/RIV2] to be (380 ± 50) and as $\approx 10^6$ based on the results of Casas *et al.* [2005CAS/CRI]. The ionic strengths of the solutions used to derive these two estimates were different, but this is a major discrepancy between the two results, and we consider that only qualitative information, limited to the speciation, is available.

IX.1.2.1.4.4 $\mathbf{FeHSO_4^{2+}}$

The existence of this weak complex has been denied by several workers [1953WHI/DAV], [1963WIL] because the small variations in the properties observed for $\mathrm{FeSO_4^+}$ formation can be easily attributed to activity-coefficient changes, especially in the case when distribution coefficients of Fe(III) between a cation-exchange resin and sulfate solutions with different acidities [1953WHI/DAV] are measured. However, as UV-visible spectroscopic changes attributable to $\mathrm{HSO_4^-}$ have been observed in the spectrum of Fe(III) solutions [1955LIS/RIV2], [2002CIA/TOM2], [2005CAS/CRI], we consider that the species $\mathrm{FeHSO_4^{2+}}$ actually can form.

The very limited number of results in the literature for the formation constant of $\mathrm{FeHSO_4^{2+}}$ have been analyzed by the SIT model and they are plotted in Figure IX-5. The number of measurements is very limited and statistically unreliable (r = − 0.39 for the unweighted linear fit, − 0.32 for the weighted linear fit).

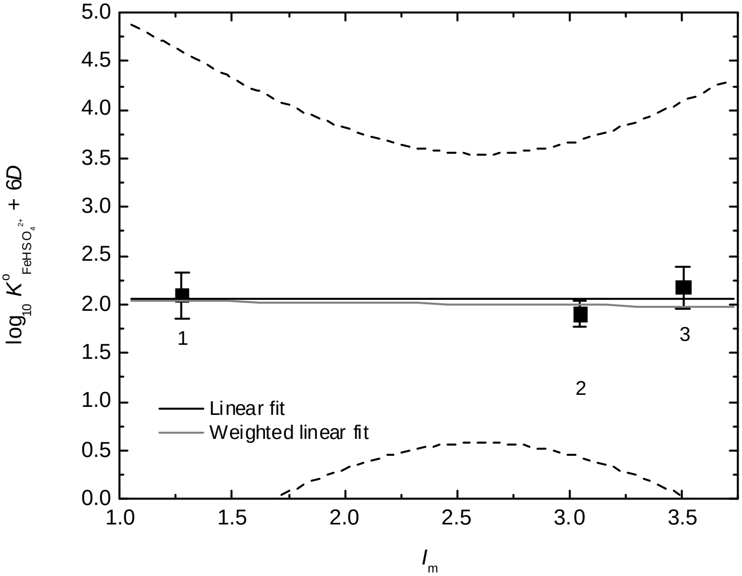
The values of $K^{\circ}_{\mathrm{FeHSO_4^{2+}}}$ and $\Delta\varepsilon$ for Reaction (IX.16)

are:

$\log_{10} K^{\circ}_{\mathrm{FeHSO_4^{2+}}} = (1.86 \pm 1.30)$; $\Delta\varepsilon = -(0.13 \pm 0.44)\ \mathrm{kg{\cdot}mol^{-1}}$ (unweighted fit)

$\log_{10} K^{\circ}_{\mathrm{FeHSO_4^{2+}}} = (1.73 \pm 0.76)$; $\Delta\varepsilon = -(0.14 \pm 0.12)\ \mathrm{kg{\cdot}mol^{-1}}$ (weighted fit).

Figure IX-5: Values of the formation constant at 298.15 K of $\mathrm{FeHSO_4^{2+}}$ treated using the SIT formalism (1 [1955LIS/RIV2], 2 [1977SAP/PAT], 3 [1973NIK/PAL], 4 [2002CIA/TOM2]).



The $\log_{10} K^{o}_{\mathrm{FeHSO_4^{2+}}}$ value assessed but not recommended by Stipp [1990STI] for incorporation in geochemical models was 2.48, and this does not differ substantially from the value from the present SIT evaluation.

With $\Delta\varepsilon = -(0.14 \pm 0.12)$ kg·mol^{-1} one can calculate $\varepsilon(\mathrm{FeHSO_4^{2+}}, \mathrm{ClO_4^-})$ using the values of $\varepsilon(\mathrm{Fe^{3+}}, \mathrm{ClO_4^-})$ and $\varepsilon(\mathrm{Na^+}, \mathrm{HSO_4^-})$ in the NEA-TDB tables, and obtain $\varepsilon(\mathrm{FeHSO_4^{2+}}, \mathrm{ClO_4^-}) = (0.58 \pm 0.13)$ kg·mol^{-1}.

This value can be taken as a first approximation, but the uncertainties are so high that it cannot be considered as a recommended value. Investigations of sulfato complexes in rather highly acidic solutions using a technique capable of specific detection of the $\mathrm{Fe^{3+}}-\mathrm{HSO_4^-}$ linkage are necessary to assess more reliable values for $\log_{10} K^{o}_{\mathrm{FeHSO_4^{2+}}}$ and $\varepsilon(\mathrm{FeHSO_4^{2+}}, \mathrm{ClO_4^-})$. For that purpose the Raman spectroscopy results reported by Cass *et al.* [2005CAS/CRI] look encouraging.

IX.1.2.1.5 Thermodynamic constants for the aqueous sulfato complexes of iron(III)

Formation constants of $\mathrm{FeSO_4^+}$ as a function of temperature have been reviewed in Section IX.1.2.1.4.2. As expected for a hard-donor – hard-acceptor complex the formation constant increases with the temperature. At temperatures below 308.15 K some agreement between the various authors sets the value of Δ_rH around 25 kJ·mol^{-1}. At higher temperatures the value of $d(\ln \beta_{1m})/d(1/T)$ increases by a factor close to 2 [1975NIK/TSV], [1977SAP/PAT]. That raises the question of a possible change of sulfate coordination mode in the temperature range 310 to 330 K.

The value of Δ_rH for the reaction $FeSO_4^+ + SO_4^{2-} \rightleftharpoons Fe(SO_4)_2^-$ is very poorly documented. From the paper of Zvyagnitsev and Lyakmanov [1969ZVY/LYA], in which values of β_{1c} and β_{2c} at 298.15, 308.15 and 318.15 K were reported, it can be deduced that $\Delta_rH_c = -15.48$ kJ·mol^{-1}. This is the sole available value (though also see the Appendix A entry for [1963BAC/LIE]), but it does not contradict chemical sense, which associates positive Δ_rH values with the dehydration of highly charged ions like Fe^{3+} in the case of $FeSO_4^+$. Here it is the less highly-charged species, $FeSO_4^+$, that is dehydrated. Therefore, when required, the Δ_rH value of Zvyagnitsev and Lyakmanov [1969ZVY/LYA] has been used to make minor temperature corrections to get values of K_2 at 298.15 K.

There is no study of the influence of temperature on the formation constant of $FeHSO_4^{2+}$.

IX.1.2.1.6 Conclusions

There are aspects of the iron(III)-sulfate system in solution that are still not firmly established. This is mainly because of the possibility of the sulfate ligand forming complexes both with the metal and with protons. Mixed hydroxido and sulfato complexes of Fe(III) also have been claimed. The formation of polymers with oxygen or sulfate bridges is also possible, but such species have not yet been proven unambiguously in aqueous solutions.

Quantitative work is difficult because of all these possible reactions. So the speciation often remains uncertain, and the calculated values of thermodynamic constants are scattered. The best known and most stable species is $FeSO_4^+$, and it is the only one for which there is sufficient experimental work to get a useful value for the standard formation constant. The stability constants of the other species are such that their concentrations in most solutions would be low, and even their existence, except for $Fe(SO_4)_2^-$ and $FeHSO_4^{2+}$, is not completely established.

IX.1.2.2 Iron sulfate compounds

IX.1.2.2.1 Anhydrous iron(II) sulfate

Anhydrous iron(II) sulfate is difficult to prepare and isolate in a pure form (although it can be prepared in contact with concentrated sulfuric acid solutions, *e.g.*, [1941BEL/SHP]). Neumann and Heintke [1937NEU/HEI] were unable to prepare the completely anhydrous stoichiometric compound using methods suggested earlier by d'Ans [1905ANS] and Greulich [1927GRE]. Moore and Kelley [1942MOO/KEL] found that at least some decomposition always accompanied the final dehydration step when the iron(II) sulfate was heated at ~ 500 K under vacuum. Skeaff and Espelund [1973SKE/ESP] provided fewer experimental details about their syntheses than might be desired, but reported a high-temperature (T/K > 700) modification of $FeSO_4$(cr), and its powder X-ray diffraction pattern. Based on electrochemical measurements of oxygen chemical potential at constant $p_{SO_2} \leq 0.1$ MPa they showed that in a closed system above 913 K $FeSO_4$(cr) is unstable with respect to decomposition to $Fe_2(SO_4)_3$(cr) and Fe_2O_3(cr, unspecified form) (Reaction (IX.19)).

$$FeSO_4(cr) \rightleftharpoons \tfrac{1}{6}\,Fe_2(SO_4)_3(cr) + \tfrac{1}{3}\,Fe_2O_3(cr) + \tfrac{1}{2}\,SO_2(g) \qquad (IX.19)$$

This decomposition temperature represents the peak of the $FeSO_4$(cr) stability field in the Fe-O-S phase diagram at p = 0.1 MPa. At lower temperatures, $FeSO_4$(cr) is limited by divariant equillibria (dependent on partial pressures of both O_2 and SO_2) such as those discussed in Section IX.1.2.2.1.2.

IX.1.2.2.1.1 $FeSO_4$(cr) entropy and heat capacity

There seems to have been only one useful study of the heat capacity of $FeSO_4$(cr) [1942MOO/KEL]. Based on a slight extrapolation of the calorimetry measurements done at 53.0 to 294.9 K,

$$C^{o}_{p,\mathrm{m}}\,(FeSO_4,\ cr,\ 298.15\ K) = (100.78 \pm 2.00)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

is selected. The JANAF compilation [1998CHA] provides an estimated value of $(120.96 \pm 1.30)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ for S^{o}_{m} ($FeSO_4$, cr, 298.15 K), based on integration of the results of Moore and Kelley [1942MOO/KEL], and an estimated contribution to the magnetic entropy. This value is likely adequate for most thermodynamic calculations, but is not selected in the present review because there is no experimental corroboration of the magnetic contribution.

IX.1.2.2.1.2 Enthalpy and dissociation of $FeSO_4$(cr)

The decomposition pressures above samples of $FeSO_4$(cr) have been studied several times as a function of temperature from ~ 500 to ~ 900 K [1908KEP/ANS], [1927GRE], [1937NEU/HEI]. The reaction

$$4\ FeSO_4(cr) \rightleftharpoons 2\ Fe_2O_3(cr) + 4\ SO_2(g) + O_2(g) \qquad (IX.20)$$

is complicated by the equilibrium

$$2\ SO_3(g) \rightleftharpoons 2\ SO_2(g) + O_2(g), \qquad (IX.21)$$

which is also important; furthermore, there is generally a lack of information on whether the iron(III) oxide product was actually α-Fe_2O_3 [1999ZBO/MAS], [2003ZBO/MAS]. The decomposition equilibrium (IX.20) and the equilibrium between $FeSO_4$(cr) and $Fe_2(SO_4)_3$(cr) (IX.22)

$$Fe_2(SO_4)_3(cr) \rightleftharpoons 2\ FeSO_4(cr) + SO_2(g) + O_2(g) \qquad (IX.22)$$

have also been investigated by electrochemical measurements of the oxygen chemical potential at constant p_{SO_2} [1973SKE/ESP].

In the absence of adequate thermal functions for $FeSO_4$(cr) and a value for S^{o}_{m} ($FeSO_4$, cr, 298.15 K), no acceptable third-law value can be calculated for $\Delta_f H^{o}_{m}$ ($FeSO_4$, cr, 298.15 K), and no value for this quantity is selected in the present review.

IX.1.2.2.2 Iron(II) sulfate hydrates

The heptahydrate and monohydrate are well-established compounds with regions of stability in the $FeSO_4$-H_2O(l) system [1907FRA], [1941BEL/SHP], 1956KOB/FRE], [1987REA/BEC]. These hydrates correspond to the minerals melanterite and szomolnokite, respectively [1987REA/BEC]. Dehydration of the heptahydrate in saturated aqueous solution occurs near 330 K [1907FRA], and at lower temperatures in aqueous mixtures with H_2SO_4 [1913WIR], [1941BEL/SHP]. Existence of the tetrahydrate (rozenite) is also well-established [1907FRA], [1914FOR], [1953CHI/SEK], [1969PRI] though it is probable that in contact with aqueous solutions this compound is formed only as a metastable intermediate [1952BUL/CAN], [1964KOH/ZAS2], [1987REA/BEC]. If $FeSO_4\cdot4H_2O$(cr) actually is an equilibrium solid in the aqueous binary system, it has a very narrow range of stability (between 325 and 333 K). There is no evidence for higher hydrates at lower temperatures, *e.g.*, Belopolskii *et al.* [1948BEL/KOL], Belopolskii and Urazov [1948BEL/URA]. Also, as suggested by Hemingway *et al.* [2002HEM/SEA], [2002CHO/SEA] it is probable that the iron(II) sulfate pentahydrate and hexahydrate (known as the minerals siderotil and ferrohexahydrite) are metastable, but might be stabilized if small amounts of cations of other metals are incorporated in the structure.

The solubility of the heptahydrate increases with increasing temperature, whereas the solubility of the monohydrate decreases. Most solubility studies did not use X-ray diffraction to determine the equilibrium solid(s). Kohler and Zäske [1964KOH/ZAS2] published X-ray diffraction patterns for the monohydrate, tetrahydrate and heptahydrate as part of their study of the temperature dependence of water vapour pressure over the hydrates. They also confirmed that the tetrahydrate forms as an intermediate on gradually heating the heptahydrate (as did Pribylov [1969PRI]). At a constant pressure of “20 torr” (2.7 kPa) the dehydration of the monohydrate was found to begin above 463 K. As noted above, this final dehydration step is not reversible [1942MOO/KEL], [1964KOH/ZAS2].

IX.1.2.2.2.1 The heat capacity and entropy of $FeSO_4\cdot7H_2O$(cr)

Lyon and Giauque [1949LYO/GIA] measured the heat capacity of $FeSO_4\cdot7H_2O$(cr) between 0.9 and 307.7 K. As discussed in Appendix A, the equation $C^{o}_{p,m}$ ($FeSO_4\cdot7H_2O$, cr)/$J\cdot K^{-1}\cdot mol^{-1}$ = 76.055 + 1.0677 (T/K) can be used to estimate heat-capacity values for temperatures between 269 and 308 K. The value for 305 K, (401.7 ± 2.0) $J\cdot K^{-1}\cdot mol^{-1}$ is almost identical to the average value for 292 to 320 K from the 1865 study of Kopp ((403 ± 14) $J\cdot K^{-1}\cdot mol^{-1}$) [1865KOP].

The following value

$$C^{o}_{p,m}(\mathrm{FeSO_4\cdot 7H_2O, cr, 298.15\ K}) = (394.4 \pm 2.0)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

based on the extensive low-temperature work of Lyon and Giauque [1949LYO/GIA], is accepted in the present review. Similarly, from the same source, the preliminary assessed value for S^{o}_{m}($FeSO_4\cdot 7H_2O$, cr, 298.15 K) is (409.1 ± 1.3) $J\cdot K^{-1}\cdot mol^{-1}$. Evaluation of the available cycles for iron species and optimization to ensure consistency with other thermodynamic quantities for iron species (Chapter XI), suggests a slight decrease in the uncertainty, and the selected value is

$$S^{o}_{m}(\mathrm{FeSO_4\cdot 7H_2O, cr, 298.15\ K}) = (409.12 \pm 0.82)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

IX.1.2.2.2.2 Enthalpy and Gibbs energy of formation of $FeSO_4\cdot 7H_2O$(cr)

There have been two solution calorimetry studies leading to values for $\Delta_f H^{o}_{m}$($FeSO_4\cdot 7H_2O$, cr, 298.15 K). As discussed in the corresponding sections of Appendix A, the values have been recalculated in the present review. Results from the work of Adami and Kelley [1963ADA/KEL], – (3014.56 ± 1.00) $kJ\cdot mol^{-1}$, and Vasil'ev *et al.* [1985VAS/DMI2], – (3015.61 ± 1.54) $kJ\cdot mol^{-1}$ are in good agreement.

In the preliminary optimization analysis of consistency between various thermodynamic quantities for iron species, the two calorimetric results for $\Delta_f H^{o}_{m}$($FeSO_4\cdot 7H_2O$, cr, 298.15 K), – (3014.56 ± 1.00) and – (3015.61 ± 1.54) $kJ\cdot mol^{-1}$, are treated separately. After evaluation of the available cycles for iron species and optimization to ensure consistency with other thermodynamic quantities for iron species (Chapter XI), this value is adjusted to

$$\Delta_f H^{o}_{m}(\mathrm{FeSO_4\cdot 7H_2O, cr, 298.15\ K}) = -(3012.51 \pm 0.60)\ \mathrm{kJ\cdot mol^{-1}}.$$

As discussed in Chapter XI, this value is markedly less negative than the two values based directly on experiments, and the reason for this disagreement is unclear. Nevertheless, the optimized value must be accepted to maintain database consistency.

Based on this value, the value selected above for S^{o}_{m}($FeSO_4\cdot 7H_2O$, cr, 298.15 K), and appropriate auxiliary data (Table IV-1):

$$\Delta_f G^{o}_{m}(\mathrm{FeSO_4\cdot 7H_2O, cr, 298.15\ K}) = -(2507.71 \pm 0.65)\ \mathrm{kJ\cdot mol^{-1}}.$$

IX.1.2.2.2.3 Osmotic coefficient measurements for aqueous Fe(II)SO_4 solutions

Osmotic coefficients for concentrated aqueous iron(II) sulfate solutions at 298.15 K were measured by Oykova and Balarew [1974OYK/BAL] and by Nikolaev *et al.* [1989NIK/DIK]. A Pitzer equation fitted to the data of Oykova and Balarew, constrained only by the need to assume a reasonable value for $\beta^{(2)}$ [1987REA/BEC], leads to values of 0.699, 0.048 and 0.952 for ϕ, $\gamma_{\pm}$, and a_w at the saturation molality, 1.9641 $mol\cdot kg^{-1}$, [1974OYK/BAL] (see Appendix A)

$$\mathrm{FeSO_4{\cdot}7H_2O(cr)} \rightleftharpoons \mathrm{Fe^{2+}} + \mathrm{SO_4^{2-}} + 7\ \mathrm{H_2O(l)}. \qquad \text{(IX.23)}$$

Thus, $\Delta_\mathrm{r}G^\circ_\mathrm{m}$ (IX.23) is (12.90 ± 0.40) kJ·mol^{-1} at 298.15 K. The results reported by Nikolaev *et al.* [1989NIK/DIK] appear to be less reliable, but lead to a similar value, (13.8 ± 1.0) kJ·mol^{-1}, for $\Delta_\mathrm{r}G^\circ_\mathrm{m}$ (IX.23). Although there are some concerns about the consistency of both sets of measurements for aqueous iron(II) sulfate solutions when they are compared to measurements for other transition metal sulfates (Appendix A), these are probably the best 298.15 K values currently available. The weighted average $\Delta_\mathrm{r}G^\circ_\mathrm{m}$ (IX.23) = (13.02 ± 0.37) kJ·mol^{-1} is used initially in the present review.

After evaluation of the available cycles for iron species and optimization to ensure consistency with other thermodynamic quantities for iron species (Chapter XI), the adjusted value is essentially identical to that from the original assessment, but with an increased uncertainty,

$$\Delta_\mathrm{sln}G^\circ_\mathrm{m}\ (\mathrm{FeSO_4{\cdot}7H_2O,\ cr,\ 298.15\ K}) = (13.0 \pm 1.3)\ \mathrm{kJ{\cdot}mol^{-1}}.$$

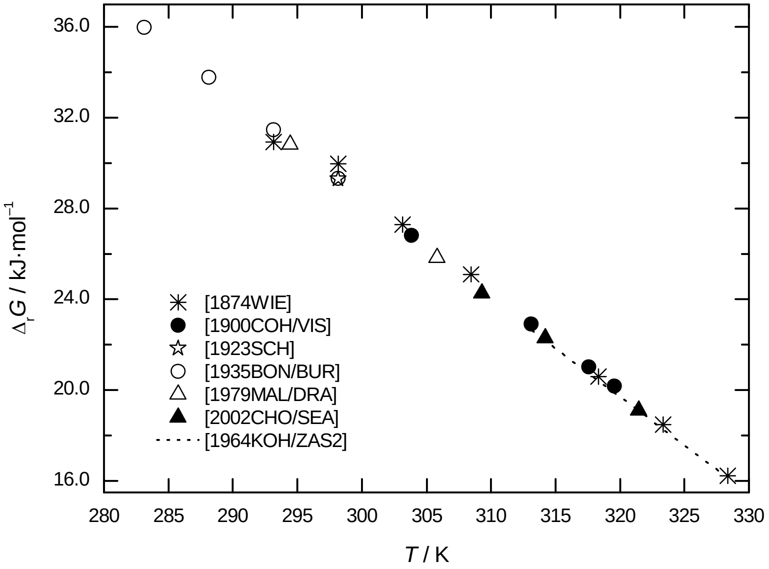
IX.1.2.2.2.4 Dehydration equilibria and enthalpies

Water Vapour-Pressure Measurements

There have been a number of sets of measurements of the vapour pressure of water over iron(II) sulfate hydrates [1874WIE], [1900COH/VIS], [1923SCH], [1935BON/BUR], [1964KOH/ZAS2], [1979MAL/DRA], [1981PAR/DAY], [2002CHO/SEA]. For measurements done at temperatures below 325 K, it is clear, in most cases, that the higher hydrate of the pair of solids was the heptahydrate. However, the identity of the lower hydrate was not usually established unequivocally, and in some cases [1923SCH], [1935BON/BUR] was incorrectly assumed to be the hexahydrate. The Gibbs energy of reaction data from these studies agree very well as shown in Figure IX-6.

The water vapour-pressure measurements for temperatures from 283.15 to 328.35 K were assigned weights as discussed in the entries in Appendix A. From a weighted least-squares fit to these values, $\Delta_\mathrm{r}G_\mathrm{m}$ and $\Delta_\mathrm{r}H_\mathrm{m}$ at 298.15 K could be determined. However, the data are inadequate to also allow $\Delta_\mathrm{r}C_{p,\mathrm{m}}$ to be calculated, as the fitted values for the three quantities are highly correlated.

Figure IX-6: Gibbs energies of dehydration of $FeSO_4·7H_2O(cr)$ to $FeSO_4·4H_2O(cr)$ with evolution of $H_2O(g)$.



Enthalpies of solution

The heat of solution of $FeSO_4·7H_2O(cr)$ in water has been reported from several studies [1908THO], [1914FOR], [1941PER2], [1965JAM/BRO], [1968LAR], [1968LAR/CER], [1985VAS/DMI], [1992PRZ/WIS], [1993PRZ/WIS]. Several of these studies were done at temperatures other than 298.15 K [1908THO], [1914FOR], [1941PER2], [1965JAM/BRO] or at a limited number of rather high molalities [1908THO], [1914FOR]. The experimental results of Larson [1968LAR], [1968LAR/CER] can be extrapolated to give a value of (11.89 ± 0.50) kJ·mol^{-1} for the heat of solution at zero ionic strength and 298.15 K, and Vasil'ev *et al.* [1985VAS/DMI] reported a similar value (see the discussions in Appendix A). The rather sparse results from Przepiera *et al.* [1993PRZ/WIS], primarily in aqueous sulfuric acid solutions, are only roughly comparable with those from the other two studies at 298.15 K. The value from Larson's work [1968LAR] is used for the preliminary assessment of consistency discussed in Chapter XI.

After evaluation of the available cycles for iron species and optimization to ensure consistency with other thermodynamic quantities for iron species, the adjusted value is essentially identical to that from the original assessment, but with an increased uncertainty,

$$\Delta_{\text{sln}}H^{\circ}_{\text{m}}(\text{FeSO}_4\cdot7\text{H}_2\text{O, cr, 298.15 K}) = (12.07 \pm 0.84)\ \text{kJ}\cdot\text{mol}^{-1}.$$

Of these studies, only three, those of de Forcrand [1914FOR], Jamieson *et al.* [1965JAM/BRO] and Larson [1968LAR], [1968LAR/CER], reported information on heats of solution of the lower iron(II) hydrates. De Forcrand's study at 286.65 K indicates that the enthalpies of solution of $FeSO_4\cdot7H_2O$(cr) and $FeSO_4\cdot4H_2O$(cr) differ by 24.78 $kJ\cdot mol^{-1}$ at some unspecified final concentration, and that the enthalpies of solution of $FeSO_4\cdot4H_2O$(cr) and $FeSO_4\cdot H_2O$(cr) differ by 24.85 $kJ\cdot mol^{-1}$. Jamieson *et al.* reported results that indicate similarly that the enthalpies of solution of $FeSO_4\cdot7H_2O$(cr) and $FeSO_4\cdot4H_2O$(cr) differ by 25.7 $kJ\cdot mol^{-1}$ at a low but not explicitly specified final concentration (~ 0.002 m), and with the same difference between the enthalpies of solution of $FeSO_4\cdot4H_2O$(cr) and $FeSO_4\cdot H_2O$(cr). Larson's heat-of-solution data for 298.15 K, extrapolated to infinite dilution and then to the stoichiometric compositions of the heptahydrate, tetrahydrate and monohydrate (see the Appendix A entry for [1968LAR]) lead to $-(13.77 \pm 1.00)$ $kJ\cdot mol^{-1}$ and $-(44.3 \pm 5.0)$ $kJ\cdot mol^{-1}$ for $\Delta_{\text{sln}}H^{\circ}_{\text{m}}$ ($FeSO_4\cdot4H_2O$, cr, 298.15 K) and $\Delta_{\text{sln}}H^{\circ}_{\text{m}}$ ($FeSO_4\cdot H_2O$, cr, 298.15 K), respectively. The difference values (heptahydrate to tetrahydrate and tetrahydrate to monohydrate) then are 25.66 $kJ\cdot mol^{-1}$ and 30.5 $kJ\cdot mol^{-1}$, very similar to those found by de Forcrand and by Jamieson *et al.*

Based on Larson's work and values for H_2O(g) and H_2O(l) from Chapter IV, the enthalpies for the reactions

$$\text{FeSO}_4\cdot7\text{H}_2\text{O(cr)} \rightleftharpoons \text{FeSO}_4\cdot4\text{H}_2\text{O(cr)} + 3\ \text{H}_2\text{O(g)}, \qquad \text{(IX.24)}$$

and

$$\text{FeSO}_4\cdot4\text{H}_2\text{O(cr)} \rightleftharpoons \text{FeSO}_4\cdot\text{H}_2\text{O(cr)} + 3\ \text{H}_2\text{O(g)}, \qquad \text{(IX.25)}$$

at 298.15 K are calculated to be (157.67 ± 0.80) $kJ\cdot mol^{-1}$ and (162.5 ± 5.1) $kJ\cdot mol^{-1}$, respectively.

IX.1.2.2.2.5 The heat capacity of $FeSO_4\cdot4H_2O$(cr)

Rolla and Accame [1913ROL/ACC] reported an average molar heat-capacity value of 266.0 $J\cdot K^{-1}\cdot mol^{-1}$ for $FeSO_4\cdot4H_2O$(cr) for the temperature range 273.1 to 291 K. This was based on measurements on six samples of hydrated $FeSO_4\cdot xH_2O$ (x = 4.89 to 7.04). For reasons discussed in Appendix A, this value is not considered to be particularly reliable. Based on the value selected for $C^{\circ}_{p,\text{m}}$ ($FeSO_4\cdot7H_2O$, cr, 298.15 K) and an estimated contribution of 40.0 $J\cdot K^{-1}\cdot mol^{-1}$ per mole of water of hydration to the heat capacity[1], a rather similar value of 274.4 $J\cdot K^{-1}\cdot mol^{-1}$ is calculated for $C^{\circ}_{p,\text{m}}$ ($FeSO_4\cdot4H_2O$, cr, 298.15 K).

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[1] Standard estimation methods [1971NAU/RYZ], [1979KUB/ALC] suggest ~36 $J\cdot K^{-1}\cdot mol^{-1}$ per water of hydration. The difference in the values selected for $FeSO_4\cdot7H_2O$(cr) and $FeSO_4$(cr) suggest ~42 $J\cdot K^{-1}\cdot mol^{-1}$ per water of hydration. The use of 40 $J\cdot K^{-1}\cdot mol^{-1}$ per water of hydration is not unreasonable.

IX.1.2.2.2.6 The Gibbs energy and enthalpy of formation of $FeSO_4{\cdot}4H_2O$

As discussed above, there are difficulties when water vapour-pressure measurements are used to determine $\Delta_r G_m$ (IX.24), $\Delta_r H_m$ (IX.24) and $\Delta_r C_{p,m}$ (IX.24), at 298.15 K. Inclusion of the value of $\Delta_r H_m$ (IX.24) from the study of Larson [1968LAR] (see Appendix A) did not circumvent these difficulties. However, if the value of $C^{\circ}_{p,m}$ ($FeSO_4{\cdot}4H_2O$, cr, 298.15 K) is constrained to (274.4 ± 15.0) $J{\cdot}K^{-1}{\cdot}mol^{-1}$, a least-squares fit leads to values of 29.24 $kJ{\cdot}mol^{-1}$ (with a variation of only ± 0.01) for $\Delta_r G_m$ (IX.24), and 158.5 $kJ{\cdot}mol^{-1}$ (with a variation of ± 0.1 $kJ{\cdot}mol^{-1}$) for $\Delta_r H_m$ (IX.24) .

In the present review, uncertainties in these values were estimated by comparison of the fitting results that were obtained both including and excluding the enthalpy of solution values [1968LAR]. Hence at 298.15 K,

$$\Delta_r G_m \text{ ((IX.24), 298.15 K)} = (29.24 \pm 0.10)\ kJ{\cdot}mol^{-1}$$

$$\Delta_r H_m \text{ ((IX.24), 298.15 K)} = (158.53 \pm 1.50)\ kJ{\cdot}mol^{-1}.$$

From these, and appropriate auxiliary data (Table IV-1), the following values are selected for $FeSO_4{\cdot}4H_2O$(cr),

$$\Delta_f H^{\circ}_m (FeSO_4{\cdot}4H_2O\text{, cr, 298.15 K}) = -\ (2128.50 \pm 1.62)\ kJ{\cdot}mol^{-1}$$

and

$$\Delta_f G^{\circ}_m (FeSO_4{\cdot}4H_2O\text{, cr, 298.15 K}) = -\ (1792.72 \pm 0.67)\ kJ{\cdot}mol^{-1}.$$

IX.1.2.2.2.7 Enthalpy and Gibbs energy of formation of $FeSO_4{\cdot}H_2O$(cr)

Adami and Kelley [1963ADA/KEL], in parallel to their study on the enthalpy of formation of $FeSO_4{\cdot}7H_2O$(cr), carried out solution calorimetry studies with $FeSO_4{\cdot}1.008H_2O$(cr), and reported results leading to a value of – (1241.8 ± 0.5) $kJ{\cdot}mol^{-1}$ for $\Delta_f H^{\circ}_m$ ($FeSO_4{\cdot}H_2O$, cr, 298.15 K). As discussed in Appendix A, the value – (1244.02 ± 0.80) $kJ{\cdot}mol^{-1}$ has been determined by recalculation in the present review.

For the reaction

$$FeSO_4{\cdot}7H_2O(cr) \rightleftharpoons FeSO_4{\cdot}H_2O(cr) + 6\ H_2O(l), \qquad \text{(IX.26)}$$

this leads to 55.87 $kJ{\cdot}mol^{-1}$ for $\Delta_r H_m$ (IX.26). This is in good agreement with the value (56.2 ± 5.2) $kJ{\cdot}mol^{-1}$ based on Larson's study [1968LAR] (and in fair agreement with the values 49.6 $kJ{\cdot}mol^{-1}$ at 286.65 K from de Forcrand [1914FOR] and 48.7 $kJ{\cdot}mol^{-1}$ at 303.15 K from Jamieson *et al.* [1965JAM/BRO]).

The value of $\Delta_f H^{\circ}_m$ ($FeSO_4{\cdot}H_2O$, cr, 298.15 K) based on the work of Adami and Kelley [1963ADA/KEL] is accepted, but with an increased uncertainty.

$$\Delta_f H^{\circ}_m (FeSO_4{\cdot}H_2O\text{, cr, 298.15 K}) = -\ (1244.0 \pm 1.5)\ kJ{\cdot}mol^{-1}.$$

The vapour-pressure equations of Kohler and Zäske [1964KOH/ZAS2] indicate that the Gibbs energy of dehydration of $FeSO_4{\cdot}7H_2O(cr)$ to $FeSO_4{\cdot}H_2O(cr)$ (also forming $H_2O(g)$) is of the order of (30.0 ± 1.0) $kJ{\cdot}mol^{-1}$ at 331 K. Assuming a reasonable value of 150 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ for the heat capacity of $FeSO_4{\cdot}H_2O(cr)$, and hence an average constant value for $\Delta_r C_{p,m}$ (IX.27) of – 43 $J{\cdot}K^{-1}{\cdot}mol^{-1}$, the value of $\Delta_r G_m$ (IX.27) at 298.15 K is calculated to be 58.7 $kJ{\cdot}mol^{-1}$.

$$FeSO_4{\cdot}7H_2O(cr) \rightleftharpoons FeSO_4{\cdot}H_2O(cr) + 6\ H_2O(g), \qquad \text{(IX.27)}$$

Even if the estimated heat capacity of reaction were incorrect by 50 $J{\cdot}K^{-1}{\cdot}mol^{-1}$, this would introduce an uncertainty in the value of $\Delta_r G_m$ (IX.27) at 298.15 K of less than 0.2 $kJ{\cdot}mol^{-1}$. On this basis, the uncertainty in $\Delta_r G_m$ (IX.27) at 298.15 K is assumed to be introduced mainly by the uncertainties in the temperature and pressure measurements in the study of Kohler and Zäske [1964KOH/ZAS2], and is estimated as ± 5.0 $kJ{\cdot}mol^{-1}$

$$\Delta_r G_m\ \text{(IX.27)} = (58.7 \pm 5.0)\ kJ{\cdot}mol^{-1}.$$

Hence,

$$\Delta_f G_m^{o}\ (FeSO_4{\cdot}H_2O,\ cr,\ 298.15\ K) = -\ (1077.52 \pm 5.05)\ kJ{\cdot}mol^{-1}.$$

IX.1.2.2.3 Anhydrous iron(III) sulfate compound

IX.1.2.2.3.1 Enthalpy of formation of $Fe_2(SO_4)_3(cr)$

Anhydrous iron(III) sulfate exists in monoclinic and trigonal modifications, the latter as the mineral mikasaite. There have been two important calorimetry studies of the enthalpy of formation of $Fe_2(SO_4)_3(cr)$. Barany and Adami [1965BAR/ADA] carried out measurements of the heat of solution of $Fe_2(SO_4)_3(cr)$ into 20 weight-% aqueous HF (at 346.85 K). From this and heats of solution of iron(III) oxide, $H_2SO_4(sln)$ and $H_2O(l)$ into the same solvent, – (2584.02 ± 5.00) $kJ{\cdot}mol^{-1}$ is calculated for the heat of formation at 298.15 K. Majzlan *et al.* [2005MAJ/NAV] determined the enthalpy of formation of monoclinic $Fe_2(SO_4)_3$ by measurement of the heats of solution of $Fe_2(SO_4)_3(cr)$, γ-FeOOH, $H_2O(l)$, MgO(cr) and α-$MgSO_4$ at 298.15 K into a 5 M HCl aqueous solution. On recalculation with auxiliary data consistent with those used in the present review, the value of $\Delta_f H_m^{o}$ is calculated to be – (2584.17 ± 6.07) $kJ{\cdot}mol^{-1}$ for 298.15 K.

Several groups have determined the equilibrium constant for the thermal decomposition of iron(III) sulfate to iron(III) oxide, sulfur oxides and oxygen using dynamic [1908KEP/ANS], [1965ALC/SUD] and static [1908WOH/PLU], [1910BOD/SUZ], [1913GRU], [1937NEU/HEI], [1960WAR/ING], [1961BLA] gas-pressure measurements. The early results were reviewed by Neumann and Heintke [1937NEU/HEI]. Kellogg [1964KEL] also reviewed the data for 700 to 1000 K, and provided an equation for $\Delta_r G_m$ (IX.28) for the equilibrium

$$Fe_2(SO_4)_3(cr) \rightleftharpoons Fe_2O_3(cr) + 3\ SO_3(g). \qquad \text{(IX.28)}$$

Electrochemical methods have also been used [1973SKE/ESP], [1977SAD/KAW], [1986HSI/CHA], [1986JAC/IYE]. Jacob and Iyengar [1986JAC/IYE] provided a useful comparison of these studies, all carried out at temperatures between 800 and 1000 K. Some further details are provided in Appendix A.

Second-law analyses of these high-temperature data generate very scattered values for $\Delta_f H_m^o$(Fe$_2$(SO$_4$)$_3$, cr, 298.15 K) and S_m^o(Fe$_2$(SO$_4$)$_3$, cr, 298.15 K). The derived values for these quantities are very strongly correlated, and cannot be used independently. Third-law analyses using S_m^o(Fe$_2$(SO$_4$)$_3$, cr, 298.15 K) from Majzlan *et al.* [2005MAJ/NAV] and enthalpy and entropy increment values tabulated by Pankratz and Weller [1969PAN/WEL] lead to values of $\Delta_f H_m^o$(Fe$_2$(SO$_4$)$_3$, cr, 298.15 K) of – 2584 kJ·mol^{-1}, – 2578 kJ·mol^{-1}, – 2576 kJ·mol^{-1} and – 2576 kJ·mol^{-1} from the 900 K results of Jacob and Iyengar [1986JAC/IYE], Kellogg [1964KEL], Hsieh and Chang [1986HSI/CHA] and Skeaff and Espelund [1973SKE/ESP], respectively. Thus, the values from the high-temperature equilibrium studies are consistent with the calorimetrically determined values.

The results from the two calorimetry studies are in good agreement. Though it is assumed here, on the basis of the description of the synthesis, that the Fe$_2$(SO$_4$)$_3$ sample used by Barany and Adami [1965BAR/ADA] was probably the trigonal form, the equally weighted average of the two measurements is selected.

$$\Delta_f H_m^o(\text{Fe}_2(\text{SO}_4)_3,\ \text{cr},\ 298.15\ \text{K}) = -(2584.1 \pm 3.9)\ \text{kJ·mol}^{-1}.$$

The selected value has a sufficient large uncertainty that, in the absence of other information, it can be assumed to apply to either crystalline form of the solid.

IX.1.2.2.3.2 Heat capacity and entropy of Fe$_2$(SO$_4$)$_3$(cr)

There have been two major studies of the heat capacities of Fe$_2$(SO$_4$)$_3$(cr). Pankratz and Weller [1969PAN/WEL] carried out adiabatic calorimetry measurements from 53 to 296 K and drop-calorimetry enthalpy measurements between 406 and 900 K (reference temperature 298.15 K). Majzlan *et al.* [2005MAJ/NAV] reported adiabatic calorimetry results for temperatures between 20 and 395 K and semi-adiabatic calorimetry results for temperatures between 0.47 and 38.2 K. Between 100 and 295 K, the values from the earlier study are approximately 0.5% less than those from the study of Majzlan *et al.*, but agreement becomes poorer at lower temperatures. Near 50 K the values from the earlier study are greater by more than 5%. There is a sharp magnetic transition near 30 K, and though the semi-adiabatic calorimetry results can be used to better resolve the shape of the anomaly, the results from the adiabatic calorimetry are in good agreement. The drop-calorimetry measurements mesh well with the adiabatic calorimetry measurements at higher temperatures, though, as discussed below, more than one equation is useful for modelling the change in heat capacity with temperature. The drop-calorimetry results also revealed what appears to be a small transition near 800 K. The value of the entropy at 298.15 K as determined by Majzlan *et al.* [2005MAJ/NAV] is accepted in the present review:

$$S^{\circ}_{\mathrm{m}}\ (\mathrm{Fe_2(SO_4)_3}, \text{monoclinic}, 298.15\ \mathrm{K}) = (305.6 \pm 0.6)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}.$$

The function

$$C^{\circ}_{p,\mathrm{m}}\ (\mathrm{Fe_2(SO_4)_3}, \text{monoclinic}, T\,)/\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}} = 202.96 + 0.33152\ (T/\mathrm{K}) - 2566800\ (T/\mathrm{K})^{-2} \qquad \text{(IX.29)}$$

was fitted to the weighted experimental adiabatic calorimetry results between 250 and 395 K, and

$$C^{\circ}_{p,\mathrm{m}}\ (\mathrm{Fe_2(SO_4)_3}, \text{monoclinic}, T\,)/\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}} = 263.77 + 0.21763\ (T/\mathrm{K}) - 5108700\ (T/\mathrm{K})^{-2} \qquad \text{(IX.30)}$$

was fitted to the weighted experimental adiabatic calorimetry and drop-calorimetry results between 350 and 800 K. The functions give similar values between 350 and 400 K, and cross at 376.5 K. Therefore, Eq. (IX.29) is recommended for temperatures between 250 and 376.5 K, and Eq. (IX.30) from 376.5 to 800 K. Thus,

$$C^{\circ}_{p,\mathrm{m}}\ (\mathrm{Fe_2(SO_4)_3}, \text{monoclinic}, 298.15\ \mathrm{K}) = (272.93 \pm 1.00)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}.$$

In the early study of Nilson and Pettersson [1880NIL/PET], an average $C^{\circ}_{p,\mathrm{m}}$ value of 277 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ was reported for temperatures between 273 and 373 K—only 2 to 3% lower than the value calculated from Eq. (IX.29).

A function also was fitted to the drop-calorimetry experiments from temperatures above the apparent transition at 800 K (see Appendix A). When combined with the enthalpy-difference equation related to Eq. (IX.30), this leads to (2.3 ± 1.0) $\mathrm{kJ{\cdot}mol^{-1}}$ for a calculated enthalpy of transition at (800 ± 10) K. However, the nature of the transition is not clear, and in the present review the enthalpy is not assigned to any specific transition (see Appendix A).

IX.1.2.2.4 Hydrated iron(III) sulfates and other solids in the $\mathrm{Fe_2O_3}$-$\mathrm{SO_3}$-$\mathrm{H_2O}$ system

There have been several detailed studies and reviews of the solids in the $\mathrm{Fe_2O_3}$-$\mathrm{SO_3}$-$\mathrm{H_2O}$ system (*e.g.*, [1907CAM/ROB3], [1907REC], [1914WIR/BAK], [1922APP/WIL], [1922POS/MER], [1935BAS/CAM], [1937MER/POS], [1938KOE/CAL]). However, some equilibria are not established except over very long times, especially in some of the very viscous saturated solutions at temperatures at and below 323 K. Recovery and analysis of most of the solids have also proven difficult, and conditions for partial dehydration of the "simple" hydrates are not well established. Tosca *et al.* [2007TOS/SMI] have attempted to apply the results of recent isopiestic studies in assessing whether equilibrium was attained in several of these earlier solubility studies.

Among the solids[1] identified in the system are:

- $3Fe_2O_3{\cdot}4SO_3{\cdot}9H_2O$
  (hydronium jarosite, $(H_3O)Fe_3(SO_4)_2(OH)_6$ [1922POS/MER], [2004MAJ/STE]. Synthesis leads to a solid with some unoccupied crystal lattice sites *e.g.*, $(H_3O)_{1.00\text{-}x}Fe_{3.00\text{-}y}(SO_4)_2(OH)_{6\text{-}3y\text{-}x}(H_2O)_{2x}$ [1922POS/MER], [2004MAJ/STE]);
- $Fe_2O_3{\cdot}2SO_3{\cdot}xH_2O$
  ($Fe(OH)(SO_4){\cdot}((x-1)/2)H_2O$ [1922POS/MER], see discussion below);
- $Fe_2O_3{\cdot}2.5SO_3{\cdot}7H_2O$ [1935BAS/CAM], $2Fe_2O_3{\cdot}5SO_3{\cdot}17H_2O$ [1937MER/POS]
  ($Fe_4(SO_4)_5(OH)_2{\cdot}13H_2O$, but more likely $Fe_{14}(SO_4)_{18}(OH)_6{\cdot}60H_2O$, ferricopiapite [2006MAJ/NAV]);
- $Fe_2O_3{\cdot}3SO_3{\cdot}5H_2O$
  ($Fe_2(SO_4)_3{\cdot}5H_2O$, lausenite, [1922POS/MER] (identified in that paper as a hexahydrate), [2005MAJ/BOT]);
- $Fe_2O_3{\cdot}3SO_3{\cdot}7.25H_2O$
  ($Fe_2(SO_4)_3{\cdot}7.25H_2O$ [1973ROB/FAN], kornelite, earlier reported as being a heptahydrate or octahydrate [1922POS/MER], [1935BAS/CAM], and probably variable with 6 to 8 waters of hydration depending on the synthesis [1973ROB/FAN], [2005MAJ/BOT]);
- $Fe_2O_3{\cdot}3SO_3{\cdot}9H_2O$
  ($Fe_2(SO_4)_3{\cdot}9H_2O$, coquimbite [1937MER/POS], [2006MAJ/NAV], paracoquimbite [1971ROB/FAN]);
- $Fe_2O_3{\cdot}3SO_3{\cdot}11H_2O$
  ($Fe_2(SO_4)_3{\cdot}11H_2O$, quenstedtite [1974THO/ROB]);
- $Fe_2O_3{\cdot}4SO_3{\cdot}3H_2O$
  ($(H_3O)Fe(SO_4)_2$, [1903REC], [1922POS/MER]);
- $Fe_2O_3{\cdot}4SO_3{\cdot}9H_2O$
  ($(H_3O)Fe(SO_4)_2{\cdot}3H_2O$, rhomboclase [1922POS/MER], [1935BAS/CAM], [2006MAJ/NAV]).

The study of Posnjak and Merwin [1922POS/MER] was carried out at temperatures between 323 and 403 K, therefore allowing a more rapid approach to equilibrium and production of more easily characterized crystals. However, the results are then not directly comparable to those from experiments at lower temperatures [1914WIR/BAK], [1935BAS/CAM]. As listed above, Posnjak and Merwin

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[1] In parts of this section, formulae shown with hydroxyl groups or monohydrogen sulfate ions are written to facilitate comparison of stoichiometries, and do not necessarily reflect the structures in the solids.

[1922POS/MER] proposed two basic hydrates, formed at temperatures above (or near) 323 K and above 348 K, formulated as $Fe_2O_3\cdot2SO_3\cdot5H_2O$ and $Fe_2O_3\cdot2SO_3\cdot H_2O$. These formulae can be rewritten as $Fe(OH)SO_4\cdot2H_2O$ and $Fe(OH)SO_4$, and the compounds, if they exist, may be related to one or more of the minerals: fibroferrite ($Fe(OH)SO_4\cdot5H_2O$) [1997BLA/DEN], hohmannite ($Fe_2O(SO_4)_2\cdot8H_2O$ [2004SCO/VEN], *i.e.*, $FeOHSO_4\cdot3.5H_2O$), amarantite ($Fe_2O(SO_4)_2\cdot7H_2O$ [1968SUS], *i.e.*, $FeOHSO_4\cdot3H_2O$ butlerite ($Fe(OH)SO_4\cdot2H_2O$) [1997BLA/DEN], parabutlerite (also $Fe(OH)SO_4\cdot2H_2O$) [1997BLA/DEN], and metahohmannite ($Fe_2O(SO_4)_2\cdot4H_2O$ [2004SCO/VEN], *i.e.*, $FeOHSO_4\cdot1.5H_2O$).

As most of these hydrated solids are very difficult to isolate in a pure form, there are few precise thermodynamic data available. Recently Majzlan *et al.* [2004MAJ/STE] synthesized and reported enthalpy of solution and heat-capacity measurements for a solid with the composition $(H_3O)_{0.91}Fe_{2.91}(SO_4)_2(OH)_{5.64}(H_2O)_{0.18}$, close to the ideal composition of hydronium jarosite. From these measurements, a set of thermodynamic values was reported for $(H_3O)Fe_3(SO_4)_2(OH)_6$, – (3770.2 ± 4.6) $kJ\cdot mol^{-1}$, (448.2 ± 0.7) $J\cdot K^{-1}\cdot mol^{-1}$, for $\Delta_f H_m^o$ and S_m^o, respectively, at 298.15 K, and (287.2 + 0.6281 (T/K) – 3286000 $(T/K)^{-2}$) for $C_{p,m}^o / J\cdot K^{-1}\cdot mol^{-1}$ for temperatures between 273 and 400 K (for details see the Appendix A entry for [2004MAJ/STE]).

The values of $\Delta_f H_m^o$ (298.15 K) (after recalculation using auxiliary data consistent with those in the present review) and $[C_{p,m}^o]_{273\text{ K}}^{400\text{ K}}$ for the non-stoichiometric compound $(H_3O)_{0.91}Fe_{2.91}(SO_4)_2(OH)_{5.64}(H_2O)_{0.18}$ [2004MAJ/STE], are accepted,

$$\Delta_f H_m^o((H_3O)_{0.91}Fe_{2.91}(SO_4)_2(OH)_{5.64}(H_2O)_{0.18}, \text{cr}, 298.15\text{ K}) = -(3693.9 \pm 6.5)\text{ kJ}\cdot\text{mol}^{-1},$$

and

$$[C_{p,m}^o]_{274.74\text{K}}^{394.94\text{K}}((H_3O)_{0.91}Fe_{2.91}(SO_4)_2(OH)_{5.64}(H_2O)_{0.18})/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 280.6 + 0.6149(T/\text{K}) - 3199700(T/\text{K})^{-2}.$$

The value of $\Delta_f H_m^o$ proposed by the authors for stoichiometric hydronium jarosite does not agree well with – (3741.6 ± 8.3) $kJ\cdot mol^{-1}$ reported by Drouet and Navrotsky [2003DRO/NAV], and in the present review no value is selected for $\Delta_f H_m^o((H_3O)Fe_3(SO_4)_2(OH)_6$, cr, 298.15 K).

The value of $S_m^o((H_3O)_{0.91}Fe_{2.91}(SO_4)_2(OH)_{5.64}(H_2O)_{0.18})$ at 298.15 K, augmented by half the maximum configurational entropy [2004MAJ/STE] at 0 K, is accepted, and the uncertainty is estimated as ± 8.0 $J\cdot K^{-1}\cdot mol^{-1}$

$$S_m^o((H_3O)_{0.91}Fe_{2.91}(SO_4)_2(OH)_{5.64}(H_2O)_{0.18}, \text{cr}, 298.15\text{K}) = (446.5 \pm 8.0)\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

As the entropy of the stoichiometric compound should not include extra configurational entropy, the values of the entropy and heat-capacity equations proposed by Majzlan *et al.* [2004MAJ/STE] are accepted for the entropy and heat capacity

$$S_m^o((H_3O)Fe_3(SO_4)_2(OH)_6, \text{cr}, 298.15\text{ K}) = (448.2 \pm 0.7)\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$[C^{\circ}_{p,\mathrm{m}}]^{400\,\mathrm{K}}_{273\,\mathrm{K}}\,((\mathrm{H_3O})\mathrm{Fe_3(SO_4)_2(OH)_6})/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = 287.2 + 0.6281\,(T/\mathrm{K}) - 3286000(T/\mathrm{K})^{-2}$$

$$C^{\circ}_{p,\mathrm{m}}\,((\mathrm{H_3O})\mathrm{Fe_3(SO_4)_2(OH)_6},\ 298.15\ \mathrm{K}) = (437.5 \pm 2.0)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

Majzlan *et al.* [2006MAJ/NAV] reported an enthalpy of formation value for $Fe_2(SO_4)_3\cdot5.03H_2O$(cr). The enthalpy of formation value for the stoichiometric pentahydrate, as calculated in Appendix A, is selected in the present review

$$\Delta_{\mathrm{f}} H^{\circ}_{\mathrm{m}}\,(\mathrm{Fe_2(SO_4)_3\cdot5H_2O,\ cr,\ 298.15\ K}) = -\,(4106.5 \pm 5.9)\ \mathrm{kJ\cdot mol^{-1}}.$$

Majzlan *et al.* [2006MAJ/NAV] also reported enthalpy of formation values for solids with the compositions $Fe_{4.78}(SO_4)_6(OH)_{2.34}\cdot20.71H_2O$ and $(H_3O)_{1.34}Fe(SO_4)_{2.17}\cdot3.06H_2O$, for a sample of natural coquimbite (with an Fe(III):Al(III) ratio of 3.44:1) [2006MAJ/NAV], and for two samples of schwertmannite (idealized formula $FeO(SO_4)_{0.125}(OH)_{0.75}$) [2004MAJ/NAV]. Schwertmannite occurs primarily as an intermediate mineral in acid-mine drainage environments [1994BIG/CAR], and at 298.15 K is metastable with respect to decomposition to a sulfate-containing goethite phase [2005SCH/CAR].

The value of $\Delta_{\mathrm{f}} H^{\circ}_{\mathrm{m}}$ (298.15 K) for the non-stoichiometric acid sulfate (after recalculation using auxiliary data consistent with those in the present review) is:

$$\Delta_{\mathrm{f}} H^{\circ}_{\mathrm{m}}\,((\mathrm{H_3O})_{1.34}\mathrm{Fe(SO_4)_{2.17}\cdot3.06H_2O,\ cr,\ 298.15\ K}) = -\,(3201.22 \pm 3.56)\ \mathrm{kJ\cdot mol^{-1}}$$

and for the other oxo- and oxohydroxy-sulfates

$$\Delta_{\mathrm{f}} H^{\circ}_{\mathrm{m}}\,(\mathrm{Fe_{4.78}(SO_4)_6(OH)_{2.34}\cdot20.71H_2O,\ cr,\ 298.15\ K}) = -\,(12046.2 \pm 12.6)\ \mathrm{kJ\cdot mol^{-1}}$$

$$\Delta_{\mathrm{f}} H^{\circ}_{\mathrm{m}}\,(\mathrm{FeO(SO_4)_{0.157}(OH)_{0.686}\cdot0.972H_2O,\ cr,\ 298.15\ K}) = -\,(884.1 \pm 2.0)\ \mathrm{kJ\cdot mol^{-1}}$$

$$\Delta_{\mathrm{f}} H^{\circ}_{\mathrm{m}}\,(\mathrm{FeO(SO_4)_{0.168}(OH)_{0.664}\cdot1.226H_2O,\ cr,\ 298.15\ K}) = -\,(960.6 \pm 2.0)\ \mathrm{kJ\cdot mol^{-1}}.$$

There have been attempts to estimate the entropies of such species [2004MAJ/NAV], [2006MAJ/NAV] and to measure the solubility of schwertmannite samples [1999YU/HEO], [2001KAW/TOM] that had somewhat different stoichiometries. However, in the absence of other measurements on pure samples, the assignment of values to further thermodynamic quantities for these poorly-crystalline metastable compounds with variable stoichiometries is beyond the scope of the present review.

IX.1.2.2.5 $(NH_4)_2Fe(SO_4)_2\cdot6H_2O$(cr)

Vasil'ev *et al.* [1978VAS/VAS2] reported heats of solution measurements for $(NH_4)_2Fe(SO_4)_2\cdot6H_2O$ in aqueous $HClO_4$ solutions. Using these, heats of dissolution of Fe(cr) and $(NH_4)_2SO_4$(cr) [1976PAR/WAG], and heats of dilution of H_2O_2(aq) and concentrated aqueous sulfuric acid H_2SO_4(sln) in similar solutions, the enthalpy of formation of $(NH_4)_2Fe(SO_4)_2\cdot6H_2O$(cr) was recalculated (see Appendix A) using CODATA-consistent auxiliary data, and is accepted in the present review:

$$\Delta_f H_m^o\ ((NH_4)_2Fe(SO_4)_2{\cdot}6H_2O, \text{cr}, 298.15\ \text{K}) = -\ (3925.58 \pm 2.40)\ \text{kJ}{\cdot}\text{mol}^{-1}.$$

The only heat-capacity measurements for this solid appear to be those of Hill and Smith [1953HIL/SMI] at temperatures from ~ 2.5 to 30 K, and no values of $C_{p,m}^o$ or S_m^o can be selected for 298.15 K.

IX.1.2.2.6 Mixed oxidation state iron sulfates

Two categories of iron(II)/iron(III) mixed sulfates have been reported, especially in mineral assemblages. First there are sulfates with more iron(III) than iron(II)—römerite ($Fe^{II}(Fe^{III})_2(SO_4)_4{\cdot}14H_2O$) and bilinite ($Fe^{II}(Fe^{III})_2(SO_4)_4{\cdot}22H_2O$), and the hydroxysulfate, copiapite ($Fe^{II}(Fe^{III})_4(SO_4)_6(OH)_2{\cdot}20H_2O$). Then, there is the so-called "green rust two", $(Fe^{II})_4(Fe^{III})_2(OH)_{12}SO_4{\cdot}{\sim}8H_2O$ [1959BER/DAS], comprised of positively charged hydroxide sheets $[(Fe^{II})_4(Fe^{III})_2(OH)_{12}]^{2+}$ and negatively charged interlayers composed of sulfate anions and water molecules [2003SIM/FRA].

No thermodynamic measurements were found for the iron(III)-rich solids, though Hemingway *et al.* [2002HEM/SEA] have estimated values for the enthalpies of formation and the entropies of römerite, bilinite and copiapite.

There have been several papers [1994HAN/BOR], [1996GEN/OLO], [1998GEN/BOU], [1999REF/BON], [2006TRO/BOU] on the thermodynamic quantities for the "green rust two" sulfate compound, all based on the regions of apparent stability of the solid(s) and voltammetric measurements of the electrochemical potential at which suspensions of $Fe(OH)_2$ are oxidized in aqueous solutions. The compound is probably best formulated as $(Fe^{III})_2(Fe^{II})_4(OH)_{12}SO_4{\cdot}nH_2O$ ($n \approx 8$). Refait *et al.* [2003REF/GEH] indicated that the solid is metastable with respect to magnetite except in a limited domain near neutral pH. Because the sulfate "green rust" has a wider range of stability than the chloride-containing "green rust one" (Section VIII.3.2.4.2), the thermodynamic properties of the sulfate-containing solid have been better established. The electrochemical studies [1998GEN/BOU], [1999REF/BON] indicate that for

$$6\ Fe(OH)_2(s) + SO_4^{2-} + 2\ H^+ + n\ H_2O(l) \rightleftharpoons (Fe^{III})_2(Fe^{II})_4(OH)_{12}SO_4{\cdot}nH_2O + H_2(g) \quad (IX.31)$$

$\Delta_r G_m^o$ (IX.31) is $-(105 \pm 2)$ kJ·mol^{-1} at 298.15 K. However, no values are selected here for the thermodynamic quantities of this hydroxysulfate.

Chapter X

Group 14 compounds and complexes

X.1 Carbon compounds and complexes

X.1.1 Aqueous iron carbonates

X.1.1.1 Carbonate as ligand

X.1.1.1.1 Acid-base equilibria

Because the earth's atmosphere contains CO_2 which forms HCO_3^- and CO_3^{2-} on dissolution in water, and because these anions strongly complex metal ions, carbon dioxide is one of the main ligands in geochemistry. Many important natural compounds are carbonates, and the estimation of the stability of iron(III) carbonates as a function of environmental conditions is a key problem for modelling the behaviour of iron (and in correlating the behaviour of other trace elements through possible oxidation reduction reactions). Reactions and related equilibrium constant values have been summarized in [1990NOR/PLU].

If the temperature and pressure of CO_2(g) are fixed and the pH is set by addition of strong bases or acid, the concentrations of CO_2(aq), HCO_3^- and CO_3^{2-} are fixed. At high CO_2 pressures, high pH values cannot be reached because they would require unattainably high salt concentrations. For example, if the partial pressure of CO_2(g) is 10 kPa at 298.15 K and the solution pH is fixed at 10, the solution activities of HCO_3^- and CO_3^{2-} would need to be 14.8 m and 7.0 m, respectively. Realistically, any attempt to generate such solutions would result in precipitation of solids such as Na_2CO_3, K_2CO_3, $NaHCO_3$, and $KHCO_3$. If excess carbonate or hydrogen carbonate solids are contacted with water (again at a constant partial pressure of CO_2(g)), both carbonate and hydrogen carbonate solids will result. The lower the fixed partial pressure of CO_2(g), the higher the resulting pH. In speciation studies investigation of non-equilibrium solutions more concentrated in CO_3^{2-} ions is also possible. However, such solutions are susceptible to changes in carbonate concentration if they absorb or release CO_2. The composition of any alkaline carbonate or hydrogen carbonate solution will change drastically if left in contact with a substantial volume of gas containing carbon dioxide.

As will be discussed below, the carbonate aqueous complexes of iron(III) are difficult to characterize because the concentrations of carbonate ions are only important at high pH values at which the hydroxido and oxo complexes are often predominant. To investigate the complexes of iron(III) and other highly charged metal cations with carbonate, it sometimes can be necessary to use highly concentrated carbonate solutions to compete with the hydrolysis. For such purposes it is preferable to use potassium carbonate. The concentrations of carbonate, hydrogen carbonate and pH of such saturated solutions at equilibrium with gaseous CO_2 are always much greater for the potassium salts because of the higher solubility of $KHCO_3$.

Another problem encountered in the investigation of carbonate complexes is the kinetics of their formation. Generally for highly hydrolyzable metals the rate of carbonate complex formation is slower than the rate of hydrolysis for the first hydrolysis steps. Therefore, mixtures of carbonate solutions with acidic solutions of these metals can lead to non-equilibrium hydrolysis products, instead of carbonate species, because of differences in the rates of association of OH^- and CO_3^{2-} with the metal ions; reaching equilibrium can take long periods of time.

X.1.1.1.2 Coordination modes of the CO_3^{2-} anion [1987OLD]

As discussed by Oldham [1987OLD], the carbonate CO_3^{2-} anion is planar with D_{3h} symmetry and an oxygen-to-carbon distance of 0.129 nm. Four kinds of bonding have been observed for the carbonate.

- Ionic in solids such as calcite: the charge on the carbonate is neutralized by the positive charge of Ca^{2+}, but there is no defined bonding between the carbonate and the metal ion.
- Unidentate, such as in $Co(NH_3)_5CO_3^+$: the CO_3^{2-} anion loses its D_{3h} symmetry. The C=O bond linked to the metal is elongated (~ 0.131 nm), while the non-coordinated C=O bonds are shortened (~ 0.12 nm).
- η^3 chelates or bidentate, such as in $Co(NH_3)_4CO_3^+$: the carbonate forms a four-member ring with the metal and again it loses its D_{3h} symmetry with the two linked C=O bonds being elongated (0.134 nm), and the free C=O shortened (0.124 nm).
- Various bridging systems, such as in the examples described by Oldham [1987OLD]. There the metal-metal distances are shorter than for a purely ionic solid, and one carbonate is shared by several metal ions. Several geometries (as determined by X-ray diffraction) have been observed.

Infra-red and Raman spectroscopy have been proposed as tools for the determination of the type of bonding. It has been claimed that the degree of splitting of the single stretching absorption band of the calcite CO_3^{2-} with D_{3h} symmetry (1430 – 1490 cm^{-1}) with carbonate bonding depends on the mode of coordination. The splitting for unidentate coordination is in the range of 80 cm^{-1}, and is much higher for chelate formation (~ 300 cm^{-1}). However, when bridging occurs interpretation of the results from vibrational spectroscopy becomes confusing, and only X-ray diffraction can lead unambiguously to the real geometry. Therefore, most of the structures described above were observed in solids. Bridging carbonate has been proposed in some polymeric species such as those with the empirical formulae $(UO_2)_3(CO_3)_3^{6-}$ and $(UO_2)_{11}(OH)_{24}(CO_2)_2^{2-}$ [1991GRE/LAG].

X.1.1.2 Aqueous iron(II) carbonato complexes

Although many references deal with the solubility of siderite and/or solids with the chemical formula $FeCO_3(s)$ (see Section X.1.2.1.2), quantitative studies describing aqueous complexes of Fe(II) with carbonate ligands are nearly absent.

X.1.1.2.1 $FeHCO_3^+$

Johnson and Baumann [1978JOH/BAU] were able to reproduce previously measured stability constants for $MgHCO_3^+$ and $MnHCO_3^+$, but they failed in attempts to measure the similar constant for $FeHCO_3^+$ according to a method described by Siebert and Hostetler [1977SIE/HOS] because the numerical evaluation did not converge. Johnson and Baumann [1978JOH/BAU] estimated the formation constant at 298.15 K to be similar to that of $MnHCO_3^+$, *i.e.*, of the order of 10 to 30.

At 298.15 K in 0.1 $mol \cdot dm^{-3}$ $NaClO_4$ Singer and Stumm [1970SIN/STU], who measured electrode potentials, did not find any indications of hydrogencarbonato complex formation. They concluded that the formation constant is less than 10.

Reanalysis of the dissolution experiments of Smith [1918SMI] can lead to the value $K^{\circ}(FeHCO_3^+, 303.15\ K) = (8 \pm 15)\ kg \cdot mol^{-1}$, but the data of [1918SMI] are even more consistent with the hypothesis that the complex $FeHCO_3^+$ does not exist (see Appendix A).

Bruno *et al.* [1992BRU/WER] concluded that their siderite solubility data are incompatible with formation of the simple hydrogencarbonato complex. Moreover, they stated that the "*additional assumption of a* $FeHCO_3^+$ *complex leads to a poorer agreement of our experimental data…*".

There is no strong evidence for formation of the hydrogencarbonato complex, and in general protonation of a monodentate carbonate ligand is a precursor step to rapid (millisecond time-scale) loss of $CO_2(aq)$ [1983PAL/ELD]. At best the complex is very weak. Further, the potential field of stability of $FeHCO_3^+$ would be expected to be very narrow because differences in $\log_{10} K_i$ for protonation of HCO_3^- and CO_3^{2-} are of the same order of magnitude as the difference $\{\log_{10} K(FeCO_3(aq)) - \log_{10} K(FeHCO_3^+)\}$. This means that any formation of $FeHCO_3^+$ likely would be accompanied by formation of $FeCO_3(aq)$ in most systems of practical relevance. Hence, the present review does not select a formation constant for $FeHCO_3^+$.

X.1.1.2.2 $FeCO_3(aq)$

There is only one study that quantitatively describes the formation of $FeCO_3(aq)$. Bruno *et al.* [1992BRU/WER] carefully measured the solubility of siderite at 298.15 K in 1.0 M $NaClO_4$ over an extended pH range from 6 to 9 and at two different CO_2 partial pressures. The analytical data in this paper were taken from the thesis of Wersin [1990WER].

The measured Fe(II) concentrations can be explained by the reactions

$$FeCO_3(s) + 2\,H^+ \rightleftharpoons Fe^{2+} + CO_2(g) + H_2O(l) \qquad (X.1)$$

$$FeCO_3(s) \rightleftharpoons FeCO_3(aq) \qquad (X.2)$$

$$FeCO_3(s) + H_2O(l) + CO_2(g) \rightleftharpoons Fe(CO_3)_2^{2-} + 2\,H^+. \qquad (X.3)$$

Recalculation using a density of 1.0735 $kg\cdot dm^{-3}$ for 1 M $NaClO_4$ at 298.15 K [1985SOH/NOV] leads to an average minimum value of $(3.89 \pm 0.38(2\sigma)) \times 10^{-6}$ $mol\cdot kg^{-1}$ for the molality of dissolved iron(II) and, hence,

$$\log_{10} K((X.2), 298.15\ K, 1.0515\ m\ NaClO_4) = -(5.41 \pm 0.04).$$

As discussed in Appendix A, the value of $\log_{10} K^\circ((X.1), 298.15\ K)$ is (7.19 ± 0.05), and $\Delta_r G_m^\circ((X.1), 298.15\ K)$ is $-(41.04 \pm 0.29)\ kJ\cdot mol^{-1}$.

To a first approximation, K(X.2) does not depend on ionic strength, provided that the interaction coefficient $\varepsilon(FeCO_3(aq), Na^+; ClO_4^-)$ can be set to zero. Therefore,

$$\log_{10} K^\circ((X.2), 298.15\ K) = -(5.41 \pm 0.04),$$

and $$\Delta_r G_m^\circ((X.2), 298.15\ K) = (30.88 \pm 0.90)\ kJ\cdot mol^{-1}.$$

Therefore

$$\Delta_f G_m^\circ(FeCO_3, aq, 298.15\ K) = \Delta_f G_m^\circ(Fe^{2+}) + \Delta_f G_m^\circ(CO_2, g) + \Delta_f G_m^\circ(H_2O, l) + \Delta_r G_m^\circ(X.2) - \Delta_r G_m^\circ(X.1).$$

Using the selected value for $\Delta_f G_m^\circ(Fe^{2+}, 298.15\ K)$ from Section VI.1.3.

$$\Delta_f G_m^\circ(FeCO_3(aq), 298.15\ K) = -(648.68 \pm 1.29)\ kJ\cdot mol^{-1}.$$

X.1.1.2.3 $Fe(CO_3)_2^{2-}$

As in the case of $FeCO_3(aq)$, only the work of Bruno *et al.* [1992BRU/WER] provides quantitative data. The fit, as mentioned in the former section, leads to a value of $-(20.82 \pm 0.06)$ for $\log_{10} K((X.3), 298.15\ K, 1.0515\ m\ NaClO_4)$, and after correction to zero ionic strength (Appendix A), the value of $\log_{10} K^\circ((X.3), 298.15\ K)$ is $-(21.80 \pm 0.12)$ and

$$\Delta_r G_m^\circ((X.3), 298.15\ K) = (124.4 \pm 0.9)\ kJ\cdot mol^{-1}.$$

Therefore

$$\begin{aligned}\Delta_f G_m^o(\mathrm{Fe(CO_3)_2^{2-}}, 298.15\ \mathrm{K}) = {} & \Delta_f G_m^o(\mathrm{Fe^{2+}}, 298.15\ \mathrm{K}) + 2\Delta_f G_m^o(\mathrm{CO_2, g}, 298.15\ \mathrm{K}) \\ & + 2\Delta_f G_m^o(\mathrm{H_2O, l}, 298.15\ \mathrm{K}) + \Delta_r G_m^o(\mathrm{X.3}) \\ & - \Delta_r G_m^o(\mathrm{X.1}).\end{aligned}$$

Using the selected value for $\Delta_f G_m^o(\mathrm{Fe^{2+}}, 298.15\ \mathrm{K})$ from Section VI.1.3

$$\Delta_f G_m^o(\mathrm{Fe(CO_3)_2^{2-}}, 298.15\ \mathrm{K}) = -(1186.67 \pm 1.30)\ \mathrm{kJ\cdot mol^{-1}}.$$

These values depend on the solid in the solubility experiments being independent of the acidity of the experimental solutions [1992BRU/WER], but are *not* dependent on that solid being identical to the most stable form of $FeCO_3$(cr).

X.1.1.3 Aqueous iron(III) carbonato complexes

For a long time information in the literature about carbonate complexes of Fe(III) was very limited. The difficulty in observing the carbonate complexes is partially a result of the competition between OH^- and CO_3^{2-}, both of which are able to enter into the first coordination sphere of Fe(III) at neutral or slightly basic pH. Almost all the evidence for iron(III)-carbonate interactions is based on an increase in solubility of hydroxide or oxide solids in the presence of carbonate. In spite of the importance of solubility information for geochemical calculations, unambiguous speciation is difficult without other types of data.

In general the environmental chemistry community has not considered Fe(III) carbonates to be important species. Byrne and Kester [1976BYR/KES] did not mention the carbonates in their list of the soluble species of iron(III) less concentrated than 10^{-7} m in seawater with pH values between 2 and 10. Millero *et al.* [1995MIL/YAO] also did not consider Fe(III) carbonates in sea water, but mentioned Fe(II) carbonates $FeHCO_3^+$, $FeCO_3$ and $Fe(CO_3)_2^{2-}$ as species between pH values 7 and 9. Waite [2001WAI] expressed the same opinion in his review.

The results of several studies of formation of Fe(III) carbonate complexes are summarized in Table X-1. Bruno *et al.* [1992BRU/STU] reported the solubility of hematite in aqueous $NaHCO_3$ solutions. The solution concentration of Fe(III) under CO_2(g) (p_{CO_2} = 98 kPa) was much greater than expected based on the equilibrium of aqueous hydrolysis species, especially at pH values between 7.0 and 7.5. The solubility data were interpreted by assuming the existence of two species with the stoichiometries $FeCO_3OH$(aq) and $Fe(CO_3)_2^-$.

$$\mathrm{Fe^{3+} + H_2O(l) + CO_3^{2-} \rightleftharpoons H^+ + FeCO_3OH(aq)} \qquad (X.4)$$

$$\log_{10} K_{111} \equiv \log_{10} K(\mathrm{X.4})$$

$$\mathrm{Fe^{3+} + 2\,CO_3^{2-} \rightleftharpoons Fe(CO_3)_2^-} \qquad (X.5)$$

$$\log_{10} \beta_{12} \equiv \log_{10} K(\mathrm{X.5})$$

The original interpretation of these data was criticized by Hummel [2000HUM], who pointed out that the solubilities were unreasonably high if the controlling solid phase had been hematite. Bruno and Duro [2000BRU/DUR] reanalysed the data, and proposed formation constants ($\log_{10} K^{\circ}_{111}$ = 7.7 and $\log_{10} \beta^{\circ}_{12}$ = 19.6) for $FeCO_3OH(aq)$ and $Fe(CO_3)_2^-$ based on the controlling solid being ferrihydrite rather than hematite.

The reanalysis did cast some doubt on the speciation, though there remained strong evidence for the formation of at least one Fe(III) carbonate-containing species. The proposed formation values are consistent with the known behaviour of iron in natural environments, and suggest that iron(III) carbonate complexes will start to play a role for $p_{CO_2} > 1$ kPa. The nature of the solid controlling the solubility was not established, nor was a satisfactory mechanism proposed for the existence of ferrihydrite when the initial solid in the experiments was the thermodynamically stable hematite. As seen from the information in Table X-1, the proposed species and formation constants based on the various interpretations of the study of Bruno *et al.* [1992BRU/STU] differ greatly.

Table X-1: Reported results of studies of formation for carbonate complexes of iron(III).

Reference	Method	Results
[1992BRU/STU]	solubility	$\log_{10}\beta_{111} = -(3.83 \pm 0.21)$ for formation of $FeCO_3OH(aq)$ $\log_{10}\beta_{12} = (7.40 \pm 0.11)$ for formation of $Fe(CO_3)_2^-$
[2000HUM]	correction and recalculation of data from [1992BRU/STU]	$\log_{10}\beta_{111} = 14.9$ for formation of $FeCO_3OH(aq)$ $\log_{10}\beta_{12} = 26.5$ for formation of $Fe(CO_3)_2^-$
[2000BRU/DUR]	reinterpretation of data from [1992BRU/STU]	(I —> 0 extrapolation) $\log_{10}\beta^{\circ}_{111} = 7.7$ for formation of $FeCO_3OH(aq)$ $\log_{10}\beta^{\circ}_{12} = 19.6$ for formation of $Fe(CO_3)_2^-$
[2005GRI]	ferrihydrite solubility	(I —> 0 extrapolation) $\log_{10}\beta^{\circ}_{111} = (10.76 \pm 0.38)$ for formation of $FeCO_3OH(aq)$ $\log_{10}\beta^{\circ}_{13} = (24.24 \pm 0.42)$ for formation of $Fe(CO_3)_3^{3-}$

Grivé [2005GRI] carried out a similar study on the solubility of solids identified as hematite and ferrihydrite. Equilibrium was established under gas streams of $N_2(g)$, to determine the effective solubility products under acidic conditions, and with $CO_2(g)$ at pressures of 1, 30.1 and 98 kPa. There is approximately a one order of magnitude difference between the Fe(III) concentrations reported by Bruno *et al.*

[1992BRU/STU], [2000BRU/DUR] and by Grivé from experiments done under very similar conditions at p_{CO_2} = 98 kPa.

Grivé interpreted her results in terms of the neutral species, $FeCO_3OH(aq)$ and a tricarbonato complex.

$$Fe^{3+} + 3CO_3^{2-} \rightleftharpoons Fe(CO_3)_3^{3-} \quad (X.6)$$

$$\log_{10}\beta_{13} \equiv \log_{10}K(X.6)$$

As discussed in Appendix A, though the solid-liquid separations were carried out with more care, and substantial attempts were made to identify the solid phases, there are reasons to regard the speciation and quantitative results of Grivé [2005GRI] (Table X-1) with considerable caution. As described in the Appendix A entry, reanalysis of the data leads to average values at 0.513 m of (8.81 ± 0.02) and (22.28 ± 0.05) for $\log_{10}\beta_{111}$ and $\log_{10}\beta_{13}$ respectively. By application of an SIT analysis, this resulted in (10.69 ± 0.04) and (24.0 ± 0.1) for $\log_{10}\beta^{o}_{111}$ and $\log_{10}\beta^{o}_{13}$, respectively.

Though increased dissolution of Fe(III) hydroxides and oxides in high-pH aqueous solutions containing carbonate is a strong argument for the existence of stable Fe(III) carbonato complexes, the speciation and the thermodynamic values for the formation of these species are difficult to obtain using only solubility data. This is primarily due to the difficulties in measuring the solubility, which depends both on achieving a satisfactory solid-liquid equilibrium and separation and on proper characterization of the surface of the solid.

The formula of the anionic complex, $Fe(CO_3)_3^{3-}$, requires confirmation by other techniques. Although it seems reasonable, as $Am(CO_3)_3^{3-}$ and $Ln(CO_3)_3^{3-}$ are well-characterized species, there are considerable differences in the M^{3+} ionic radii— ~ 0.06 nm for Fe^{3+} and ~ 0.09 - 0.11 nm for the trivalent actinides and lanthanides [1976SHA].

The stability of a soluble neutral species, $FeCO_3OH(aq)$, in equilibrium with ferrihydrite or hematite is highly improbable, because it would require 1 or 3 water molecules to fulfil the coordination number of 4 or 6 for iron. As there is a strong tendency of OH^- to act as a bridging ligand, it is unlikely that $FeCO_3OH(aq)$ prefers water to complete its coordination sphere. Also the apparent extended region of stability of $FeCO_3OH(aq)$ from a pH value of approximately 4.5 to a pH value of approximately 7 (corresponding to five orders of magnitude in CO_3^{2-} concentration) is puzzling. It would seem to require a stabilizing effect such as bridging, yet the solubility dependence on p_{CO_2} does not fit with a predominantly polymeric iron(III) species.

In the present review, it is concluded that the recalculated complexation constants based on the work of Grivé [2005GRI] are probably the best available estimates. However, the statistical uncertainties given by the data treatment are small compared to the other major uncertainties discussed in Appendix A. Therefore the estimated uncertainties have been increased substantially to ±2.0. The values proposed in the present review are

$$\log_{10} \beta^{\circ}_{111} = (10.7 \pm 2.0)$$

and $$\log_{10} \beta^{\circ}_{13} = (24.0 \pm 2.0).$$

No formation constant for $\mathrm{Fe(CO_3)_2^-}$ has been proposed in the present review because the work of Grivé [2005GRI] did not confirm the existence of such a species; the strong increase of Fe(III) solubility at high pH has been interpreted in terms of formation of $\mathrm{Fe(CO_3)_3^{3-}}$ rather than $\mathrm{Fe(CO_3)_2^-}$.

X.1.2 Iron carbonate compounds

X.1.2.1 $FeCO_3$(cr) (siderite)

Compared to the iron oxides, the number of reported experimental measurements of chemical thermodynamic quantities for $FeCO_3$(cr) is rather small. However, the diverse measurements provide independent estimates of values of $\Delta_f G^{\circ}_m$ (from solubility studies [1918SMI], [1969LAN], [1970SIN/STU], [1971FRE], [1976BAR/PER], [1981REI/JOH], [1991BRA], [1992BRU/WER], [1992GRE/TOM], [1992PTA/REA], [2002SIL/LIU], [2002JEN/BOD] (Table X-2) and thermal decomposition studies [1989STU/TOG], [2004KOZ]), of $\Delta_f H^{\circ}_m$ (from drop-calorimetry measurements [1994CHA/NAV] and the temperature dependence of equilibrium measurements [1989STU/TOG], [1992GRE/TOM]), and S°_m based on low-temperature heat-capacity measurements [1984ROB/HAS]. The values do not mesh very well, and there are questions concerning the uncertainties that should be assigned to the primary data.

X.1.2.1.1 Heat-capacity measurements and the value of S°_m at 298.15 K

There have been several reports of studies in which values of the heat capacity of $FeCO_3$(cr) have been obtained [1934AND], [1963KAL], [1964KOS/KAL], [1984ROB/HAS]. However, all of these studies were carried out using samples of natural siderite. In each case several per cent $MnCO_3$ was present, and in the sample used in the earliest study [1934AND] there was ~ 5% $MnCO_3$ and ~ 5% $MgCO_3$.

The sparse heat-capacity values from Kostryukov and Kalinkina [1964KOS/KAL] only were presented graphically, but for temperatures above 100 K appear to be ~ 5% greater than the values from Anderson [1934AND] and from Robie *et al.* [1984ROB/HAS]. For reasons discussed in Appendix A, the quantitative results from Anderson [1934AND] and Kostryukov and Kalinkina [1964KOS/KAL] are not used in the present review. The extensive adiabatic calorimetry and differential scanning calorimetry results of Robie *et al.* [1984ROB/HAS] are used to obtain

$$[C^{\circ}_{p,\mathrm{m}}]^{500\,\mathrm{K}}_{230\,\mathrm{K}}(\mathrm{FeCO_3, cr}, T)/\mathrm{J \cdot K^{-1} \cdot mol^{-1}} = 52.390 + 125.798 \times 10^{-3}\,(T/\mathrm{K}) - 4.004 \times 10^{5}\,(T/\mathrm{K})^{-2} - 0.3308 \times 10^{-4}\,(T/\mathrm{K})^{2}$$

and hence,

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{FeCO_3, cr, 298.15\ K}) = (82.45 \pm 2.00)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

In the present review, the assessed value for S°_{m} ($FeCO_3$, cr, 298.15 K) is the value reported by Robie *et al.* [1984ROB/HAS], but with an increased uncertainty ((95.47 ± 1.00) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, see Appendix A).

After evaluation of the available cycles for iron species and optimization to ensure consistency with other thermodynamic quantities for iron species (Chapter XI), the selected value is essentially the same except for a decrease in the uncertainty:

$$S^{\circ}_{\mathrm{m}}(\mathrm{FeCO_3, cr, 298.15\ K}) = (95.54 \pm 0.65)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

In some publications [1994CHA/NAV], [2004KOZ] there is mention of a larger value, 105 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, for S°_{m} ($FeCO_3$, cr, 298.15 K). That value can be traced to an estimate [1965ROB] based on the early measurements of Anderson [1934AND] for temperatures ≥ 54 K. The estimate included what, on the basis of later measurements [1963KAL], [1964KOS/KAL], [1984ROB/HAS], was undoubtedly an overestimate of the magnetic contribution to the entropy from 0 to 54 K.

X.1.2.1.2 The solubility of $FeCO_3$(cr)[1]

The results of available solubility measurements are summarized in Table X-2.

$$\mathrm{FeCO_3(cr)} \rightleftharpoons \mathrm{Fe^{2+}} + \mathrm{CO_3^{2-}} \qquad (X.7)$$

$$\mathrm{FeCO_3(cr)} + 2\ \mathrm{H^+} \rightleftharpoons \mathrm{Fe^{2+}} + \mathrm{H_2O(l)} + \mathrm{CO_2(g)}. \qquad (X.8)$$

The early result of Ehlert and Hempel [1912EHL/HEM] does not appear to be credible. The values of Braun [1991BRA] are inconsistent with all the others, especially for temperatures above 320 K (see Appendix A). There are insufficient experimental data available in the papers of Langmuir [1969LAN], and Singer and Strum [1970SIN/STU] to allow recalculation of the solubility constants. The values obtained by Silva *et al.* [2002SIL/LIU] at different ionic strengths are not consistent. Jensen *et al.* [2002JEN/BOD] showed that solutions supersaturated in $FeCO_3$(cr) approach equilibrium only very slowly. Ptacek and Reardon [1992PTA], [1992PTA/REA], and Jensen *et al.* [2002JEN/BOD] confirmed that solubilities measured from undersaturated solutions depend strongly on the method used to prepare the $FeCO_3$(cr) solid. There is a marked difference of approximately half an order of magnitude in the solubilities of unheated solids prepared by precipitation at room temperature [1970SIN/STU],

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[1] After this Section of the review was completed, Bénézeth *et al.*, published a paper [2009BEN/DAN] describing measurements of the solubility of siderite (in 0.1 $\mathrm{mol\cdot kg^{-1}}$ NaCl aqueous solutions) as a function of temperature between 298 and 525 K. At the lower temperatures, the reported values are consistent with those selected in the current review. At higher temperatures the measurements are in better agreement with those of Greenberg and Tomson [1992GRE/TOM], than with those of Braun [1991BRA].

[1976BAR/PER] and solids prepared at higher temperatures or by heat treatment of a precipitated solid [1981REI/JOH], [1992BRU/WER], [1992PTA]. As other thermodynamic measurements [1984ROB/HAS], [1994CHA/NAV] were carried out on the more crystalline heat-treated samples, only the results for the heat-treated samples of siderite are evaluated in the present review.

Table X-2: Solubility studies of $FeCO_3$(cr) in aqueous solutions (the units of all ionic strength values (I) are $mol\cdot kg^{-1}$)

T /K	reported		recalculated	Reference
	$\log_{10} K_{s,0}$ (X.7)	$\log_{10} {}^{*}K^{o}_{p,s,0}$ (X.8)	$\log_{10} {}^{*}K^{o}_{p,s,0}$ (X.8)	
287 (?)	~ − 7 (recalculated)			[1912EHL/HEM]
303.15	− 10.46 (I ~ 0.007)		7.492 ± 0.014	[1918SMI]
298.15	− 10.55 ($I \rightarrow 0$)			[1969LAN]
290.15	− 10.12 (I = 0.1)			[1970SIN/STU]
295.15	− 10.21 (I = 0.05)			
295.65	− 10.28 (I = 0.1)			
303.15	− 10.25 (I = 0.1)			
293.15	−10.40 ($I \rightarrow 0$)		7.778 ± 0.013	[1976BAR/PER]
323.15		7.61 (I = 1.0, $NaClO_4$)	7.280 ± 0.032	[1981REI/JOH]
303.15	− 11.11 (I = 0.1)			[1991BRA]
313.15	− 11.27 (I = 0.1)			
323.15	− 11.88 (I = 0.1)			
333.15	− 12.43 (I = 0.1)			
343.15	− 12.31 (I = 0.1)			
353.15	− 12.57 (I = 0.1)			
298.15	−10.8 (I = 1.05, $NaClO_4$)		7.19 ± 0.05	[1992BRU/WER]
298.15	− 10.76 (I ~ 0.006)		7.59 ± 0.05	[1992GRE/TOM]
316.15	− 10.94 (I ~ 0.005)		7.37 ± 0.05	
335.15	− 11.03 (I ~ 0.003)		7.33 ± 0.05	
356.15	− 11.25 (I ~ 0.002)		7.24 ± 0.05	
367.15	− 11.41 (I ~ 0.002)		7.16 ± 0.05	
298.15	−11.06 ($I \rightarrow 0$, NaCl)			[1992PTA/REA]
	−11.08 ($I \rightarrow 0$, Na_2SO_4)			
	−11.03 ($I \rightarrow 0$, $FeSO_4$)			
298.15‡	−11.03 ($I \rightarrow 0$; dried crystals)			[2002JEN/BOD]
	−11.43 ($I \rightarrow 0$; wet crystals)			

(Continued on next page)

Table X-2: (continued)

T /K	reported		recalculated	Reference
	$\log_{10} K_{s,0}$ (X.7)	$\log_{10} {}^{*}K^{\circ}_{p,s,0}$ (X.8)	$\log_{10} {}^{*}K^{\circ}_{p,s,0}$ (X.8)	
298.15	− 10.22 (I = 0.1, NaCl)	7.26 (I = 0.1, NaCl)	7.03 ± 0.14	[2002SIL/LIU]
	− 9.53 (I = 0.7, NaCl)	7.52	7.09 ± 0.04	
	− 8.58 (I = 1.4, NaCl)	8.39	7.83 ± 0.12	
	− 8.61 (I = 2.0, NaCl)	8.41	7.78 ± 0.06	
	− 8.55 (I = 2.5, NaCl)	8.52	7.83 ± 0.14	
	− 8.56 (I = 4.0, NaCl)	8.81		
	− 8.61 (I = 5.5, NaCl)	9.25		

‡ The measurements were done at 288.15 K, but the reported solubility products were those corrected by the authors [2002JEN/BOD] to 298.15 K.

An unweighted linear extrapolation of the logarithm of the equilibrium solubility product values ($\log_{10} {}^{*}K_{p,s,0}$ (X.8)), based on the data of Smith [1918SMI], Reiterer *et al.* [1981REI/JOH], Bruno *et al.* [1992BRU/WER], and Greenberg and Tomson [1992GRE/TOM], leads to (8.469 − 0.00350 (T/K)) within 0.25 (thus, (7.42 ± 0.25), $\Delta_r G^{\circ}_m$ (X.8) = − (42.4 ± 1.4) kJ·mol^{-1}, $\Delta_r H^{\circ}_m$ (X.8) = − (5.96 ± 3.08) kJ·mol^{-1} at 298.15 K). The value $\Delta_r G^{\circ}_m$ (X.8) = − (42.4 ± 1.4) kJ·mol^{-1} appears to be reasonable and was used in the consistency assessment in the present review (Chapter XI). However, we note that Preis and Gamsjäger [2002PRE/GAM] carried out a similar analysis using a somewhat different ionic strength correction and obtained $\Delta_r G^{\circ}_m$ (X.8) = − (43.2 ± 0.6) kJ·mol^{-1} and $\Delta_r H^{\circ}_m$ (X.8) = − (17.3 ± 1.2) kJ·mol^{-1} at 298.15 K). In their analysis they included an average value based on the measurements of Silva *et al.* [2002SIL/LIU] at ionic strengths (NaCl(sln)) from 1.4 to 2.5 mol·kg^{-1}. Both calculations were carried out assuming the value of $\Delta_r C^{\circ}_{p,m}$ (X.8) to be zero (a good approximation as at 298.15 K, based on CODATA [1989COX/WAG] and values from the present review, it is ~ (6 ± 10) J·K^{-1}·mol^{-1}). These relatively minor differences in data selection and treatment, without additional constraints, lead to ranges of − 763 to − 752 kJ·mol^{-1} in $\Delta_f H^{\circ}_m$ ($FeCO_3$, cr, 298.15 K) and 62 to 95 J·K^{-1}·mol^{-1} in S°_m ($FeCO_3$, cr, 298.15 K).

If the same set of values for $\Delta_r G^{\circ}_m$ is combined with the entropy and heat-capacity values for $FeCO_3$(cr) from Robie *et al.* [1984ROB/HAS], with values for Fe^{2+} from Parker and Khodakovskii [1995PAR/KHO] and Hovey [1988HOV] (his Eq. 9.24), and with CODATA consistent values for other species, all of the calculated values of $\Delta_f H^{\circ}_m$ ($FeCO_3$, cr, 298.15 K) are between − 750.9 and − 753.5 kJ·mol^{-1}. The low ionic-strength measurements of Silva *et al.* [2002SIL/LIU] (I = 0.1 and 0.7 mol·kg^{-1}) lead to values of $\Delta_f H^{\circ}_m$ ($FeCO_3$, cr, 298.15 K) ~ − 755 kJ·mol^{-1}, whereas their measurements at higher ionic strengths (I = 1.4, 2.0 and 2.5 mol·kg^{-1}) lead to values of ~ − 751 kJ·mol^{-1}.

X.1.2.1.3 Other measurements

Chai and Navrotsky [1994CHA/NAV] reported a calorimetrically determined value of $-(750.6 \pm 1.1)$ kJ·mol^{-1} for $\Delta_f H_m^\circ$ (FeCO$_3$, cr, 298.15 K), in reasonable agreement with the solubility work. As discussed in Appendix A, the value as recalculated in the present review is $-(750.5 \pm 2.7)$ kJ·mol^{-1} based on a value for the enthalpy of decomposition of $-(56.14 \pm 2.30)$ kJ·mol^{-1}.

$$\mathrm{FeCO_3(cr)} + \tfrac{1}{4}\,\mathrm{O_2(g)} \rightleftharpoons \tfrac{1}{2}\,\alpha\text{-}\mathrm{Fe_2O_3} + \mathrm{CO_2(g)} \qquad (X.9)$$

However, high-temperature high-pressure equilibrium studies [1971FRE], [1993KOZ/NEW], [2004KOZ], have suggested substantially more negative values between -760 and -776 kJ·mol^{-1}. The early heat of precipitation results of Berthelot [1875BER2] suggest a value of approximately -760 kJ·mol^{-1}, while the combustion work of Le Chatelier [1895CHA] leads to a similar value of ~ -765 kJ·mol^{-1}.

Stubina and Toguri [1989STU/TOG] monitored the equilibrium decomposition pressure of FeCO$_3$(cr) as a function of temperature, and reported values for $\Delta_r S_m^\circ$ (X.10) and $\Delta_r H_m^\circ$ (X.10)

$$3\,\mathrm{FeCO_3(cr)} \rightleftharpoons \mathrm{Fe_3O_4(cr)} + \mathrm{CO(g)} + 2\,\mathrm{CO_2(g)}. \qquad (X.10)$$

They then derived a value of $-(750.6 \pm 1.1)$ kJ·mol^{-1} for $\Delta_f H_m^\circ$ (FeCO$_3$, cr, 298.15 K). However, their results for $\Delta_r S_m^\circ$ (X.10) lead to an unreasonably high value for S_m° (FeCO$_3$, cr, 298.15 K), ~ 127 J·K^{-1}·mol^{-1}, more than 25% greater than the values determined from calorimetry results. Their experimental work appears to be more reliable than earlier siderite thermal decomposition studies [1929ROT], [1935KRU]. However, it is not clear that equilibrium was established in any of these studies, nor was there a proper analysis of the composition of the species in the gas phase.

Even considering the impurities in the experimental samples, it appears highly unlikely that the entropy of FeCO$_3$(cr) can be less than 90 J·K^{-1}·mol^{-1} or greater than 100 J·K^{-1}·mol^{-1}. Also, considering the large number of solubility experiments approaching equilibrium from both above and below saturation, it is unlikely that $\log_{10}{}^*K_{p,s,0}$ (X.8) is greater than 7.8, and hence the value of $\Delta_f H_m^\circ$ (FeCO$_3$, cr, 298.15 K) is almost surely less than -749.6 kJ·mol^{-1}. Conversely, assuming a value of -760 kJ·mol^{-1} for $\Delta_f H_m^\circ$ (FeCO$_3$, cr, 298.15 K) leads to values of $\log_{10}{}^*K_{p,s,0}$ (X.8) between 6.45 and 5.93 (for values of 90 and 100 J·K^{-1}·mol^{-1} for S_m° (FeCO$_3$, cr, 298.15 K)). These would reflect solubilities approximately a factor of two lower than the lowest values derived from the experimental studies.

Based on this discussion, in the optimization calculations done to ensure consistency with other thermodynamic quantities for iron species (Chapter XI) the enthalpy of decomposition value, $\Delta_r H$ (X.9), (*i.e.*, $\Delta_{\mathrm{decomp}} H$ (FeCO$_3$, cr) in tables in Chapter XI) from the work of Chai and Navrotsky [1994CHA/NAV] ($-(56.14 \pm 2.30)$ kJ·mol^{-1}) is used. A less negative value, $-(54.00 \pm 1.60)$ kJ·mol^{-1}, is found from the optimization[1], though the uncertainty limits overlap. This optmization calculation also leads to $-(42.68 \pm 1.12)$ kJ·mol^{-1} and (7.49 ± 0.19) for $\Delta_{\mathrm{sln}}G^{\circ}_{\mathrm{m}}$ (FeCO$_3$, cr, 298.15 K) and $\log_{10}{}^{*}K^{\circ}_{\mathrm{p,s,0}}$ (X.8) respectively, as well as the selected value

$$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{FeCO_3, cr, 298.15\ K}) = -(752.61 \pm 0.90)\ \mathrm{kJ\cdot mol^{-1}}.$$

These values suggest a slightly lower stability for FeCO$_3$(cr) than results from the values selected previously by Robie and Hemingway [1995ROB/HEM].

X.1.2.2 Iron hydroxidocarbonates

X.1.2.2.1 Iron(II) hydroxidocarbonate

Erdös and Altorfer [1976ERD/ALT] reported a solid corrosion product of steel with a stoichiometry corresponding approximately to Fe$_2$(OH)$_2$CO$_3$. The same iron(II) hydroxidocarbonate has been reported to be formed as a transformation product of biogenic magnetite (itself formed from ferrihydrite and nanocrystalline akaganeite) [2005KUK/ZAC], and as the mineral chukanovite [2007PEK/PER] (in association with a weathered iron meteorite). On heating in oxygen above 470 K [1976ERD/ALT] an oxidocarbonate "Fe$_2$O$_2$CO$_3$(s)" was formed. The solids were characterised using chemical analysis, X-ray diffraction, differential thermal analysis and thermogravimetric analysis, but no thermodynamic quantities were reported.

X.1.2.2.2 Mixed Fe(II)/Fe(III) hydroxidocarbonates ("green rust one") and derivative compounds

There have been many papers (*e.g.*, [1969STA], [1995DRI/REF], [2002ONA/ABD], [2006GEN/ABD], [2006TRO/BOU]) on the synthesis and characterization of an Fe(II)-Fe(III) hydroxide carbonate ("green rust one"). The material has been identified with the mineral fougerite [2005GEN/AIS], and can be produced by bioreduction of the iron(III) oxyhydroxide, lepidocrocite [2002ONA/ABD], as well as by electrochemical oxidation of iron in aqueous $\mathrm{CO_3^{2-}/HCO_3^-}$ solutions [2001LEG/SAG] or by coprecipitation from solutions also containing sulfate or chloride [1995DRI/REF], [2005GEN/AIS]. Most natural samples, and material synthesized by precipitation, have a limiting stoichiometry of $(\mathrm{Fe^{III}})_2(\mathrm{Fe^{II}})_4(\mathrm{OH})_{12}\mathrm{CO_3}\cdot\sim 3\mathrm{H_2O(s)}$ (though the ratio of $\mathrm{Fe^{III}}$:$\mathrm{Fe_{TOTAL}}$ can be as low as ¼, with the minimum value defined by the solubility of Fe(OH)$_2$(s)). It is likely part of "the family of layered double hydroxides with trivalent cations all surrounded by six divalent cations in their hexagonal layer" [2005GEN/AIS], [2006TRO/BOU]. However, Trolard and Bourrié [2006TRO/BOU] suggested that the interlayer contains both $\mathrm{CO_3^{2-}}$ and $\mathrm{HCO_3^-}$, and formulated the "green rust" as $[(\mathrm{Fe^{III}})_2(\mathrm{Fe^{II}})_4(\mathrm{OH})_{12}]_3(\mathrm{CO_3})(\mathrm{HCO_3})_4\cdot x\mathrm{H_2O(s)}$ (*i.e.*, a solid with a much greater ratio of

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[1] After the first cycle of the optimization process, the value calculated for $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ (FeCO$_3$, cr, 298.15 K) was outside the originally estimated uncertainty bounds; and the uncertainty of the input value was increased by 20% to ± 2.76 kJ·mol^{-1} in the second cycle (Chapter XI).

C:Fe). Benali *et al.* [2001BEN/ABD] earlier presented arguments as to why a compound with HCO_3^- is unlikely to be formed.

Génin *et al.* [2005GEN/AIS] described oxidation of a suspension of $(Fe^{III})_2(Fe^{II})_4(OH)_{12}CO_3\cdot{\sim}3H_2O(s)$ with peroxide solution, and of dried samples of $(Fe^{III})_2(Fe^{II})_4(OH)_{12}CO_3\cdot{\sim}3H_2O(s)$ with air, to form (in the limit) a partially deprotonated iron(III) compound with stoichiometry $(Fe^{III})_6O_8(H_2O)_4CO_3\cdot xH_2O(s)$ (also formulated as $(Fe^{III})_6O_{12}H_8CO_3\cdot xH_2O$). Legrand *et al.* [2001LEG/SAG], [2004LEG/MAZ], reported a related solid [2005GEN/AIS] with a Fe^{III}:Fe_{TOTAL} ratio of ~1.

Gradual oxidation of $(Fe^{III})_2(Fe^{II})_4(OH)_{12}CO_3\cdot{\sim}3H_2O(s)$ in contact with an aqueous solution containing excess Fe(II) and carbonate leads to formation of ferrihydrite (see Section VII.2.15) and then goethite. In contrast, $Fe(OH)_2(s)$ is gradually oxidized to magnetite, and then to maghemite, whereas rapid (peroxide) oxidation can lead to feroxyhite (Section VII.2.12) [2005GEN/AIS].

There have been several papers [1995DRI/REF], [2002ONA/ABD], [2006TRO/BOU] on the thermodynamic quantities for a Fe(II)-Fe(III) hydroxide carbonate ("green rust one") based on the apparent region of stability of the solid. Descriptions of the syntheses indicate that for equal anion concentrations the green rust formulated as $(Fe^{III})_2(Fe^{II})_4(OH)_{12}CO_3\cdot{\sim}3H_2O(s)$ is definitely more stable than the sulfate-containing "green rust two"; the chloride-containing "green rust one" also is less stable, and is easily oxidized to form the carbonate-containing species [1997REF/DRI]. There seems to be little evidence for the formation of mixed green rusts. Mixtures of magnetite with siderite, $FeCO_3(cr)$, should be stable with respect to the carbonate-containing "green rust one" [2001BEN/ABD]. Also, the work of Ona-Nguema *et al.* [2002ONA/ABD] indicates that the partially deprotonated carbonate-containing "green rust" solid with a Fe^{III}:Fe_{TOTAL} greater than ⅓, when mixed with lepidocrocite in aqueous suspension, is metastable with respect to magnetite.

The electrochemical studies [1995DRI/REF] indicate that for

$$6\ Fe(OH)_2(s) + CO_3^{2-} + 2\ H^+ + n\ H_2O(l) \rightleftharpoons (Fe^{III})_2(Fe^{II})_4(OH)_{12}CO_3\cdot nH_2O(s) + H_2(g) \tag{X.11}$$

$\Delta_r G_m^\circ$ ((X.11), 298.15 K) ~ −(121 ± 2) $kJ\cdot mol^{-1}$. However, no values are selected here for the thermodynamic quantities of the mixed iron(II)/iron(III) hydroxidocarbonates.

X.2 Silicon compounds and complexes[1]

X.2.1 Iron silicate compounds

Numerous solids are known in the Fe-Si-O-H system [1997BLA/DEN]. These include: (a) the simple ternary iron(II) solids, α-Fe_2SiO_4, (fayalite), γ-Fe_2SiO_4 (the high-pressure form with a spinel structure, ringwoodite), and $FeSiO_3$ (at least four forms); (b) the iron(II) solids that also contain hydrogen (as hydroxide ligands or water of hydration), $Fe_7Si_8O_{22}(OH)_2$ (grunerite and ferro-anthophyllite), $Fe_3Si_4O_{10}(OH)_2$ (minnesotaite), iron(III) solids $Fe_2Si_4O_{10}(OH)_2$ (ferripyrophyllite) and $Fe_2Si_2O_5(OH)_4{\cdot}2H_2O$ (hisingerite); and (c) minerals containing both iron(II) and iron(III), $Fe^{II}Fe_2^{III}(SiO_4)_2$ (laihunite), $(Fe^{II}/Fe^{III})_{2\text{ to }3}Si_2O_5(OH)_4$ (greenalite), $Fe_2^{II}Fe_2^{III}OSiO_4(OH)_4$ (cronstedtite), $Fe_6^{II}Fe_3^{III}O_3(Si_6O_{17})(OH)_5$ (deerite). In many natural samples Mg^{II} or Mn^{II} cations substitute for Fe^{II}, and Al^{III} cations for Fe^{III}, and the ideal end-member compositions (containing only iron cations) may not exist. Many of the forms exist only at high temperatures (> 1000 K) and/or high pressures (> 1 GPa). Because of the substantial geochemical interest in materials in the Fe-Si-O system, especially with respect to the nature of the earth's mantle, there have been many publications and reviews of chemical thermodynamic data directed towards conditions that fall far outside the scope of the present review (*e.g.*, [1992HAA/HEM], [1996SAX], [1997FAB/SUN], [1997SEL], [2001JAC/JON]).

X.2.1.1 α-Fe_2SiO_4 (fayalite)

X.2.1.1.1 Heat capacity and entropy of α-Fe_2SiO_4

There have been several measurements of the heat capacity [1941KEL], [1980OSA], [1982ROB/FIN], [1982WAT] and heat content ($H^{\circ}_T - H^{\circ}_{T_{\mathrm{ref}}}$) [1929ROT/BER], [1933ESS/AVE], [1953ORR], [1984STE/CAR] of fayalite. As discussed by Aggarwal *et al.* [1997AGG/TOP] fayalite is not strictly a stoichiometric compound, though it is possible to synthesize material with a Si : (Si+Fe) atomic ratio very near ⅓ (*i.e.*, α-Fe_2SiO_4). Fayalite melts[2, 3] at 1490 K [1984STE/CAR]. Thus, in the present review, the properties of Fe_2SiO_4 are not assessed for temperatures above 1450 K. The earliest studies [1929ROT/BER], [1933ESS/AVE] used natural or impure samples, and the differential scanning calorimetry results of Osako [1980OSA] over a limited

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[1] In this Section, as it appears here, we are dealing with solids (only). Any discussion of aqueous complexes will be deferred to the TDB-Iron Part 2.

[2] Jacobs *et al.* [2001JAC/JON] concluded that within the constraints imposed by the available data for the liquid it is possible to assume that melting of α-Fe_2SiO_4 is congruent (despite earlier indications to the contrary [1967HSU], [1984STE/CAR]).

[3] Several authors indicate a lower melting temperature, 1478 K [1967AKI/KOM], [1967HSU], [1997FAB/SUN].

temperature range are badly scattered. Low-temperature calorimetry measurements indicate that there is a λ-transition near 65 K. Molar heat-capacity values based on the study of Kelley [1941KEL] above the transition are systematically greater (by ~ 0.5%) than those reported by Robie *et al.* [1982ROB/FIN]. The differential scanning calorimetry results of Watanabe [1982WAT] (350 to 700 K) are reasonably consistent with the drop-calorimetry results of Orr [1953ORR], but the heat-capacity values between 350 and 380 K are again greater than those of Robie *et al.* [1982ROB/FIN] (by ~ 1%). Stebbins and Carmichael [1984STE/CAR] carried out drop-calorimetry experiments at temperatures from 985 to 1705 K on carefully characterized material in an attempt to improve on the value of the heat of fusion of fayalite as reported earlier by Orr [1953ORR]. Their values near 1350 K agree well with those of Orr, but Stebbins and Carmichael's results at 985 K (measurements done in triplicate, but badly scattered) are greater by 1.6 to 4.6 $kJ\cdot mol^{-1}$, and seem inconsistent with a smooth extrapolation from lower temperatures. The reported heat-capacity values from the different studies (230 to 700 K) and reported enthalpy-difference values (adjusted to a reference temperature of 298.15 K) are shown in Figure X-1 and Figure X-2, respectively.

Figure X-1: Values of $C^{\circ}_{p,\mathrm{m}}(Fe_2SiO_4, \alpha)$: ■ [1941KEL], ○ [1982ROB/FIN], ▲ [1982WAT] and values of $C^{\circ}_{p,\mathrm{m}}(Fe_2SiO_4, \gamma)$: × [1982WAT]. The line illustrates values from the equation for $C^{\circ}_{p,\mathrm{m}}(Fe_2SiO_4, \alpha)$ from the present review.

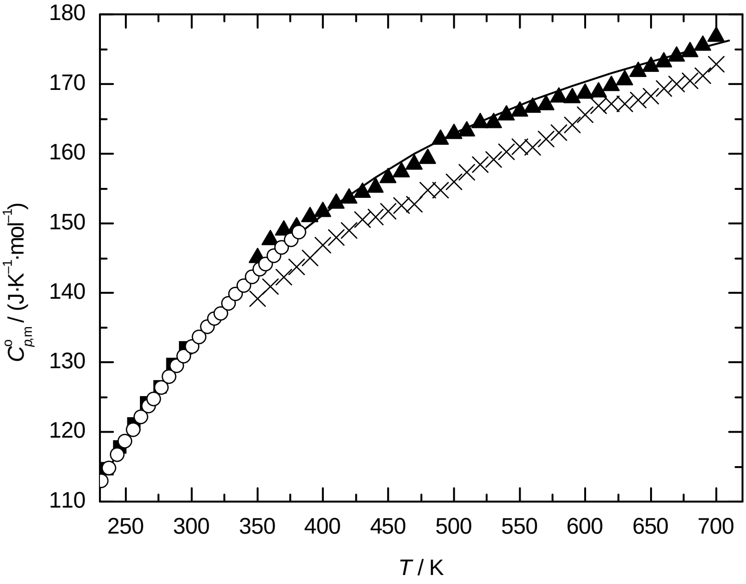
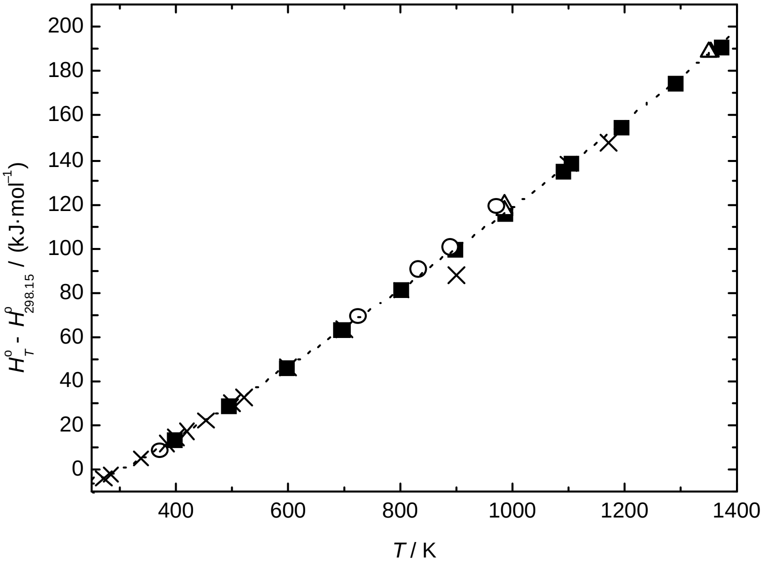


Figure X-2: Values of $(H^{\circ}_{T} - H^{\circ}_{298.15\,\mathrm{K}})$ for α-Fe_2SiO_4: ■ [1953ORR], ○ [1929ROT/BER], Δ [1984STE/CAR] and values of $(H^{\circ}_{T} - H^{\circ}_{298.15\,\mathrm{K}})$ for γ-Fe_2SiO_4: × [1985AGO]. The line illustrates values from the equation for $(H^{\circ}_{T} - H^{\circ}_{298.15\,\mathrm{K}})$ (Fe_2SiO_4, α) from the present review.



Polynomial functions were fitted to the combined results of Kelley [1941KEL], Orr [1953ORR], Robie *et al.* [1982ROB/FIN], Watanabe [1982WAT], and Stebbins and Carmichael [1984STE/CAR], weighted as discussed in Appendix A for temperatures between 231 and 1371 K.

$$[C^{\circ}_{p,\mathrm{m}}]^{1450\,\mathrm{K}}_{230\,\mathrm{K}}\,(\mathrm{Fe_2SiO_4},\ \alpha,\ T)/\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}} = 315.41 - 0.14343\,(T/\mathrm{K}) + 6.9541\times10^{-5}\,(T/\mathrm{K})^2$$
$$-\,5.6959\times10^{4}\,(T/\mathrm{K})^{-1} + 3.9323\times10^{6}\,(T/\mathrm{K})^{-2}$$

$$\begin{aligned}[H^{\circ}_{\mathrm{m}}(T) - H^{\circ}_{\mathrm{m}}(298.15\,\mathrm{K})]^{1450\,\mathrm{K}}_{230\,\mathrm{K}}\,(\mathrm{Fe_2SiO_4},\ \alpha,\ T)/\mathrm{kJ{\cdot}mol^{-1}} = {} & 0.31541\,(T/\mathrm{K}) \\ & - 7.1716\times10^{-5}\,(T/\mathrm{K})^2 \\ & + 2.3180\times10^{-8}\,(T/\mathrm{K})^3 \\ & - 56.959\,\ln\,(T/\mathrm{K}) \\ & - 3.9323\times10^{3}\,(T/\mathrm{K})^{-1} \\ & + 2.4944\times10^{2}\end{aligned}$$

and hence,

$$C^{\circ}_{p,\mathrm{m}}\,(\mathrm{Fe_2SiO_4},\ \alpha,\ 298.15\ \mathrm{K}) = (132.03 \pm 0.30)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}.$$

The uncertainty is an estimate chosen to reflect, in part, the minor inconsistencies near 300 K between the measurements of Robie *et al.* [1982ROB/FIN] and those from other studies [1941KEL], [1982WAT]. It is worth noting that Fei and Saxena [1986FEI/SAX] provided equations, based primarily on the work of Watanabe [1982WAT], that extrapolate to an unreasonably high molar heat-capacity value, 138.9 $J\cdot K^{-1}\cdot mol^{-1}$ for α-Fe_2SiO_4 at 298.15 K (primarily to maintain the difference between the heat capacities of the α- and γ-forms (see below)).

The following entropy value, derived by Robie *et al.* [1982ROB/FIN] from their heat-capacity measurements, is accepted in the present review (see Appendix A)[1].

$$S^{\circ}_{m}(Fe_2SiO_4, \alpha, 298.15\ K) = (151.0 \pm 0.2)\ J\cdot K^{-1}\cdot mol^{-1}$$

X.2.1.1.2 Enthalpy of formation of α-Fe_2SiO_4

The early calorimetric measurements by Roth and Troitzsch [1932ROT/TRO] were done with impure samples. King [1952KIN] reported careful measurements of the heat of solution of α-Fe_2SiO_4 into HF(sln) and, as discussed in Appendix A, these measurements can be used to calculate $-(1477.65 \pm 2.06)\ kJ\cdot mol^{-1}$ for $\Delta_f H^{\circ}_{m}(Fe_2SiO_4, \alpha, 298.15\ K)$.

Most subsequent values have been obtained using high-temperature equilibrium measurements (900 to 1450 K) with third-law extrapolations. The work at low pressures (through the mid-1980s) was well summarized by O'Neill [1987NEI2], and there have been more recent reviews [1989JAC/KAL], [1997SEL], [1997FAB/SUN]. The equilibrium measurements fall into two groups. First, there are the experiments in which the oxygen fugacity was controlled by gas-phase couples, *e.g.*, $CO(g)/CO_2(g)$ [1962LEB/LEV], [1966SCH/MUA], $H_2(g)/H_2O(g)$ [1966BER/SHA], $H_2(g)/CO_2(g)$ [1967NAF/MUA], [1968KIT/KAT], [1971WIL] (Figure X-3). Second, there are potential-difference measurements of cells using a number of different metal-metal oxide reference electrodes, *e.g.*, Fe/"FeO" [1964TAY/SCH], [1967ERE/FIL], [1970LEV/RAT], [1975SHI/SAN], [1977SCH/SOH], [1981SCH/KUS], [1983MYE/EUG], [1983ROG/KOZ], [1987NEI2], [1989JAC/KAL], Cu/Cu_2O or Mo/MoO_2 [1987NEI2]. The experiments have investigated two of the key equilibria which establish the stability field of α-Fe_2SiO_4

$$2\ Fe(cr) + SiO_2(cr) + O_2(g) \rightleftharpoons \alpha\text{-}Fe_2SiO_4(cr) \qquad (X.12)$$

and

$$2\ Fe_3O_4(cr) + 3\ SiO_2(cr) \rightleftharpoons 3\,\alpha\text{-}Fe_2SiO_4(cr) + O_2(g). \qquad (X.13)$$

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[1] After this review was essentially completed, Dachs *et al.* [2007DAC/GEI] reported extensive heat-capacity measurements using 20 to 48 mg samples between 5 and 302 K. Their values are in reasonable agreement with those of Robie *et al.* [1982ROB/FIN] (see the Appendix A entry for [2007DAC/GEI]).

O’Neill [1987NEI2] and Jacob *et al.* [1989JAC/KAL] showed that most experimental results for the fayalite-SiO_2-iron equilibrium (Reaction (X.12)) [1962LEB/LEV], [1964TAY/SCH], [1966SCH/MUA], [1968KIT/KAT], [1970LEV/RAT], [1977SCH/SOH], [1981SCH/KUS], [1987NEI2], [1989JAC/KAL] are in good agreement with the exception of those of Berliner and Shapovalova [1966BER/SHA], Myers and Eugster [1983MYE/EUG], and Róg and Kozinski [1983ROG/KOZ] for which $\Delta_r G$(X.12) is systematically more negative. The agreement is even better [1981SCH/KUS], [1987NEI2] if a common set of values is used for the Fe/“FeO”/O_2 reference electrode. As discussed in Appendix A, values of $\Delta_f H_m^o$ (Fe_2SiO_4, α, 298.15 K) from both the gas-equilibrium and electrochemical potential-difference studies have been recalculated using auxiliary data consistent with the present review. Figures X-3 to X-5 illustrate that the measurements done over a range of more than 400 K lead to essentially the same enthalpy value for 298.15 K, indicating that the third-law analysis is satisfactory. The results of the reanalyses are also summarized in Table X-3.

Figure X-3: Recalculated values of $\Delta_f H_m^o$ (Fe_2SiO_4, α, 298.15 K) based on high-temperature equilibrium measurements using gas mixtures to set the oxygen fugacity for the iron-SiO_2(cr)-α-Fe_2SiO_4 system: ■ [1932SCH/FRA], ✳ [1946CIR], ✯ [1962LEB/LEV], × [1966BER/SHA], ● [1966SCH/MUA], ⊠ [1967NAF/MUA], ◊ [1968KIT/KAT], ∇ [1971WIL].

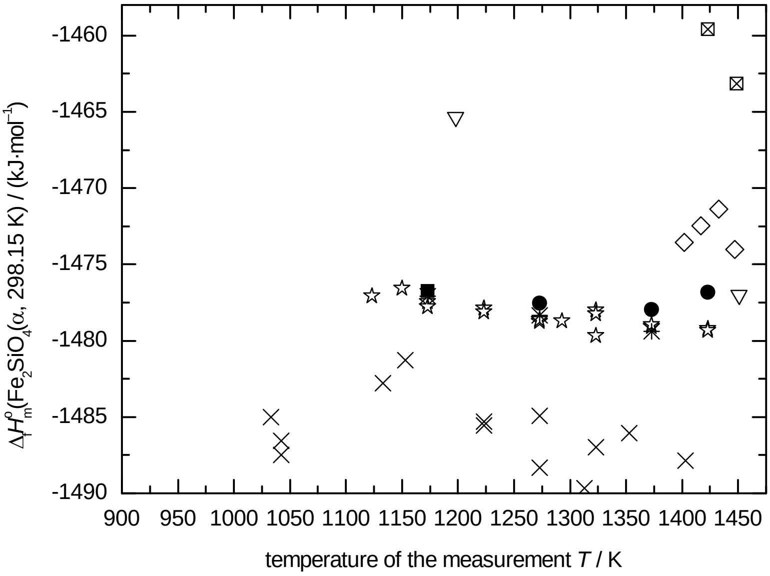


Figure X-4: A selection of values of $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{Fe_2SiO_4}, \alpha, 298.15\ \mathrm{K})$ based on high-temperature electrochemical cell-potential-difference measurements for the iron-$\mathrm{SiO_2}$(cr)-α-$\mathrm{Fe_2SiO_4}$ system. Except for values for the reference electrode potentials, the values have been recalculated using auxiliary data for the present review: ✳ [1964TAY/SCH], ■ [1977SCH/SOH], × [1981SCH/KUS], ◊ [1983MYE/EUG], □ [1989JAC/KAL]. The line illustrates the average values of O'Neill [1987NEI2].

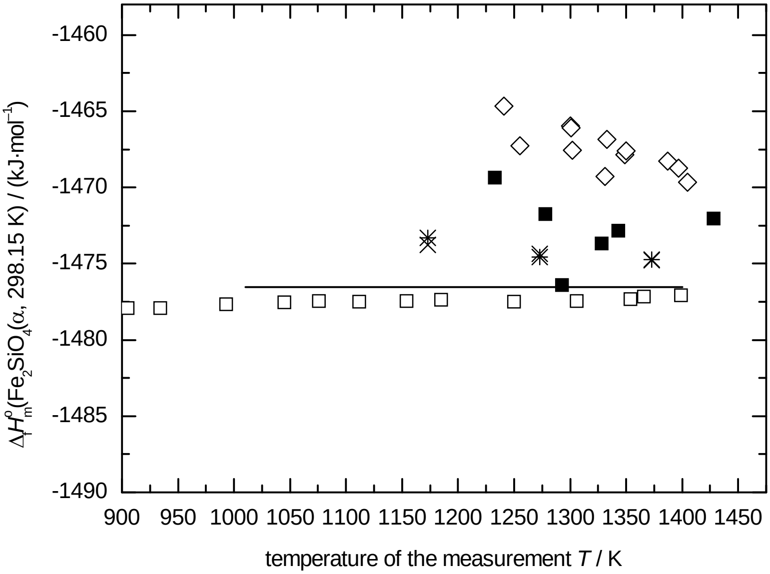
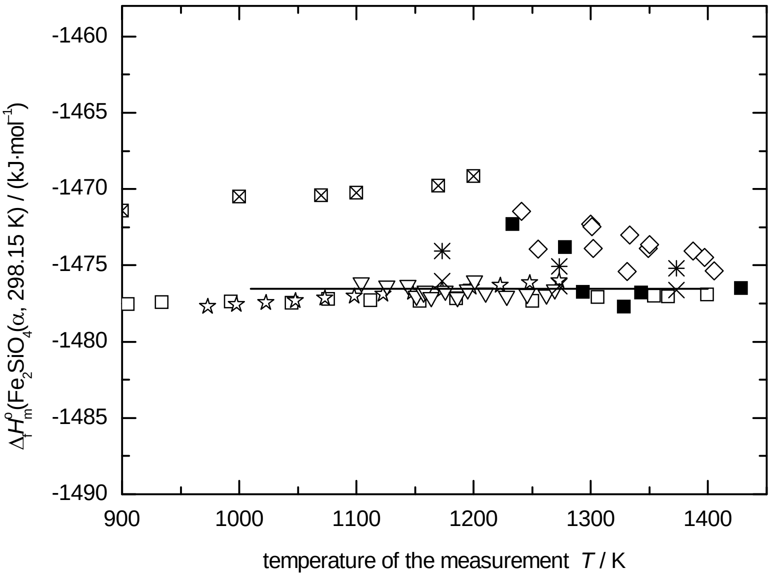


Figure X-5: Values of $\Delta_f H_m^o$ (Fe_2SiO_4, α, 298.15 K) based on high-temperature electrochemical cell-potential-difference measurements for the iron-SiO_2(cr)-α-Fe_2SiO_4 system. The values have been recalculated relative to the reference electrode values used by O'Neill [1987NEI2]: ✳ [1964TAY/SCH], ∇ [1970LEV/RAT], ✯ [1975SHI/SAN], ■ [1977SCH/SOH], × [1981SCH/KUS], ◊ [1983MYE/EUG], ☒ [1983ROG/KOZ], ☐ [1989JAC/KAL]. The line illustrates the average values of O'Neill [1987NEI2].



Results for the fayalite-SiO_2-magnetite Reaction (X.13) [1966SCH/MUA], [1969WON/GIL], [1978CHO], [1978HEW], [1981SCH/KUS], [1983MYE/EUG], [1987NEI2], [1989JAC/KAL], are more scattered, and achieving stable results with the cell can be difficult [1987NEI2]. Also, values for the thermodynamic quantities for α-Fe_2SiO_4 should not be determined independently of those for magnetite [1987NEI2]. In general, the best measurements [1978HEW], [1987NEI2], [1989JAC/KAL] lead to calculated values of $\Delta_f H_m^o$ (Fe_2SiO_4, α, 298.15 K) that are in good agreement (within 2 $kJ\cdot mol^{-1}$) with values from the fayalite-SiO_2-iron equilibrium measurements (Reaction (X.12)). However, the fayalite-SiO_2-magnetite results are not used further in the present review.

Table X-3: Summary of values of $\Delta_f H_m^\circ$ (Fe$_2$SiO$_4$, α, 298.15 K) as recalculated using a third-law analysis

reference	temperature range/K	$\Delta_f H_m^\circ$ (Fe$_2$SiO$_4$, α)/kJ·mol^{-1}	2σ/kJ·mol^{-1}
$\Delta_f H_m^\circ$ (Fe$_2$SiO$_4$, α, 298.15 K) as recalculated from galvanic cell measurements shifted to correspond to the reference electrode potentials from [1987NEI2]			
[1964TAY/SCH]	1173 – 1373	− 1474.79	1.50
[1970LEV/RAT]	1104 – 1269	− 1476.67	0.68
[1975SHI/SAN]	973 – 1273	− 1476.89	1.09
[1977SCH/SOH]	1233 – 1428	− 1475.64	4.18
[1981SCH/KUS]	1173 – 1373	− 1476.34	0.57
[1983MYE/EUG]	1241 – 1405	− 1473.66	2.38
[1983ROG/KOZ] *	900 – 1200	− 1470.26	1.09
[1987NEI2]	971 – 1398	− 1476.55	0.39
[1989JAC/KAL]	905 – 1399	− 1477.25	0.46
weighted average − (1476.65 ± 0.67) kJ·mol^{-1}			
$\Delta_f H_m^\circ$ (Fe$_2$SiO$_4$, α, 298.15 K) as recalculated from gas-equilibrium measurements			
[1932SCH/FRA] *	1173 –	− 1476.74	
[1946CIR]	1173 – 1373	− 1478.28	2.31
[1962LEB/LEV]	1123 – 1423	− 1478.38	3.00
[1966BER/SHA] *	1033 – 1403	− 1485.98	4.51
[1966SCH/MUA]	1273 – 1423	− 1477.45	1.50
[1967NAF/MUA] *	1423 – 1449	− 1461.36	5.03
[1968KIT/KAT]	1402 – 1447	− 1472.86	3.39
[1971WIL] *	1198	− 1465.33	
[1971WIL] *	1451	− 1477.01	
weighted average − (1476.84 ± 2.08) kJ·mol^{-1}			

* not used in determining the average, see Appendix A

O’Neill [1987NEI2] showed that the galvanic potentials found using two different reference electrodes were essentially identical, and carried out cross comparisons of the electrodes. Use of the reference potential values of Jacob *et al.* [1989JAC/KAL] would result in slightly more negative values (by 0.2 to 0.3 kJ·mol^{-1}) for $\Delta_f H_m^\circ$ (Fe$_2$SiO$_4$, α, 298.15 K). Therefore, the uncertainty in the average value for $\Delta_f H_m^\circ$ (Fe$_2$SiO$_4$, α, 298.15 K) calculated from the galvanic cell results is larger, and is estimated here as ± 0.9 kJ·mol^{-1}. The results from the gas-equilibrium, calorimetry and electrochemical potential-difference measurements are in good agreement, and the weighted average is selected in the present review,

$$\Delta_f H_m^\circ (\mathrm{Fe_2SiO_4}, \alpha, 298.15\ \mathrm{K}) = -(1476.79 \pm 1.07)\ \mathrm{kJ \cdot mol^{-1}}.$$

X.2.1.2 γ-Fe_2SiO_4

X.2.1.2.1 Heat capacity and entropy of γ-Fe_2SiO_4

The γ-form of Fe_2SiO_4 is formed as a high-pressure phase (spinel structure) which is metastable at 100 kPa and temperatures to 1200 K [1985AGO]. Watanabe [1982WAT] reported a differential scanning calorimetric determination of the heat capacity from 350 to 700 K (Figure X-1), and Agoshkov [1985AGO] reported Calvet immersion calorimetry results ($H_T - H_{T_{\text{ref}}}$) for temperatures from 240 to 1170 K (Figure X-2). The results agree within ~ 3%. The work of Agoshkov leads to heat-capacity values above 350 K that are approximately mid-way between those of Watanabe for γ-Fe_2SiO_4 and the results of Orr [1953ORR] for α-Fe_2SiO_4 (except above 1000 K). However, at lower temperatures, the results of Agoshkov are close to all the literature results for α-Fe_2SiO_4 [1941KEL], [1953ORR], [1982ROB/FIN], [1982WAT]. Watanabe has shown that the heat capacities of the more dense spinel forms of several A_2SiO_4 solids (A = Mg, Co, Fe, Ni) are 2 to 6 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ less than the heat capacities of the corresponding olivine forms at all temperatures between 350 and 700 K, with the difference *increasing* marginally at lower temperatures. Agoshkov also reported, from measurements on α-Fe_2SiO_4 from 400 to 900 K, that the heat capacity of α-Fe_2SiO_4 is greater than the heat capacity of γ-Fe_2SiO_4 below 800 K. Thus, the possibilities seem to be that:

a) the results of Agoshkov [1985AGO] are too positive, especially at low temperatures (*i.e.*, there may have been a systematic error in the method used by Agoshkov to do enthalpy-difference measurements at temperatures below 337 K);

b) the assessed results for α-Fe_2SiO_4 are too low between 300 and 600 K;

c) the heat capacities of the α- and γ- forms are essentially identical below 350 K.

In the present review, it is assumed that the heat capacity of γ-Fe_2SiO_4 at 298.15 K is less than the heat capacity of α-Fe_2SiO_4 at 298.15 K by (4.0 ± 3.0) $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$,

$$C^{\circ}_{p,\text{m}}(\text{Fe}_2\text{SiO}_4, \gamma, 298.15\text{ K}) = (128.0 \pm 3.0)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

and the temperature dependence of γ-Fe_2SiO_4 is determined by a weighted least-squares fit to the results of Watanabe [1982WAT] and Agoshkov [1985AGO] (for 337 K and higher temperatures only).

$$[C^{\circ}_{p,\text{m}}]^{1000\text{K}}_{298.15\text{K}}(\text{Fe}_2\text{SiO}_4, \gamma, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 11.34 + 0.13821\,(T/\text{K}) + 6.1650 \times 10^{4}\,(T/\text{K})^{-1} - 1.1674 \times 10^{7}\,(T/\text{K})^{-2}$$

The temperature range is restricted because the fit is not particularly good, especially for temperatures above 800 K. In any case, the γ-form is metastable at 100 kPa pressure, and some conversion to the α- form begins near 1200 K [1985AGO].

X.2.1.2.2 Enthalpy of formation of γ-Fe_2SiO_4

The selection of a value of $\Delta_f H_m^o$ for the high-pressure phase γ-Fe_2SiO_4 at 298.15 K and 1 bar falls outside the scope of the present review; however, some experimental determinations have been reported. Navrotsky *et al.* [1979NAV/PIN] used solution calorimetry to determine the enthalpy of conversion of γ-Fe_2SiO_4 to α-Fe_2SiO_4 at 101 kPa (1 atm) and 986 K as $-(2.94 \pm 1.66)$ $kJ\cdot mol^{-1}$, and estimated the entropy of the conversion as 20.0 $J\cdot K^{-1}\cdot mol^{-1}$ based on calculations using thermal expansion and bulk-modulus data. Akaogi *et al.* [1989AKA/ITO] reported a value of $-(6.61 \pm 2.43)$ $kJ\cdot mol^{-1}$ for $\Delta_{tr}H$ at 298.15 K based on reverse drop-calorimetry measurements from 1052 K. Values of $\Delta_{tr}H$ (298.15 K, 100 kPa) from recent reviews of (primarily) high-pressure data vary considerably, from -5.4 to -12.3 $kJ\cdot mol^{-1}$ [2001JAC/JON].

X.2.1.3 $FeSiO_3$ (ferrosilite)

X.2.1.3.1 Heat capacity and entropy of $FeSiO_3$

Four forms of ferrosilite have been reported [1997WOO/ANG] (orthoferrosilite (space group *Pbca*), low-pressure clinoferrosilite (space group $P2_1/c$), high-temperature clinoferrosilite (space group $C2/c$) and a high-pressure clinoferrosilite (also, space group $C2/c$)). As indicated by the work of Lindsley [1965LIN3] and Hugh-Jones *et al.* [1994HUG/WOO], only the orthoferrosilite (space group *Pbca*) and low-pressure clinoferrosilite phases are experimentally accessible (but probably not stable) at near-atmospheric pressures for temperatures below 1300 K. The clinoferrosilite is converted to the orthoferrosilite at temperatures below 1100 K. However, even the clinoferrosilite is probably marginally unstable with respect to a mixture of fayalite + quartz near room temperature [1965AKI/KAT], [1996SAX], [1997WOO/ANG], [1997FAB/SUN].

Watanabe [1982WAT] reported heat-capacity measurements (differential-scanning calorimetry) on a “clinoferrosilite” (350 to 610 K at a constant but unstated pressure). Bohlen *et al.* [1983BOH/MET] reported an entropy value for “a synthetic ferrosilite” from low-temperature adiabatic calorimetry (8 to 350 K), but did not report the experimental heat-capacity data. In neither case is it clear which form of ferrosilite was used. The synthesis conditions used by Watanabe would be expected to lead initially to a high-pressure form ($C2/c$), but it may well be that the measurements were done on a sample that had been transformed to the $P2_1/c$ structure (see Appendix A).

Watanabe [1982WAT] fit a function of temperature to his values,

$$[C_{p,m}^{o}]_{350\,K}^{610\,K}\ (FeSiO_3, cr, 298.15\ K)/J\cdot K^{-1}\cdot mol^{-1} = 124.26 + 14.54 \times 10^{-3}\ (T/K) - 3.3777 \times 10^{6}\ (T/K)^{-2}.$$

The value from this equation, extrapolated to 298.15 K (Appendix A),

$$C_{p,m}^{o}\ (FeSiO_3, clino, 298.15\ K) = (90.6 \pm 5.0)\ J\cdot K^{-1}\cdot mol^{-1}$$

is accepted in the present review for clinoferrosilite ($P2_1/c$), but with substantial uncertainty to reflect the lack of structural information in the original source.

The reported entropy value from Bohlen *et al.* [1983BOH/MET]

$$S^{\circ}_{m}(\mathrm{FeSiO_3}, \text{ortho}, 298.15\ \mathrm{K}) = (94.6 \pm 3.0)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$$

likely refers to the orthoferrosilite (see Appendix A), and is accepted in this review. Again the uncertainty has been increased to reflect the lack of details for the sample preparation and the incomplete set of the reported results. Several authors [1979NAV/PIN], [1987NEI2], [1997FAB/SUN] have suggested slightly larger S°_{m} values (*e.g.*, 96 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ [1997FAB/SUN]) based on molar volumes, bulk-modulus data and thermal-expansion data. The evaluation of such properties for a high-pressure phase falls outside the scope of the present review, but such values of S°_{m}($FeSiO_3$, ortho, 298.15 K) are within the estimated uncertainties.

X.2.1.3.2 Enthalpy of formation of $FeSiO_3$

Values reported from the early combustion calorimetry work of Le Chatelier [1895CHA] and Wologdine [1913WOL] do not provide useful values because analyses of the final products were not reported. Reviews by Saxena [1996SAX] and by Fabrichnaya and Sundman [1997FAB/SUN] provide values, respectively, of − 1193.4 and − 1192.6 $\mathrm{kJ \cdot mol^{-1}}$ for $\Delta_{f} H^{\circ}_{m}$($FeSiO_3$, “ferrosilite”, 298.15 K, 100 kPa). In each case the value was derived from a Gibbs-energy minimization calculation that included data for many species and covered wide ranges of temperature and pressure. Therefore, the values of $\Delta_{f} H^{\circ}_{m}$($FeSiO_3$) from these sources should be used only with other values and auxiliary data from the same assessment. The solution calorimetry work of Navrotsky *et al.* [1979NAV/PIN] (using a quenched sample of orthoferrosilite) leads (Appendix A) to a more negative value (− 1197.9 $\mathrm{kJ \cdot mol^{-1}}$) that is inconsistent with (α-Fe_2SiO_4 + SiO_2) being stable with respect to $FeSiO_3$ at 298.15 K. In all cases the calculations are hampered by the large uncertainties in the heat capacities (and, except in the case of the calorimetry, the entropy) of $FeSiO_3$. No enthalpy of formation value for any of these high-pressure phases is selected in the present review.

X.2.1.4 Other iron silicates

X.2.1.4.1 Heat capacity and entropy of deerite and grunerite

The end-member solids are very difficult to isolate in a pure form, and there are few precise thermodynamic data available. Komada *et al.* [1995KOM/WES] measured the heat-capacity values of natural samples of deerite (composition $(\mathrm{Fe^{2+}_{4.87}Fe^{3+}_{2.76}Mn_{1.07}Mg_{0.15}Ti_{0.15}O_3})(\mathrm{Si_{5.94}Al_{0.03}Ti_{0.03}O_{17}})(\mathrm{OH})_5)$) and grunerite (composition $(\mathrm{Fe^{2+}_{5.38}Fe^{3+}_{0.66}Mn_{0.08}Mg_{0.80}Ca_{0.05}})(\mathrm{Si_8O_{22}})\ \{(\mathrm{OH})_{1.37}\mathrm{Cl_{0.03}O_{0.60}}\}$) over a wide range of temperature. From the smoothed adiabatic calorimetry measurements the following values were reported for 298.15 K

$$C^{\circ}_{p,\mathrm{m}}((\mathrm{Fe}^{2+}_{4.87}\mathrm{Fe}^{3+}_{2.76}\mathrm{Mn}_{1.07}\mathrm{Mg}_{0.15}\mathrm{Ti}_{0.15}\mathrm{O}_3)(\mathrm{Si}_{5.94}\mathrm{Al}_{0.03}\mathrm{Ti}_{0.03}\mathrm{O}_{17})(\mathrm{OH})_5, 298.15\ \mathrm{K}) = (786.1 \pm 0.8)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

$$C^{\circ}_{p,\mathrm{m}}((\mathrm{Fe}^{2+}_{5.38}\mathrm{Fe}^{3+}_{0.66}\mathrm{Mn}_{0.08}\mathrm{Mg}_{0.80}\mathrm{Ca}_{0.05})(\mathrm{Si}_8\mathrm{O}_{22})\{(\mathrm{OH})_{1.37}\mathrm{Cl}_{0.03}\mathrm{O}_{0.60}\}, 298.15\ \mathrm{K}) = (684.9 \pm 2.6)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}.$$

The values of $C^{\circ}_{p,\mathrm{m}}$ at 298.15 K for the solids with these compositions are accepted. The authors also used their results to estimate values of S°_{m} for the end-member compounds. However, there are unresolved complications associated with the calculation of these values (*cf.*, Appendix A), and the entropy values are not included in the database derived from the present review.

Earlier, Bennington *et al* [1978BEN/FER] carried out heat of solution measurements, adiabatic calorimetry measurements (7.76 to 309.33 K) and drop-calorimetry measurements (402.9 to 851.7 K, reference temperature 298.15 K) on a grunerite solid with the composition $\{(\mathrm{Fe}^{2+}_{5.2766}\mathrm{Fe}^{3+}_{0.1200}\mathrm{Mn}_{0.0825}\mathrm{Mg}_{1.5209})(\mathrm{Si}_{7.9163}\mathrm{Al}_{0.0837}\mathrm{O}_{22.0363})(\mathrm{OH})_{1.9637}\}$ ≡ “amosite”. The drop-calorimetry and adiabatic calorimetry results, weighted as discussed in Appendix A, lead to:

$$[C^{\circ}_{p,\mathrm{m}}]^{850\,\mathrm{K}}_{240\,\mathrm{K}}(\text{“amosite”})/\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}} = 614.27 + 0.57172\,(T/\mathrm{K}) - 8.88035 \times 10^{6}\,(T/\mathrm{K})^{-2}$$

and hence,

$$C^{\circ}_{p,\mathrm{m}}(\{(\mathrm{Fe}^{2+}_{5.2766}\mathrm{Fe}^{3+}_{0.1200}\mathrm{Mn}_{0.0825}\mathrm{Mg}_{1.5209})(\mathrm{Si}_{7.9163}\mathrm{Al}_{0.0837}\mathrm{O}_{22.0363})(\mathrm{OH})_{1.9637}\}, 298.15\ \mathrm{K}) = (684.8 \pm 3.0)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

The values of $C^{\circ}_{p,\mathrm{m}}$ for the solid with this composition are accepted for temperatures from 240 to 850 K. However, as discussed in Appendix A, no value is selected for the entropy of amosite in the present review, nor for the enthalpy of formation of the same solid from the HF solution-calorimetry measurements.

X.2.1.5 The Fe_2SiO_4-Fe_3O_4 system

At temperatures above 1473 K, if the pressure is greater than 9 GPa, γ-Fe_2SiO_4 is completely miscible with Fe_3O_4 [1992ROS/ARM], [1997OHT/TOB]. At lower pressures (> 3 GPa), a spinelloid phase $Fe_{3-x}Si_xO_4$ forms for $Fe_3O_4:Fe_2SiO_4$ ratios near 1:1. In the present review, no thermodynamic quantities are selected for these high-pressure phases.

Chapter XI

Resolution of values from different chemical thermodynamic cycles

The experimentally determined values of thermodynamic quantities for many iron species are linked (Figure XI-1). After completion of the initial assessments for iron compounds and species in the previous sections, re-examination is necessary to try to ensure that the values from different thermodynamic cycles are consistent. For example, the value of $\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{Fe}^{2+})$ is related not only to the heats of solution of $FeCl_2$(cr), $FeBr_2$(cr), $FeSO_4 \cdot 7H_2O$(cr), and the heats of formation of these solids, but also, among many other quantities, to the solubility and entropy for $FeCO_3$(cr). Re-evaluation is done as part of the selection process to determine final database values. Inconsistencies within each cycle must be resolved, usually by changing the value and increasing the uncertainty for one or more reactions or formation quantities.

In the re-evaluation process a computer programme has been developed to use the preliminary re-assessed values (either experimental or composite) and their uncertainties, and to optimize the values using a weighted least-squares procedure[1]. When several experimental results for a key quantity were found to differ by more than the assessed uncertainties, the optimization program was used with each of the values and its uncertainty. After the optimization, in some cases it was clear that certain experimental results were inconsistent, and their assessed uncertainties were increased, or in a few cases a reassessment of an experimental paper was done, and if necessary the results were rejected. The optimization resulted in “best” values and uncertainties, and these are used in the final iron database (as noted in the discussions elsewhere in the text).

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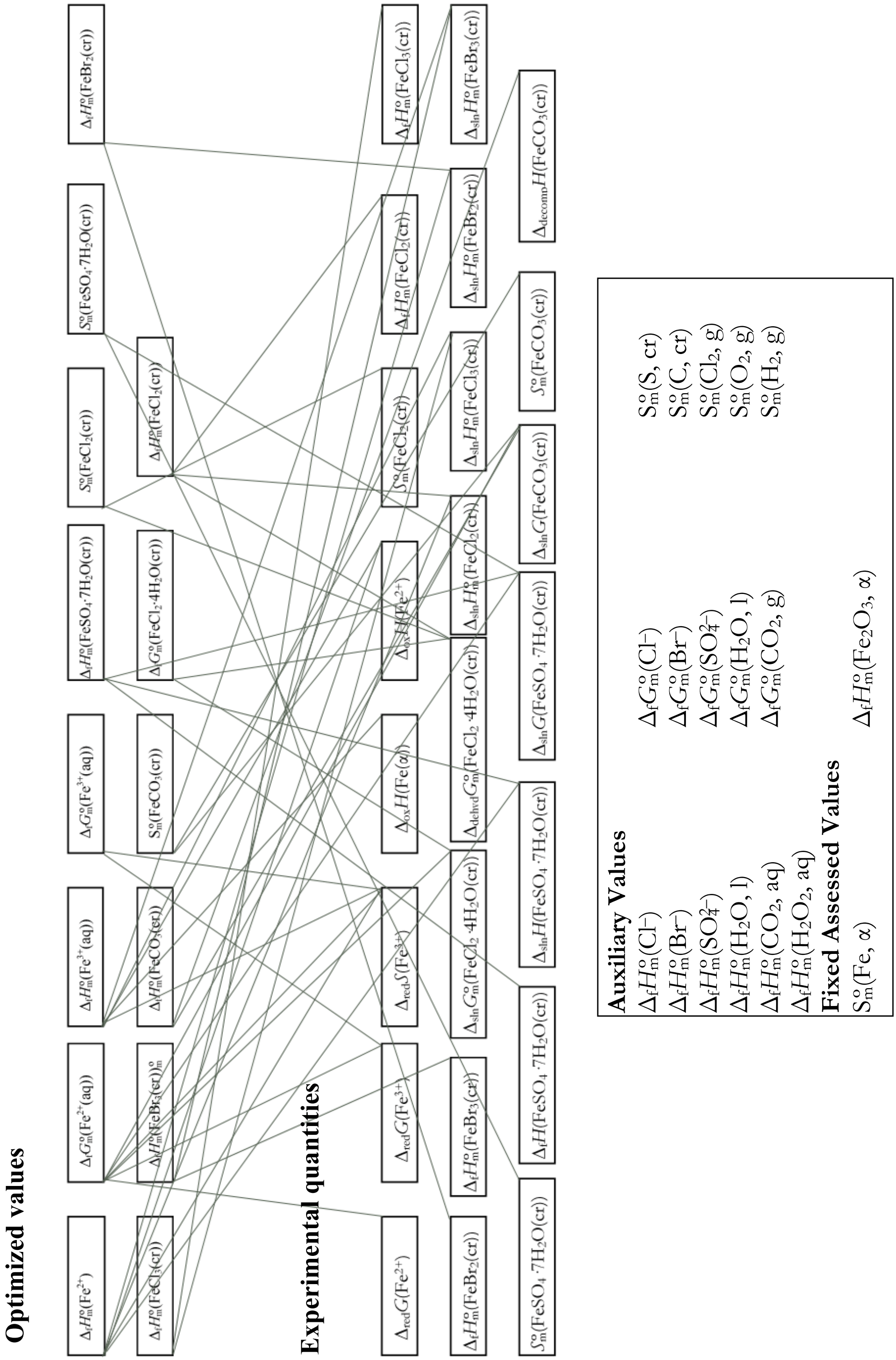
[1] A copy of this program (CYCLES, written in Fortran 77) has been deposited with the NEA Data Bank for reference purposes. It is *not* a general minimization code, but is specific to the current assessment for thermodynamic quantities for iron species. It is strictly a utility program, and has *not* undergone quality assurance to the extent that would be required to meet current national or international standards.

Figure XI-1: Related chemical thermodynamic quantities for iron species.



The values used for the following quantities are from the standard tables of TDB auxiliary data: $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{Cl}^-)$, $\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ}(\mathrm{Cl}^-)$, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{Br}^-)$, $\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ}(\mathrm{Br}^-)$, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{SO}_4^{2-})$, $\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ}(\mathrm{SO}_4^{2-})$, $\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ}(\mathrm{CO_2, g})$, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{CO_2, g})$, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{H_2O, l})$, $\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ}(\mathrm{H_2O, l})$, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{H_2O_2, aq})$, $S_{\mathrm{m}}^{\circ}(\mathrm{Cl_2, g})$, $S_{\mathrm{m}}^{\circ}(\mathrm{Br_2, l})$, $S_{\mathrm{m}}^{\circ}(\mathrm{S, cr})$, $S_{\mathrm{m}}^{\circ}(\mathrm{O_2, g})$, $S_{\mathrm{m}}^{\circ}(\mathrm{H_2, g})$, $S_{\mathrm{m}}^{\circ}(\mathrm{C, cr})$. T_{r} is the reference temperature, 298.15 K.

The input data for the optimization are listed in Table XI-1, and the preliminary optimized quantities from the output are listed in Table XI-2. Details of the equations used and the differences between the initially assessed experimental values and results of this preliminary optimization are listed in Table XI-3 and Table XI-4.

Table XI-1: Input experimental values or values based on assessment of experimental data as used in the iron database optimization.

$\Delta_{\mathrm{red}}G$ (Fe(II))	(91.56 ± 1.70) kJ·mol^{-1}	Section VI.1.1.2.4, from E°
$\Delta_{\mathrm{red}}G$ (Fe(III))	$-(74.49 \pm 0.19)$ kJ·mol^{-1}	Section VI.1.2.4, Eq. (VI.14) SIT$_2$[1]
$\Delta_{\mathrm{red}}G$ (Fe(III))	$-(74.49 \pm 0.38)$ kJ·mol^{-1}	Section VI.1.2.5, Eq. (VI.14)
$\Delta_{\mathrm{red}}S$ (Fe(III))	(117.7 ± 8.6) J·K^{-1}·mol^{-1}	Section VI.1.2.4, Eq. (VI.14) SIT$_2$
$\Delta_{\mathrm{ox}}H$ (Fe(II))	$-(149.0 \pm 4.0)$ kJ·mol^{-1}	Section VI.3.1, Eq. (VI.23)
$\Delta_{\mathrm{ox}}H$ (Fe, cr)	$-(617.8 \pm 2.5)$ kJ·mol^{-1}	Section VI.3.2, Eq. (VI.24)
S_{m}° $(\mathrm{FeCl_2, cr})_{\mathrm{e}}$	(118.2 ± 0.8) J·K^{-1}·mol^{-1}	Section VIII.1.4.1
$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}$ $(\mathrm{FeCl_3, cr})_{\mathrm{e1}}$	$-(399.51 \pm 0.56)$ kJ·mol^{-1}	Section VIII.3.2.3.2; [1959KOE/COU]
$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}$ $(\mathrm{FeCl_3, cr})_{\mathrm{e2}}$	$-(394.14 \pm 2.19)$ kJ·mol^{-1}	Section VIII.3.2.3.2; [1934ROT/WIE]
$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}$ $(\mathrm{FeCl_3, cr})_{\mathrm{e3}}$	$-(395.57 \pm 0.74)$ kJ·mol^{-1}	Section VIII.3.2.3.2; [1989EVD/EFI2]
$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}$ $(\mathrm{FeCl_3, cr})_{\mathrm{e4}}$	$-(396.00 \pm 0.14)$ kJ·mol^{-1}	Section VIII.3.2.3.2; [1984LAV/TIM2]
$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}$ $(\mathrm{FeCl_2, cr})_{\mathrm{e1}}$	$-(341.84 \pm 0.48)$ kJ·mol^{-1}	Section VIII.3.2.1.2; [1959KOE/COU]
$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}$ $(\mathrm{FeCl_2, cr})_{\mathrm{e2}}$	$-(341.04 \pm 0.53)$ kJ·mol^{-1}	Section VIII.3.2.1.2; [1989EVD/EFI2]
$\Delta_{\mathrm{sln}}G$ $(\mathrm{FeCl_2{\cdot}4H_2O, cr})$	$-(17.16 \pm 0.40)$ kJ·mol^{-1}	Section VIII.3.2.2, Eq. (VIII.24)
$\Delta_{\mathrm{dehyd}}G$ $(\mathrm{FeCl_2{\cdot}4H_2O, cr})$	(33.3 ± 3.9) kJ·mol^{-1}	Section VIII.3.2.2, Eq. (VIII.28)
$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}$ $(\mathrm{FeBr_2, cr})_{\mathrm{e}}$	$-(245. \pm 4.)$ kJ·mol^{-1}	Section VIII.3.3.1.2
$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}$ $(\mathrm{FeBr_3, cr})_{\mathrm{e}}$	$-(262.63 \pm 1.00)$ kJ·mol^{-1}	Section VIII.3.3.3
$\Delta_{\mathrm{sln}}H$ $(\mathrm{FeCl_2, cr})$	$-(82.91 \pm 0.31)$ kJ·mol^{-1}	Section VIII.3.5.1
$\Delta_{\mathrm{sln}}H$ $(\mathrm{FeBr_2, cr})$	$-(85.3 \pm 1.4)$ kJ·mol^{-1}	Section VIII.3.5.2
$\Delta_{\mathrm{sln}}H$ $(\mathrm{FeCl_3, cr})$	$-(158.3 \pm 3.0)$ kJ·mol^{-1}	Section VIII.3.5.4; [1995PAR/KHO]
$\Delta_{\mathrm{sln}}H$ $(\mathrm{FeBr_3, cr})$	$-(152.2 \pm 3.0)$ kJ·mol^{-1}	Section VIII.5.5.5; [1995PAR/KHO]
S_{m}° $(\mathrm{FeSO_4{\cdot}7H_2O, cr})_{\mathrm{e}}$	(409.1 ± 1.3) J·K^{-1}·mol^{-1}	Section IX.1.2.2.2.1
$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}$ $(\mathrm{FeSO_4{\cdot}7H_2O, cr})_{\mathrm{e1}}$	$-(3014.56 \pm 1.00)$ kJ·mol^{-1}	Section IX.1.2.2.2.2; [1963ADA/KEL]
$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}$ $(\mathrm{FeSO_4{\cdot}7H_2O, cr})_{\mathrm{e2}}$	$-(3015.61 \pm 1.54)$ kJ·mol^{-1}	Section IX.1.2.2.2.2; [1985VAS/DMI2]

(Continued on next page)

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[1] The SIT$_2$ value is used, as it is a better extrapolation for low ionic strengths. Overall, only minor differences result (within the final uncertainties) if the SIT$_1$ value, $(-(74.78 \pm 0.48)$ kJ·mol$^{-1})$, is used.

Table XI-1 (continued)

$\Delta_{\text{sln}}G$ ($FeSO_4{\cdot}7H_2O$, cr)$_{e1}$	(12.9 ± 0.4) $kJ{\cdot}mol^{-1}$	Section IX.1.2.2.2.3
$\Delta_{\text{sln}}G$ ($FeSO_4{\cdot}7H_2O$, cr)$_{e2}$	(13.8 ± 1.0) $kJ{\cdot}mol^{-1}$	Section IX.1.2.2.2.3
$\Delta_{\text{sln}}H$ ($FeSO_4{\cdot}7H_2O$, cr)	(11.89 ± 0.50) $kJ{\cdot}mol^{-1}$	Section IX.1.2.2.2.4
S°_{m} ($FeCO_3$, cr)$_{e}$	(95.47 ± 1.00) $J{\cdot}K^{-1}{\cdot}mol^{-1}$	Section X.1.2.1.1
$\Delta_{\text{sln}}G$ ($FeCO_3$, cr)	– (42.4 ± 1.1) $kJ{\cdot}mol^{-1}$	Section X.1.2.1.2; Eq. X.2
$\Delta_{\text{decomp}}H$ ($FeCO_3$, cr)	– (56.14 ± 2.30) $kJ{\cdot}mol^{-1}$	Section X.1.2.1.3; Appendix A [1994CHA/NAV]
TDB iron species values accepted from the present review		
S°_{m} (Fe, α)	(27.085 ± 0.160) $J{\cdot}K^{-1}{\cdot}mol^{-1}$	Section V.2
$\Delta_{\text{f}}H^{\circ}_{\text{m}}$ (Fe_2O_3, α)	– (826.29 ± 2.63) $kJ{\cdot}mol^{-1}$	Section VII.2.2.1

Table XI-2: Quantities from the output of the first optimization cycle of experimental data assessed in the iron database review.

$\Delta_{\text{f}}H^{\circ}_{\text{m}}$ (Fe^{2+})	– (90.60 ± 0.82) $kJ{\cdot}mol^{-1}$
$\Delta_{\text{f}}G^{\circ}_{\text{m}}$ (Fe^{2+})	– (91.36 ± 1.39) $kJ{\cdot}mol^{-1}$
$\Delta_{\text{f}}H^{\circ}_{\text{m}}$ (Fe^{3+})	– (50.15 ± 2.41) $kJ{\cdot}mol^{-1}$
$\Delta_{\text{f}}G^{\circ}_{\text{m}}$ (Fe^{3+})	– (16.87 ± 1.42) $kJ{\cdot}mol^{-1}$
$\Delta_{\text{f}}G^{\circ}_{\text{m}}$ ($FeCl_2{\cdot}4H_2O$, cr)	– (1285.18 ± 1.63) $kJ{\cdot}mol^{-1}$
$\Delta_{\text{f}}H^{\circ}_{\text{m}}$ ($FeCl_2$, cr)	– (341.66 ± 0.61) $kJ{\cdot}mol^{-1}$
$\Delta_{\text{f}}H^{\circ}_{\text{m}}$ ($FeSO_4{\cdot}7H_2O$, cr)	– (3013.45 ± 1.02) $kJ{\cdot}mol^{-1}$
$\Delta_{\text{f}}H^{\circ}_{\text{m}}$ ($FeBr_2$, cr)	– (247.77 ± 2.56) $kJ{\cdot}mol^{-1}$
$\Delta_{\text{f}}H^{\circ}_{\text{m}}$ ($FeCl_3$, cr)	– (396.17 ± 0.24) $kJ{\cdot}mol^{-1}$
$\Delta_{\text{f}}H^{\circ}_{\text{m}}$ ($FeBr_3$, cr)	– (262.59 ± 1.75) $kJ{\cdot}mol^{-1}$
$\Delta_{\text{f}}H^{\circ}_{\text{m}}$ ($FeCO_3$, cr)	– (753.07 ± 2.25) $kJ{\cdot}mol^{-1}$
S°_{m} ($FeCO_3$, cr)	(95.58 ± 1.82) $J{\cdot}K^{-1}{\cdot}mol^{-1}$
S°_{m} ($FeCl_2$, cr)	(118.21 ± 1.46) $J{\cdot}K^{-1}{\cdot}mol^{-1}$
S°_{m} ($FeSO_4{\cdot}7H_2O$, cr)	(408.92 ± 2.30) $J{\cdot}K^{-1}{\cdot}mol^{-1}$

The following cycles were considered in the review of Parker and Khodakovskii [1995PAR/KHO], but in the present review the available data have not been deemed suitable for the optimization process.

a. $\Delta_{\text{f}}H^{\circ}_{\text{m}}$ (Fe^{2+}) from $\Delta_{\text{f}}H^{\circ}_{\text{m}}$ (FeI_2, cr) from solution calorimetry, with values for $\Delta_{\text{sln}}H^{\circ}_{\text{m}}$ (FeI_2, cr) in water and $\Delta_{\text{f}}H^{\circ}_{\text{m}}$ (I^{-}), because values for $\Delta_{\text{f}}H^{\circ}_{\text{m}}$ (FeI_2, cr) in the literature are badly scattered;

b. $\Delta_{\text{f}}H^{\circ}_{\text{m}}$ (Fe^{2+}) from $\Delta_{\text{f}}H^{\circ}_{\text{m}}$ ($(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$, cr) from solution calorimetry with $\Delta_{\text{f}}H^{\circ}_{\text{m}}(SO_4^{2-})$, $\Delta_{\text{f}}H^{\circ}_{\text{m}}$ ($(NH_4)_2SO_4$, sln) and $\Delta_{\text{f}}H^{\circ}_{\text{m}}$ (H_2O, l), because the ionic strength correction is not well defined;

c. $\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ}(\mathrm{Fe}^{2+})$ from chemical equilibrium of Fe(cr) with Tl^{+}, as it requires correction from $I = 1\ \mathrm{mol\cdot kg^{-1}}$, and 323 K, and values for Tl^{+} also are required;

d. $\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ}(\mathrm{Fe}^{2+})$ from magnetite solubility 373 to 573 K, because it requires good heat-capacity values, $\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ}(\mathrm{Fe_3O_4}, \mathrm{cr})$ and hydrolysis constants for Fe^{2+} as a function of temperature;

e. $\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ}(\mathrm{Fe}^{3+})$ from goethite solubility;

f. $\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ}(\mathrm{Fe}^{3+})$ from hematite solubility;

g. $\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ}(\mathrm{Fe}^{3+}) - \Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ}(\mathrm{Fe}^{2+})$ from chemical equilibrium of Fe^{2+} with Ag^{+} in nitrate medium.

Also, cycles involving values for gas-phase iron halide species have not been used [1995PAR/KHO]. Most of these involve gas-phase species of iron(III). These cycles require good third-law calculations, and hence values for $C_{p,\mathrm{m}}^{\circ}(T)$ and S_{m}° for $\mathrm{FeCl_3(g)}$ and/or $\mathrm{Fe_2Cl_6(g)}$. These quantities are not assessed in the present review. There are many papers on the relevant reactions. However, as discussed in the sections on the halide solids, difficulties have been encountered in evaluating the experimental work on the bromide and iodide species.

A cycle based on the reaction

$$\mathrm{FeOCl(cr)} + 2\,\mathrm{HCl(sln)} \rightleftharpoons \mathrm{FeCl_3(cr)} + \mathrm{H_2O(l)},$$

which also is related to values of $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{Fe_2O_3}, \mathrm{cr})$ and $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{Fe_2Cl_6}, \mathrm{g})$, is available, but some of the experiments for $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{FeOCl}, \mathrm{cr})$ are associated with those used to determine quantities for $\mathrm{FeCl_3(cr)}$. Furthermore, the uncertainties in $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{FeOCl}, \mathrm{cr}, 288.15\ \mathrm{K})$ are large enough that the cycle is unlikely to add much to the optimization.

Any cycle based on heats of solution of iron fluorides is unlikely to be helpful, because of the strong association of the simple iron aqueous species Fe^{3+} with F^{-}.

In the analysis, the value assessed for $S_{\mathrm{m}}^{\circ}(\mathrm{Fe}, \alpha)$ was accepted because it was felt that it was less prone to error than the values being refined. Also, the value assessed for $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{Fe_2O_3}, \alpha)$ was not allowed to vary because of the many cross-linkages with values for other iron solids.

Table XI-3: Summary of the equations used in the first optimization, and results from the optimization cycle. The equations in the main text that are related to the thermodynamic quantities are those noted in Table XI-1.

	Numbered equations used in the first optimization assessment cycle	(LHS) value† from the first assessment cycle	(RHS) optimized value†	difference
1	$\Delta_{\mathrm{red}}G$ (Fe(II)) = $-\Delta_{\mathrm{f}}G^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{Fe^{2+}}$)	91.56 ± 1.70	91.36	0.20
2	$\Delta_{\mathrm{red}}G$ (Fe(III)) = $\Delta_{\mathrm{f}}G^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{Fe^{2+}}$) $-$ $\Delta_{\mathrm{f}}G^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{Fe^{3+}}$)	$-$ 74.49 ± 0.17	$-$ 74.49	0.00
3	$\Delta_{\mathrm{red}}S$ (Fe(III)) = ($\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{Fe^{2+}}$) $-$ $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{Fe^{3+}}$) $-$ $\Delta_{\mathrm{f}}G^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{Fe^{2+}}$) + $\Delta_{\mathrm{f}}G^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{Fe^{3+}}$))/T_{r}	117.7 ± 8.6	114.2	3.5
4	$\Delta_{\mathrm{ox}}H$ (Fe, cr) + 1.5$\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{H_2O_2}$, aq) $-$ 3$\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{H_2O}$, l) = $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{Fe^{3+}}$)	$-$ 47.06 ± 2.51	$-$ 49.79	3.09*
5	$\Delta_{\mathrm{ox}}H$ (Fe(II)) + 0.5$\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{H_2O_2}$, aq) $-$ $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{H_2O}$, l) = $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{Fe^{3+}}$) $-$ $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{Fe^{2+}}$)	41.24 ± 4.00	40.45	0.80
6	$\Delta_{\mathrm{sln}}H$ ($\mathrm{FeCl_2}$, cr) $-$ 2$\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{Cl^-}$) = $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{Fe^{2+}}$) $-$ $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeCl_2}$, cr)	251.25 ± 0.37	251.06	0.19
7	$S^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeCl_2}$, cr)$_{\mathrm{e}}$ = $S^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeCl_2}$, cr)	118.20 ± 0.80	118.21	$-$ 0.01
8	$\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeCl_2}$, cr)$_{\mathrm{e1}}$ = $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeCl_2}$, cr)	$-$ 341.84 ± 0.48	$-$ 341.66	$-$ 0.18
	$\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeCl_2}$, cr)$_{\mathrm{e2}}$ = $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeCl_2}$, cr)	$-$ 341.04 ± 0.53		0.62*
9	$\Delta_{\mathrm{sln}}H$ ($\mathrm{FeCl_2{\cdot}4H_2O}$, cr) $-$ 2$\Delta_{\mathrm{f}}G^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{Cl^-}$) $-$ 4$\Delta_{\mathrm{f}}G^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{H_2O}$, l) = $\Delta_{\mathrm{f}}G^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{Fe^{2+}}$) $-$ $\Delta_{\mathrm{f}}G^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeCl_2{\cdot}4H_2O}$, cr)	1193.83 ± 0.49	1193.82	0.02
10	$\Delta_{\mathrm{dehyd}}G$ ($\mathrm{FeCl_2{\cdot}4H_2O}$, cr) $-$ 4$\Delta_{\mathrm{f}}G^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{H_2O}$, l) $-$ T_{r}($S^{\mathrm{o}}_{\mathrm{m}}$ (Fe, α) + $S^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{Cl_2}$, g)) = $-$ $\Delta_{\mathrm{f}}G^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeCl_2{\cdot}4H_2O}$, cr) + $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeCl_2}$, cr) $-$ $T_{\mathrm{r}}\,S^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeCl_2}$, cr)	907.27 ± 3.90	908.28	$-$ 1.00
11	$\Delta_{\mathrm{sln}}H$ ($\mathrm{FeBr_2}$, cr) $-$ 2 $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{Br^-}$) = $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{Fe^{2+}}$) $-$ $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeBr_2}$, cr)	157.52 ± 1.43	157.16	0.35
12	$\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeBr_2}$, cr)$_{\mathrm{e}}$ = $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeBr_2}$, cr)	$-$ 245.00 ± 4.00	$-$ 247.77	2.77
13	$\Delta_{\mathrm{sln}}H$ ($\mathrm{FeCl_3}$, cr) $-$ 3$\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{Cl^-}$) = $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{Fe^{3+}}$) $-$ $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeCl_3}$, cr)	342.94 ± 3.01	346.02	$-$ 3.08*
14	$\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeCl_3}$, cr)$_{\mathrm{e1}}$ = $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeCl_3}$, cr)	$-$ 399.51 ± 0.56	$-$ 396.17	$-$ 3.34*
	$\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeCl_3}$, cr)$_{\mathrm{e2}}$ = $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeCl_3}$, cr)	$-$ 394.14 ± 2.19		2.03
	$\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeCl_3}$, cr)$_{\mathrm{e3}}$ = $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeCl_3}$, cr)	$-$ 395.57 ± 0.74		0.60
	$\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeCl_3}$, cr)$_{\mathrm{e4}}$ = $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeCl_3}$, cr)	$-$ 396.00 ± 0.14		0.17*
15	$\Delta_{\mathrm{sln}}H$ ($\mathrm{FeBr_3}$, cr) $-$ 3$\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{Br^-}$) = $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{Fe^{3+}}$) $-$ $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeBr_3}$, cr)	212.03 ± 3.03	212.43	$-$ 0.40
16	$\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeBr_3}$, cr)$_{\mathrm{e}}$ = $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeBr_3}$, cr)	$-$ 262.63 ± 1.00	$-$ 262.59	$-$ 0.04
17	$\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeSO_4{\cdot}7H_2O}$, cr)$_{\mathrm{e1}}$ = $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeSO_4{\cdot}7H_2O}$, cr)	$-$ 3014.56 ± 1.00	$-$ 3013.45	$-$ 1.11*
	$\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeSO_4{\cdot}7H_2O}$, cr)$_{\mathrm{e2}}$ = $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeSO_4{\cdot}7H_2O}$, cr)	$-$ 3015.61 ± 1.54		$-$ 2.16*
18	$S^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeSO_4{\cdot}7H_2O}$, cr)$_{\mathrm{e}}$ = $S^{\mathrm{o}}_{\mathrm{m}}$ ($\mathrm{FeSO_4{\cdot}7H_2O}$, cr)	409.10 ± 1.30	408.92	0.18

(Continued on next page)

Table XI-3 (continued)

Numbered equations used in the first optimization assessment cycle	(LHS) value† from the first assessment cycle	(RHS) optimized value†	difference
19 $\Delta_{\mathrm{sln}}G\ (\mathrm{FeSO_4{\cdot}7H_2O, cr})_{\mathrm{e1}} - \Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}\ (\mathrm{SO_4^{2-}}) - 7\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}\ (\mathrm{H_2O, l}) + T_{\mathrm{r}}(S^{\circ}_{\mathrm{m}}\ (\mathrm{Fe}, \alpha) + S^{\circ}_{\mathrm{m}}\ (\mathrm{S, cr}) + 7S^{\circ}_{\mathrm{m}}\ (\mathrm{H_2, g}) + 5.5S^{\circ}_{\mathrm{m}}\ (\mathrm{O_2, g})) = \Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}\ (\mathrm{Fe^{2+}}) - \Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}\ (\mathrm{FeSO_4{\cdot}7H_2O, cr}) + T_{\mathrm{r}}\, S^{\circ}_{\mathrm{m}}\ (\mathrm{FeSO_4{\cdot}7H_2O, cr})$	3043.67 ± 0.65	3044.00	− 0.34
$\Delta_{\mathrm{sln}}G\ (\mathrm{FeSO_4{\cdot}7H_2O, cr})_{\mathrm{e2}} - \Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}\ (\mathrm{SO_4^{2-}}) - 7\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}\ (\mathrm{H_2O, l}) + T_{\mathrm{r}}(S^{\circ}_{\mathrm{m}}\ (\mathrm{Fe}, \alpha) + S^{\circ}_{\mathrm{m}}\ (\mathrm{S, cr}) + 7S^{\circ}_{\mathrm{m}}\ (\mathrm{H_2, g}) + 5.5S^{\circ}_{\mathrm{m}}\ (\mathrm{O_2, g})) = \Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}\ (\mathrm{Fe^{2+}}) - \Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}\ (\mathrm{FeSO_4{\cdot}7H_2O, cr}) + T_{\mathrm{r}}\, S^{\circ}_{\mathrm{m}}\ (\mathrm{FeSO_4{\cdot}7H_2O, cr})$	3044.57 ± 1.12		0.56
20 $\Delta_{\mathrm{sln}}H\ (\mathrm{FeSO_4{\cdot}7H_2O, cr}) - \Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}\ (\mathrm{SO_4^{2-}}) - 7\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}\ (\mathrm{H_2O, l}) = \Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}\ (\mathrm{Fe^{2+}}) - \Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}\ (\mathrm{FeSO_4{\cdot}7H_2O, cr})$	2922.04 ± 0.70	2922.85	− 0.81
21 $S^{\circ}_{\mathrm{m}}\ (\mathrm{FeCO_3, cr})_{\mathrm{e}} = S^{\circ}_{\mathrm{m}}\ (\mathrm{FeCO_3, cr})$	95.47 ± 1.00	95.58	− 0.11
22 $\Delta_{\mathrm{sln}}G\ (\mathrm{FeCO_3, cr}) + 2\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}\ (\mathrm{H^+}) - \Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}\ (\mathrm{CO_2, g}) - \Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}\ (\mathrm{H_2O, l}) = \Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}\ (\mathrm{Fe^{2+}}) - \Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}\ (\mathrm{FeCO_3, cr})$	690.65 ± 1.11	690.20	0.45
23 $\Delta_{\mathrm{decomp}}H\ (\mathrm{FeCO_3, cr}) + 0.25\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}\ (\mathrm{O_2, g}) - \Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}\ (\mathrm{CO_2, g}) - \Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}\ (\mathrm{Fe_2O_3}, \alpha) = -\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}\ (\mathrm{FeCO_3, cr})$	750.52 ± 2.65	753.07	− 2.56

† Values of ΔH and ΔG are in $\mathrm{kJ{\cdot}mol^{-1}}$; values of S are in $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, T_{r} is 298.15 K.

* Calculated differences exceed the uncertainties based on the preliminary assessments

Table XI-4: Comparison of input and output values from the first cycle optimization of experimental data as assessed in the iron database. The equations in the main text that are related to the thermodynamic quantities are those noted in Table XI-1.

Quantity	unit	input	output	difference
$\Delta_{\mathrm{red}}G$ (Fe(II))	$\mathrm{kJ\cdot mol^{-1}}$	91.56 ± 1.70	91.38	0.18
$\Delta_{\mathrm{red}}G$ (Fe(III))	$\mathrm{kJ\cdot mol^{-1}}$	-74.49 ± 0.17	-74.49	0.00
$\Delta_{\mathrm{red}}S$ (Fe(III))	$\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	117.7 ± 8.6	112.9	4.8
$\Delta_{\mathrm{ox}}H$ (Fe, cr)	$\mathrm{kJ\cdot mol^{-1}}$	-617.8 ± 2.5	-620.5	2.7*
$\Delta_{\mathrm{ox}}H$ (Fe(II))	$\mathrm{kJ\cdot mol^{-1}}$	-149.0 ± 4.0	-149.4	0.4
S°_{m} ($FeCl_2$, cr)$_{\mathrm{e}}$	$\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	118.2 ± 0.8	118.2	0.0
$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($FeCl_2$, cr)$_{\mathrm{e1}}$	$\mathrm{kJ\cdot mol^{-1}}$	-341.84 ± 0.48	-341.68	-0.16
$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($FeCl_2$, cr)$_{\mathrm{e2}}$	$\mathrm{kJ\cdot mol^{-1}}$	-341.04 ± 0.53		0.64*
$\Delta_{\mathrm{sln}}H$ ($FeCl_2$, cr)	$\mathrm{kJ\cdot mol^{-1}}$	-82.91 ± 0.31	-83.11	0.20
$\Delta_{\mathrm{sln}}G$ ($FeCl_2\cdot 4H_2O$, cr)	$\mathrm{kJ\cdot mol^{-1}}$	-17.16 ± 0.40	-17.18	0.02
$\Delta_{\mathrm{dehyd}}G$ ($FeCl_2\cdot 4H_2O$, cr)	$\mathrm{kJ\cdot mol^{-1}}$	33.3 ± 3.9	34.3	-1.0
$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($FeBr_2$, cr)$_{\mathrm{e}}$	$\mathrm{kJ\cdot mol^{-1}}$	-245 ± 4	-247.8	2.8
$\Delta_{\mathrm{sln}}H$ ($FeBr_2$. cr)	$\mathrm{kJ\cdot mol^{-1}}$	-85.3 ± 1.4	-85.7	0.4
$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($FeCl_3$, cr)$_{\mathrm{e1}}$	$\mathrm{kJ\cdot mol^{-1}}$*	-399.51 ± 0.56	-396.17	-3.34*
$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($FeCl_3$, cr)$_{\mathrm{e2}}$	$\mathrm{kJ\cdot mol^{-1}}$	-394.14 ± 2.19		2.03
$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($FeCl_3$, cr)$_{\mathrm{e3}}$	$\mathrm{kJ\cdot mol^{-1}}$	-395.57 ± 0.74		0.60
$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($FeCl_3$, cr)$_{\mathrm{e4}}$	$\mathrm{kJ\cdot mol^{-1}}$*	-396.00 ± 0.14		0.17*
$\Delta_{\mathrm{sln}}H$ ($FeCl_3$, cr)	$\mathrm{kJ\cdot mol^{-1}}$*	-158.3 ± 3.0	-154.9	-3.4*
$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($FeBr_3$, cr)$_{\mathrm{e}}$	$\mathrm{kJ\cdot mol^{-1}}$	-262.63 ± 1.00	-262.59	-0.04
$\Delta_{\mathrm{sln}}H$ ($FeBr_3$, cr)	$\mathrm{kJ\cdot mol^{-1}}$	-152.2 ± 3.0	-151.5	-0.7
S°_{m} ($FeSO_4\cdot 7H_2O$, cr)$_{\mathrm{e}}$	$\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	409.1 ± 1.3	408.9	0.2
$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($FeSO_4\cdot 7H_2O$, cr)$_{\mathrm{e1}}$	$\mathrm{kJ\cdot mol^{-1}}$*	-3014.56 ± 1.00	-3013.46	-1.10*
$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($FeSO_4\cdot 7H_2O$, cr)$_{\mathrm{e2}}$	$\mathrm{kJ\cdot mol^{-1}}$*	-3015.61 ± 1.54		-2.15*
$\Delta_{\mathrm{sln}}G$ ($FeSO_4\cdot 7H_2O$, cr)$_{\mathrm{e1}}$	$\mathrm{kJ\cdot mol^{-1}}$	12.9 ± 0.4	13.2	-0.3
$\Delta_{\mathrm{sln}}G$ ($FeSO_4\cdot 7H_2O$, cr)$_{\mathrm{e2}}$	$\mathrm{kJ\cdot mol^{-1}}$	13.8 ± 1.0		0.6
$\Delta_{\mathrm{sln}}H$ ($FeSO_4\cdot 7H_2O$, cr)	$\mathrm{kJ\cdot mol^{-1}}$*	11.89 ± 0.50	12.69	-0.80*
S°_{m} ($FeCO_3$, cr)$_{\mathrm{e}}$	$\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	95.47 ± 1.00	95.58	0.11
$\Delta_{\mathrm{sln}}G$ ($FeCO_3$, cr)	$\mathrm{kJ\cdot mol^{-1}}$	-42.4 ± 1.1	-42.8	0.4
$\Delta_{\mathrm{decomp}}H$ ($FeCO_3$, cr)	$\mathrm{kJ\cdot mol^{-1}}$*	-56.14 ± 2.30	-53.58	-2.56*

* Differences exceed the uncertainties from the preliminary assessments

XI.1 Evaluation of the results from the first assessment cycle and input values for the second assessment cycle

The majority of the values are consistent within the stated uncertainties. Among the exceptions are $\Delta_{\mathrm{ox}}H$ (Fe, cr) and $\Delta_{\mathrm{decomp}}H$ ($FeCO_3$, cr), each a result from a single study with uncertainties estimated in the present review, and $\Delta_{\mathrm{sln}}H$ ($FeCl_2$, cr), $\Delta_{\mathrm{sln}}H$ ($FeCl_3$, cr) and $\Delta_{\mathrm{sln}}H$ ($FeSO_4\cdot 7H_2O$, cr) for which our initial estimated enthalpies of dilution may be open to question. In each of these cases, for the second assessment cycle, the estimated uncertainties were increased by 20%.

The optimized value for $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($FeSO_4\cdot7H_2O$, cr) is less negative than either experimentally based value [1963ADA/KEL], [1985VAS/DMI2]. Similarly, the optimized value of $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($FeCl_3$, cr) is considerably less negative than the experimentally based value [1959KOE/COU] for $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($FeCl_3$, cr_{e1}). The most problematic measurement in the work of Koehler and Coughlin [1959KOE/COU] appears to be the enthalpy of solution of Fe(α) in 4.36 $mol\cdot kg^{-1}$ HCl(sln), and this experimental value also was used in the calculation of $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($FeSO_4\cdot7H_2O$, cr_{e1}) [1963ADA/KEL]. However, although the discrepancies are in the same direction, there appears to be an additional discrepancy in the Koehler and Coughlin value for $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($FeCl_3$, cr_{e1}), and the value for $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($FeSO_4\cdot7H_2O$, cr) from Vasil'ev *et al.* also seems to be inconsistent. Therefore, for the second assessment cycle, the value for $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($FeCl_3$, cr) from Koehler and Coughlin was discarded, and a weighted average of the other three values $-(395.98 \pm 0.14)$ $kJ\cdot mol^{-1}$ was used. For the value of $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($FeSO_4\cdot7H_2O$, cr), the weighted average -3014.87 $kJ\cdot mol^{-1}$ was used, but the estimated uncertainty was increased to 3.00 $kJ\cdot mol^{-1}$.

For $\Delta_{\mathrm{sln}}G$ ($FeSO_4\cdot7H_2O$, cr), the result of the first optimization is bracketed by the two experimental values, and the weighted average value, (13.02 ± 0.37) $kJ\cdot mol^{-1}$, is used in the second cycle. The two experimentally based values for $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($FeCl_2$, cr) are in only marginal agreement and, rather than the weighted average, the simple average was selected and the uncertainty was chosen to span those of the two values ($-(341.42 \pm 0.90)$ $kJ\cdot mol^{-1}$).

XI.2 Results from the second optimization cycle

The results of the second cycle of optimization calculations are provided in Table XI-5 and Table XI-6. The internally consistent set of values in Table XI-6 has been used in the preparation of the table of selected iron data, Table III-1. Table XI-7 provides a consistent set of thermodynamic quantities that correspond to the experimental values used in the optimization, but calculated from the values in Table XI-6 and auxiliary data used in the present review. These are consistent with the input experimental quantities within the stated uncertainties.

Table XI-5: Comparison of input and output values from the second cycle optimization of experimental data as used in the iron database optimization. The equations in the main text that are related to the thermodynamic quantities are those noted in Table XI-1.

Quantity	unit	input	output	difference
$\Delta_{\mathrm{red}}G(\mathrm{Fe(II)})$	$\mathrm{kJ\cdot mol^{-1}}$	91.56 ± 1.70	90.72	0.84
$\Delta_{\mathrm{red}}G(\mathrm{Fe(III)})$	$\mathrm{kJ\cdot mol^{-1}}$	-74.49 ± 0.17	-74.49	0.00
$\Delta_{\mathrm{red}}S(\mathrm{Fe(III)})$	$\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	117.7 ± 8.6	114.9	2.8
$\Delta_{\mathrm{ox}}H(\mathrm{Fe, cr})$	$\mathrm{kJ\cdot mol^{-1}}$	-617.8 ± 3.0	-620.8	3.0
$\Delta_{\mathrm{ox}}H(\mathrm{Fe(II)})$	$\mathrm{kJ\cdot mol^{-1}}$	-149.0 ± 4.0	-150.0	1.0
$S^{\circ}_{\mathrm{m}}(\mathrm{FeCl_2, cr_e})$	$\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	118.2 ± 0.8	118.2	0.0
$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{FeCl_2, cr})$	$\mathrm{kJ\cdot mol^{-1}}$	-341.44 ± 0.93	-341.53	-0.09
$\Delta_{\mathrm{sln}}H(\mathrm{FeCl_2, cr})$	$\mathrm{kJ\cdot mol^{-1}}$	-82.91 ± 0.31	-82.92	0.01
$\Delta_{\mathrm{sln}}G(\mathrm{FeCl_2\cdot 4H_2O, cr})$	$\mathrm{kJ\cdot mol^{-1}}$	-17.16 ± 0.40	-17.17	0.01
$\Delta_{\mathrm{dehyd}}G(\mathrm{FeCl_2\cdot 4H_2O, cr})$	$\mathrm{kJ\cdot mol^{-1}}$	33.3 ± 3.9	33.8	-0.5
$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{FeBr_2, cr_e})$	$\mathrm{kJ\cdot mol^{-1}}$	$-245. \pm 4.$	-247.5	2.5
$\Delta_{\mathrm{sln}}H(\mathrm{FeBr_2, cr})$	$\mathrm{kJ\cdot mol^{-1}}$	-85.3 ± 1.4	-85.6	0.3
$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{FeCl_3, cr})$	$\mathrm{kJ\cdot mol^{-1}}$	-395.98 ± 0.14	-395.98	0.00
$\Delta_{\mathrm{sln}}H(\mathrm{FeCl_3, cr})$	$\mathrm{kJ\cdot mol^{-1}}$	-158.3 ± 3.6	-155.3	-3.4
$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{FeBr_3, cr_e})$	$\mathrm{kJ\cdot mol^{-1}}$	-262.63 ± 1.00	-262.59	-0.04
$\Delta_{\mathrm{sln}}H(\mathrm{FeBr_3, cr})$	$\mathrm{kJ\cdot mol^{-1}}$	-152.2 ± 3.6	-151.7	-0.5
$S^{\circ}_{\mathrm{m}}(\mathrm{FeSO_4\cdot 7H_2O, cr_e})$	$\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	409.1 ± 1.3	409.1	0.0
$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{FeSO_4\cdot 7H_2O, cr})$	$\mathrm{kJ\cdot mol^{-1}}$	-3014.87 ± 3.00	-3012.5	-2.4
$\Delta_{\mathrm{sln}}G(\mathrm{FeSO_4\cdot 7H_2O, cr})$	$\mathrm{kJ\cdot mol^{-1}}$	13.02 ± 0.37	13.01	0.01
$\Delta_{\mathrm{sln}}H(\mathrm{FeSO_4\cdot 7H_2O, cr})$	$\mathrm{kJ\cdot mol^{-1}}$	11.89 ± 0.60	12.07	-0.18
$S^{\circ}_{\mathrm{m}}(\mathrm{FeCO_3, cr_e})$	$\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	95.47 ± 1.00	95.54	0.07
$\Delta_{\mathrm{sln}}G(\mathrm{FeCO_3, cr})$	$\mathrm{kJ\cdot mol^{-1}}$	-42.4 ± 1.1	-42.7	0.3
$\Delta_{\mathrm{decomp}}H(\mathrm{FeCO_3, cr})$	$\mathrm{kJ\cdot mol^{-1}}$	-56.14 ± 2.76	-54.0	-2.1

Table XI-6: Quantities from the output of the second cycle optimization calculation.

$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{Fe}^{2+})$	$-(90.29 \pm 0.52)\ \mathrm{kJ\cdot mol^{-1}}$
$\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ}(\mathrm{Fe}^{2+})$	$-(90.72 \pm 0.64)\ \mathrm{kJ\cdot mol^{-1}}$
$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{Fe}^{3+})$	$-(50.06 \pm 0.97)\ \mathrm{kJ\cdot mol^{-1}}$
$\Delta_{\mathrm{f}}\mathrm{G}_{\mathrm{m}}^{\circ}(\mathrm{Fe}^{3+})$	$-(16.23 \pm 0.65)\ \mathrm{kJ\cdot mol^{-1}}$
$\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ}(\mathrm{FeCl_2\cdot 4H_2O,\ cr})$	$-(1284.54 \pm 0.71)\ \mathrm{kJ\cdot mol^{-1}}$
$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{FeCl_2,\ cr})$	$-(341.53 \pm 0.50)\ \mathrm{kJ\cdot mol^{-1}}$
$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{FeSO_4\cdot 7H_2O,\ cr})$	$-(3012.51 \pm 0.60)\ \mathrm{kJ\cdot mol^{-1}}$
$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{FeBr_2,\ cr})$	$-(247.50 \pm 0.99)\ \mathrm{kJ\cdot mol^{-1}}$
$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{FeCl_3,\ cr})$	$-(395.98 \pm 0.09)\ \mathrm{kJ\cdot mol^{-1}}$
$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{FeBr_3,\ cr})$	$-(262.59 \pm 0.63)\ \mathrm{kJ\cdot mol^{-1}}$
$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{FeCO_3,\ cr})$	$-(752.61 \pm 0.90)\ \mathrm{kJ\cdot mol^{-1}}$
$S_{\mathrm{m}}^{\circ}(\mathrm{FeCO_3,\ cr})$	$(95.54 \pm 0.65)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$
$S_{\mathrm{m}}^{\circ}(\mathrm{FeCl_2,\ cr})$	$(118.21 \pm 0.52)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$
$S_{\mathrm{m}}^{\circ}(\mathrm{FeSO_4\cdot 7H_2O,\ cr})$	$(409.12 \pm 0.82)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$

Table XI-7: Recalculated experimental quantities and uncertainties. The equations in the main text that are related to the thermodynamic quantities are those noted in Table XI-1.

$\Delta_{\mathrm{red}}G(\mathrm{Fe(III)})$	$-(74.49 \pm 0.91)\ \mathrm{kJ\cdot mol^{-1}}$
$\Delta_{\mathrm{red}}S(\mathrm{Fe(III)})$	$(114.9 \pm 4.8)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$
$\Delta_{\mathrm{ox}}H(\mathrm{Fe,\ cr})$	$-(620.8 \pm 1.0)\ \mathrm{kJ\cdot mol^{-1}}$
$\Delta_{\mathrm{ox}}H(\mathrm{Fe(II)})$	$-(150.0 \pm 1.1)\ \mathrm{kJ\cdot mol^{-1}}$
$\Delta_{\mathrm{sln}}H(\mathrm{FeCl_2,\ cr})$	$-(82.92 \pm 0.86)\ \mathrm{kJ\cdot mol^{-1}}$
$\Delta_{\mathrm{sln}}G(\mathrm{FeCl_2\cdot 4H_2O,\ cr})$	$-(17.17 \pm 1.00)\ \mathrm{kJ\cdot mol^{-1}}$
$\Delta_{\mathrm{dehyd}}G(\mathrm{FeCl_2\cdot 4H_2O,\ cr})$	$(33.8 \pm 1.0)\ \mathrm{kJ\cdot mol^{-1}}$
$\Delta_{\mathrm{sln}}H(\mathrm{FeBr_2,\ cr})$	$-(85.6 \pm 1.2)\ \mathrm{kJ\cdot mol^{-1}}$
$\Delta_{\mathrm{sln}}H(\mathrm{FeCl_3,\ cr})$	$-(155.3 \pm 1.0)\ \mathrm{kJ\cdot mol^{-1}}$
$\Delta_{\mathrm{sln}}H(\mathrm{FeBr_3,\ cr})$	$-(151.7 \pm 1.2)\ \mathrm{kJ\cdot mol^{-1}}$
$\Delta_{\mathrm{sln}}G(\mathrm{FeSO_4\cdot 7H_2O,\ cr})$	$(13.0 \pm 1.3)\ \mathrm{kJ\cdot mol^{-1}}$
$\Delta_{\mathrm{sln}}H(\mathrm{FeSO_4\cdot 7H_2O,\ cr})$	$(12.07 \pm 0.84)\ \mathrm{kJ\cdot mol^{-1}}$
$\Delta_{\mathrm{sln}}G(\mathrm{FeCO_3,\ cr})$	$-(42.7 \pm 1.1)\ \mathrm{kJ\cdot mol^{-1}}$
$\Delta_{\mathrm{decomp}}H(\mathrm{FeCO_3,\ cr})$	$-(54.0 \pm 1.6)\ \mathrm{kJ\cdot mol^{-1}}$

XI.3 Further considerations

The type of analysis done here involves many, sometimes highly correlated, values. Using the thermodynamic cycles described, the correlation between the following pairs of derived thermodynamic quantities is found to be particularly high (correlation coefficients greater or equal to 0.80):

$\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\circ}$ (Fe^{2+}) with $\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\circ}$ ($\mathrm{FeCl_2}$, cr)

$\Delta_{\mathrm{f}} G_{\mathrm{m}}^{\circ}$ (Fe^{2+}) with $\Delta_{\mathrm{f}} G_{\mathrm{m}}^{\circ}$ (Fe^{3+})

$\Delta_{\mathrm{f}} G_{\mathrm{m}}^{\circ}$ (Fe^{2+}) with $\Delta_{\mathrm{f}} G_{\mathrm{m}}^{\circ}$ ($\mathrm{FeCl_2{\cdot}4H_2O}$, cr)

$\Delta_{\mathrm{f}} G_{\mathrm{m}}^{\circ}$ (Fe^{3+}) with $\Delta_{\mathrm{f}} G_{\mathrm{m}}^{\circ}$ ($\mathrm{FeCl_2{\cdot}4H_2O}$, cr)

In lieu of a protracted Monte Carlo treatment, a rather crude sensitivity analysis has been attempted by sequentially varying each of the input experimental values by amount equal to the final assigned $+2\sigma$ and -2σ. This should indicate, for the selected set of cycles only, the experimenatl uncertainties that have the greatest impact on the derived thermodynamic quantities. Thus a future similar analysis likely would best benefit from more accurate experimental determinations of the values (as listed in Tables XI-1 and XI-5) for $\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\circ}$ ($\mathrm{FeCl_2}$, cr) and $\Delta_{\mathrm{red}} G$ (Fe(II)), and to a lesser extent for $\Delta_{\mathrm{sln}} H$ ($\mathrm{FeSO_4{\cdot}7H_2O}$, cr), $\Delta_{\mathrm{decomp}} H$ ($\mathrm{FeCO_3}$, cr) and $\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\circ}$ ($\mathrm{FeSO_4{\cdot}7H_2O}$, cr).

Part 4

Appendices

Appendix A

Discussion of selected references

This appendix comprises discussions relating to a number of key publications which contain experimental information cited in this review. These discussions are fundamental in explaining the accuracy of the data concerned and the interpretation of the experiments, but they are too lengthy or are related to too many different sections to be included in the main text. The notation used in this appendix is consistent with that used in the present book, and not necessarily consistent with that used in the publication under discussion.

[1857DEB]

This paper is of some historical interest as an early study of reactions between controlled-ratio gas mixtures (H_2-H_2O and CO-CO_2), metals (including iron) and their oxides. This is not a quantitative study.

[1870DEV]

This series of three papers (the companion papers are [1870DEV2] and [1870DEV3]) is of historical interest as the first attempt to measure equilibrium constants for the reaction between H_2-H_2O mixtures, iron and magnetite. Iron specimens in a glass (up to 440 °C) or porcelain tube (up to an estimated 1600 °C) were allowed to react with water vapour (constant p_{H_2O}, controlled by a water or ice bath) and the resulting p_{H_2} was determined from the equilibrium total pressure. Specimen temperature was maintained by heroic but relatively inaccurate methods, *e.g.*, by baths of boiling Hg, S, Cd, or Zn.

The results were inaccurate for a variety of reasons: *e.g.*, diffusion effects in gas mixtures; the role of wüstite was not understood at the time, nor were the kinetic limitations at lower temperatures; gaseous impurities from outgassing of solid surfaces doubtless affected pressure measurements; temperature control was difficult. Nevertheless, the basic experimental procedure was adapted and improved in many subsequent studies spanning half a century.

[1874WIE]

Wiedemann reported values for the vapour pressure of water in equilibrium with hydrated Fe(II) sulfate for temperatures from 20 to 75 °C. The measurements are rather scattered at the lower temperatures, and decomposition occurred above 70 °C.

Nevertheless, based on reanalysis of the values between 30 and 55.2 °C an average enthalpy of reaction for

$$FeSO_4{\cdot}7H_2O(cr) \rightleftharpoons FeSO_4{\cdot}4H_2O(cr) + 3\,H_2O(l), \qquad (A.1)$$

is calculated to be $\Delta_r H_m^o$ (A.1) = (161.2 ± 2.0) $kJ{\cdot}mol^{-1}$, in quite reasonable agreement with later work (*e.g.*, [1964KOH/ZAS2]). For weighting purposes, the vapour pressures are estimated to have uncertainties of 270 Pa.

[1875BER2]

Berthelot reported the heat of precipitation of $FeCO_3$ on mixing aqueous solutions of ~ 0.5 $mol{\cdot}kg^{-1}$ in $FeSO_4$ with solutions of K_2CO_3 and Na_2CO_3 at 16 °C. The reactions were found to be endothermic (~7.5 $kJ{\cdot}mol^{-1}$). The results suggest a value of approximately – 760 $kJ{\cdot}mol^{-1}$ for the enthalpy of formation of poorly crystalline $FeCO_3$. However, no characterization of the final solid and the initial iron(II) sulfate was reported, nor were any precautions noted to preclude oxidation of the solution. It also would be difficult to correct the enthalpy values to $I = 0$ from the rather high and variable ionic strengths. The results are not used further in the present review.

[1881BER]

Berthelot measured the heat of dissolution in aqueous HCl of a specimen of the most reactive form of synthetic magnetite obtained by Moissan [1880MOI]. He calculated $\Delta_f H_m^o$ (Fe_3O_4, cr) from these heats of dissolution and known, but uncited (possibly from Thomsen) enthalpies of formation for hydrated forms of FeO and Fe_2O_3, nominally $Fe(OH)_2$(s) and $Fe(OH)_3$(s).

Of mainly historic interest, this is probably the first determination of $\Delta_f H_m^o$ (Fe_3O_4, cr). Berthelot admitted that the value he obtained (about – 1122 $kJ{\cdot}mol^{-1}$ using modern atomic mass values) is not corrected for the heats of hydration of FeO and Fe_2O_3, nor for the heat of transformation of magnetite from a reactive state to a stable form. He also recognized the need for knowledge of $C_p(T)$ in order to predict or interpret high-temperature reactions involving magnetite. He thus foresaw many of the key issues of the current assessment of Fe-O-H thermochemistry! While the value he obtained differs from modern values by only about 2 $kJ{\cdot}mol^{-1}$ Fe, this appears to be due to a fortuitous cancellation of errors, and the value is not included in the current assessment. A slightly different value attributed to Le Châtelier [1895CHA] by others (*e.g.*, [1921CHA], [1925MCC]) reflects only a different rounding of Berthelot's data by Le Châtelier and is not an independent determination.

[1881SAB]

In this and a later paper [1889SAB] Sabatier reported a limited number of heat of solution measurements of $FeCl_2{\cdot}2H_2O$, $FeCl_2{\cdot}4H_2O$, $FeCl_3{\cdot}2.5H_2O$ and $FeCl_3{\cdot}6H_2O$ at temperatures between 290 and 294 K and water to salt ratios between 300 and 1200. The values for the Fe(III) salts are reasonably consistent with later measurements

[1984NOV/BEL], but are not sufficiently accurate or detailed to be used in the present review. The difference in the enthalpies of formation for the two Fe(II) hydrates differs markedly (by about 10 $\text{kJ}\cdot\text{mol}^{-1}$) from what was later reported by Schäfer [1949SCH], and the value for the dissolution of the tetrahydrate is inconsistent with other reports [1908THO], [1941PER], but in a direction that suggests even poorer agreement with Schäfer for the dihydrate [1949SCH].

[1884BEL]

This chapter is of historic interest as a pioneering, systematic study of the Fe-C-O system, based on analyses of blast furnace gases including CO and CO_2 content.

[1889SAB]

See the entry for [1881SAB].

[1892ROO]

This paper contains solubility results for the $FeCl_3$-H_2O-NH_4Cl system, and includes some results for the $FeCl_3$-H_2O system, which was discussed in more detail in [1892ROO2].

[1892ROO2]

Careful, detailed solubility measurements were reported for the $FeCl_3$-H_2O system from – 55 to 100 °C. The following hydrates were identified: $FeCl_3\cdot6H_2O$, $FeCl_3\cdot3.5H_2O$, $FeCl_3\cdot2.5H_2O$ and $FeCl_3\cdot2H_2O$ (also see [1892ROO], [1894ROO/SCH]). All were found to melt congruently, at 37, 32, 56 and 73.5 °C, respectively. An excellent discussion of the results was provided by Findlay [1931FIN]. Linke [1956LIN] later identified another hydrate $FeCl_3\cdot10H_2O$, and augmented and reinterpreted the results for lower temperatures.

[1893LEM]

Approximate successive heats of dilution at 286 K were measured for concentrated (3 M) aqueous solutions of $FeCl_3$. The final concentration of Fe(II) was 0.17 M. The enthalpy of dilution from 3 to 1 M was found to be more than twice the enthalpy of dilution from 1 to 0.17 M. Somewhat smaller molar heats of dilution were reported for aqueous solutions of $Fe_2(SO_4)_3$. The solutions were not acidified to inhibit hydrolysis, and the results are not used further in the present review.

[1894LES]

The partial pressures of water measured above samples of the lower hydrates of iron(II) chloride are in rough agreement with values from the more careful later study of Schäfer [1949SCH], but the values from [1894LES] were not used further in the present review.

[1894ROO/SCH]

This paper contains results for the $FeCl_3$-H_2O-HCl system. See the discussion for [1892ROO2].

[1895CHA]

Le Châtelier reported a number of heat-of-combustion measurements involving "FeO"(cr), Fe_2O_3(cr), $FeCO_3$(cr), and $FeSiO_3$(cr), relative to Fe_3O_4(cr), and used Berthelot's [1881BER] value for $\Delta_f H^o_m$ (Fe_3O_4, cr) to derive $\Delta_f H^o_m$ values for these solids.

This paper is of historical interest, but the results were inaccurate by modern standards. Difficulties appear to include incomplete conversion in the bomb calorimeter, limited understanding of "FeO" at the time, and lack of analytical data. The enthalpy of oxidation of magnetite to hematite differs from modern values by about 9 $kJ \cdot mol^{-1}$ Fe. It appears that the two forms of Fe_2O_3 studied by Le Châtelier were poorly- and well-crystallized hematite specimens, rather than maghemite and hematite as recently suggested in [2001DRO].

Le Châtelier reported that the heat of combustion of a natural sample of $FeCO_3$ to form Fe_3O_4(cr) and CO_2(g) was 0.0 $kcal \cdot mol^{-1}$ (probably at "room" temperature). No estimate of the uncertainty was provided. Using auxiliary data from the present review for an assumed temperature of 298 K, the calculated value of $\Delta_f H^o_m$ ($FeCO_3$, cr) is $-$ 765 $kJ \cdot mol^{-1}$. This is more negative than the value selected in the present review (Section X.1.2.1.3).

Combustion of a 1:1 molar mixture of $FeCO_3$(cr) with α-SiO_2 was assumed to form $FeSiO_3$(cr), but no analysis of the final product was reported. The reaction was found to be endothermic (~ 32 $kJ \cdot mol^{-1}$), but markedly less endothermic than the ~ 75 - 90 $kJ \cdot mol^{-1}$ (depending on the value used for $\Delta_f H^o_m$ ($FeCO_3$, cr)) that might be expected for formation of either α-Fe_2SiO_4 or ferrosilite [1997FAB/SUN].

None of these results are used further in the present review.

[1896GOO]

Conductance measurements were made at 25 °C over a range of $FeCl_3$ concentrations. The molar conductances of well-mixed solutions were found to change with time accompanied by a change in colour that is consistent with gradual colloid formation. This pioneering work was a warning to subsequent studies of the ease with which Fe(III) can form colloids.

No quantitative results could be gleaned from this paper.

[1900COH/VIS]

Cohen and Visser reported a limited set of values for the vapour pressure of water in equilibrium with hydrated Fe(II) sulfate for temperatures from 30.7 to 46.4 °C. Based on reanalysis of the values, $\Delta_r H_m^o$ (A.2), the average enthalpy of reaction for

$$FeSO_4{\cdot}7H_2O(cr) \rightleftharpoons FeSO_4{\cdot}4H_2O(cr) + 3\,H_2O(g) \qquad (A.2)$$

is calculated to be 154.9 $kJ{\cdot}mol^{-1}$, in quite reasonable agreement with later work over a similar temperature range (*e.g.*, [2002CHO/SEA]). For weighting purposes, the vapour pressures are estimated to have uncertainties of 130 Pa.

The same paper was also published as [1901COH/VIS].

[1903BAU/GLA]

This was an early attempt to measure equilibria in CO-CO_2 atmospheres between Fe and "FeO" (11 measurements at 803 to 1153 K), and between "FeO" and Fe_3O_4 (25 measurements at 623 to 1223 K). This study predates understanding of the wüstite phase field and non-stoichiometry (*e.g.*, [1921CHA], [1927SCH/DIN]), and some data lie below the Fe-Fe_3O_4-wüstite eutectoid. Some of the data were obtained at temperatures too low for equilibrium to have been readily attained. This study is not considered further in the current review.

[1905ANS]

This thesis was unavailable to the present reviewers, but some of the data on equilibria between iron sulfates, sulfur oxides, oxygen, and iron oxides were tabulated in papers by Keppeler and D'Ans [1908KEP/ANS] and by Neumann and Heintke [1937NEU/HEI].

[1907FRA]

Fraenckel [1907FRA] reported the solubilities of hydrated iron sulfates in water for temperatures from – 1.82 to 90.13 °C. The equilibrium solids were stated to be $FeSO_4{\cdot}7H_2O$ from – 1.82 to 56.6 °C and $FeSO_4{\cdot}4H_2O$ from 56.6 to 64.4 °C, with $FeSO_4{\cdot}H_2O$ at higher temperatures. This appears to have been very careful work. Omission of the data point for 68.02 °C (marked by the authors as "instabl", suggests transformation of the heptahydrate to the monohydrate near 58 °C (in reasonable agreement with Bullough *et al.* [1952BUL/CAN]), with no evidence for the tetrahydrate. However, this temperature is 7 K lower than the transition temperature based on the equations of Reardon and Beckie [1987REA/BEC]. The results at higher temperatures are higher than found later by others [1952BUL/CAN], [1956KOB/FRE], probably because insufficient time was allowed for equilibrium to be attained.

[1908KEP/ANS]

The equilibria between anhydrous iron sulfates and iron oxides were studied by a dynamic method in which the sulfur oxides from thermal decomposition (~750 to

1000 K) were collected and analyzed. The iron(II) sulfate was probably impure [1937NEU/HEI], [1942MOO/KEL]. A basic iron(III) sulfate ($Fe_2O(SO_4)_2$) was reported, but its existence was not supported by later investigations [1973SKE/ESP], [1986JAC/IYE]. Results of the study on $Fe_2(SO_4)_3$(cr) are not considered to be as accurate as those from later static vapour-pressure measurements [1937NEU/HEI], [1960WAR/ING] or electrochemical [1986JAC/IYE] studies. The results were not used further in the present review.

[1908THO]

Thomsen reported the molar enthalpies of solution of $FeCl_2$(cr) (salt: water ratio 1:350) and $FeCl_2\cdot4H_2O$ (salt: water ratio 1:400) at 18 °C as $-$ 74.9 $kJ\cdot mol^{-1}$ ($-$ 17.9 $kcal\cdot mol^{-1}$) and $-$ 11.5 $kJ\cdot mol^{-1}$ ($-$ 2.75 $kcal\cdot mol^{-1}$). These values are consistent with later, more accurate measurements, *e.g.*, [1941PER], [1977CER/HEP]. Assuming each additional water of hydration increases the value of $C^{o}_{p,m}$ of the salt by 40 $J\cdot K^{-1}\cdot mol^{-1}$, the value of the heat capacity of hydration to form the tetrahydrate is approximately $-$ 0.14 $J\cdot K^{-1}\cdot mol^{-1}$. Therefore, neglecting the enthalpy of dilution of water in the ~ 0.15 m iron chloride solution, at 25 °C the enthalpy of hydration is $-$ (64.4 ± 4.0) $kJ\cdot mol^{-1}$, where the uncertainty is estimated in the present review. This is within 4.4 $kJ\cdot mol^{-1}$ of the difference calculated based on Schäfer's vapour-pressure measurements [1949SCH].

The heat of dissolution of Fe(cr) in aqueous hydrochloric acid solution (initially 200 H_2O, 1.0 HCl—the final solution probably had a very low concentration of HCl and was, in essence, $FeCl_2$(sln), salt:water ratio 1:350) was reported as $-$ 89.2 $kJ\cdot mol^{-1}$ ($-$ 21.32 $kcal\cdot mol^{-1}$). Using this and the reported heat of solution of the anhydrous salt, Parker and Khodakovskii [1995PAR/KHO] calculated $-$ (345.2 ± 2.0) $kJ\cdot mol^{-1}$ for $\Delta_f H^{o}_{m}$ ($FeCl_2$, cr, 298.15 K). The final acid concentration in Thomsen's dissolution of Fe(cr) is not clear from the tabulations in [1908THO]. Although the data can be used to calculate a value for $\Delta_f H^{o}_{m}$ ($FeCl_2$, cr, 298.15 K) similar to the values found from other studies [1959KOE/COU], [1989EVD/EFI2], the uncertainties are large, and this work is not used further in the present review.

Thomsen reported a value of 18.9 $kJ\cdot mol^{-1}$ (4.510 $kcal\cdot mol^{-1}$) for the heat of solution of $FeSO_4\cdot7H_2O$ in water (one mole of salt per 400 moles of water) at 18 °C. This single value is comparable to those in later work [1914FOR], [1992PRZ/WIS], but is not used further in the present review.

[1908WOH/PLU]

The equilibria between anhydrous iron(III) sulfates and iron(III) and sulfur oxides were studied by a static method. Results of the study are not considered to be as accurate as those from later static vapour-pressure measurements [1937NEU/HEI], [1960WAR/ING] or electrochemical [1986JAC/IYE] studies. The results were not used further in the present review.

[1910BOD/SUZ]

A limited set of measurements was carried out to attempt to resolve differences between the results of two studies [1908KEP/ANS], [1908WOH/PLU] related to the equilibria between anhydrous iron(III) sulfate and iron and sulfur oxides. Both dynamic and static methods were used. The results emphasized the need to use low flow rates and long flow times in the dynamic studies. The sparse results were not used further in the present review.

[1912EHL/HEM]

The solubility of $FeCO_3$ was measured in water at ~ 14 °C under a 0.2 MPa (2 atm) pressure of $CO_2(g)$. However, the method of synthesis of the solid was not specified, the solution was equilibrated only for 24 hours, the analysis procedures are not described, and it is not clear whether oxygen was scrupulously excluded from the solutions. The reported solution concentration of iron is an order of magnitude greater than found in rather similar experiments by Greenberg and Tomson [1992GRE/TOM], and leads to a value of 10^{-7} $\text{mol}^2\cdot\text{dm}^{-6}$ for the equilibrium constant of the reaction

$$FeCO_3(cr) \rightleftharpoons Fe^{2+} + CO_3^{2-}\,.$$

The result is not credited in the present review.

[1912NOY/BRA]

To obtain the value of the standard potential $E^\circ\,(Fe^{3+}/Fe^{2+})$, Noyes and Brann determined the equilibrium constant value of Reaction (A.3) at 25 °C.

$$Fe^{3+} + Ag(s) \rightleftharpoons Fe^{2+} + Ag^{+} \qquad (A.3)$$

The medium was nitric acid at concentrations between 0 and 0.1 M, total iron concentrations between 0.03 and 0.23 M and Ag^+ between 0.025 and 0.2 M. Activity effects for species in such solutions are relatively difficult to calculate using simple forms of the SIT formalism, because for many samples, especially those with higher iron concentrations, the ionic strength is mostly due to the metal salts. The extrapolation by the authors to zero ionic strength yielded an equilibrium constant value of 0.128 for Reaction (A.3).

At 25 °C, $E^\circ\,(Fe^{3+}/Fe^{2+})$ and $K^\circ\,(A.3)$ are correlated by Eq. (A.4)

$$E^\circ\,(Fe^{3+}/Fe^{2+}) = E^\circ\,(Ag^{+}/Ag(s)) - 0.05916\ \log_{10} K^\circ\,(A.3). \qquad (A.4)$$

Hydrolysis of Fe^{3+} was not taken into account by the authors, and the results were reinterpreted by [1934BRA/HER] and again in the present review after recalculation of the Fe^{3+} concentrations. Two different methods derived from the SIT have been used.

1) A linear regression plot was done of the logarithm of the molal equilibrium constant + $4D$ as a function of I_m to get the value of $K^\circ\,(A.3)$ by extrapolation to $I = 0$.

Thirteen data points for the higher acidities (0.05 to 0.1 M HNO_3) and total metal (Fe^{3+} + Fe^{2+} + Ag^+) concentrations (0.054 to 0.29 m) were selected for that plot.

That yielded $-(0.391 \pm 0.046)$ for $\log_{10} K^{\circ}$ (A.3), and using the TDB value for E° (Ag^+/Ag(s))

$$E^{\circ}\,(Fe^{3+}/Fe^{2+}) = (0.7990 \pm 0.0016) - (0.0231 \pm 0.0027) = (0.7759 \pm 0.0032)\text{ V}$$

(which can be rounded to (0.776 ± 0.003) V) and the value of $-\Delta\varepsilon$ is (0.30 ± 0.08) kg·mol^{-1}. The linearity of the plot is poor, $R^2 = 0.832$.

2) Activities of the Fe^{3+}, Fe^{2+} and Ag^+ ions were calculated for the selected data points treated above by applying the SIT formula:

$$\log_{10} \gamma_{M^{z+}} = -D z^2 + \varepsilon(M^{z+}, NO_3^-)\, m_{NO_3^-} \qquad (A.5)$$

and then calculating K° (A.3) ($= a_{Fe^{2+}}\, a_{Ag^+}/a_{Fe^{3+}} = K_m{\cdot}\gamma_{Fe^{2+}}\, \gamma_{Ag^+}/\gamma_{Fe^{3+}}$) for each data point.

The values of $\varepsilon(M^{z+}, NO_3^-)$ listed in Table B-4 were used. As no value of $\varepsilon(Fe^{2+}, NO_3^-)$ is available, the value (0.182 ± 0.010) kg·mol^{-1} of $\varepsilon(Ni^{2+}, NO_3^-)$ has been used.

This process yielded a preliminary value of (0.429 ± 0.035) mol·kg^{-1} for K° (A.3) and (0.777 ± 0.003) V for E° (Fe^{3+}/Fe^{2+}). However, in this recalculation it was clear that the values of K° (A.3) seemed to increase with increasing ionic strength, and mostly for those solutions with higher total metal concentrations. So there is a deviation from the SIT model, for which most of the interaction coefficients have been evaluated in dilute solutions of metal cations in salt solutions. To get a more realistic K° (A.3) value, we used a linear fit of K'° *vs.* $I_m^{1/2}$ where the values used for K'° were the preliminary, anomalously variable K° values. This linear regression yielded: K° = (0.336 ± 0.064) mol·kg^{-1} for $I = 0$ which leads to E° (Fe^{3+}/Fe^{2+}) = (0.771 ± 0.005) V. Here the linear correlation was even poorer, $R^2 = 0.42$.

So in spite of the unusual set of solution compositions, the results of the SIT treatments are in fair agreement with that of Bray and Hershey [1934BRA/HER] (E° (Fe^{3+}/Fe^{2+}) = (0.7725 ± 0.0010) V), although the uncertainties probably were underestimated. The E° (Fe^{3+}/Fe^{2+}) values, derived using the SIT, also are close to those derived from electrochemical cell-potential measurements. However, we did not use these results to determine the recommended value of E° (Fe^{3+}/Fe^{2+}) because of the abundance of other useful data and possible systematic errors from partial oxidation of Fe^{2+} by the NO_3^- ions.

[1912RUF/GER]

This paper includes a direct (heat of combustion) measurement of $\Delta_f H_m^{\circ}$ (Fe_3O_4, cr), corrected for incomplete conversion (wüstite is treated as "FeO") and for impurities.

See the Appendix A entry of [1913RUF/GER], which presents further corrections based on new data for the oxidation of “FeO” to Fe_3O_4.

[1913GRU]

This thesis was not available to the present reviewer, but a few of the data points were reported by Wöhler and Grünzweig [1913WOH/GRU] and Neumann and Heintke [1937NEU/HEI].

[1913MIX]

Various reaction enthalpies, including $\Delta_f H^\circ_m$ for “FeO”(cr), Fe_3O_4(cr), and α-Fe_2O_3, were obtained by measuring heats of fusion in sodium peroxide (Na_2O_2) in the presence of elemental sulfur. The value of $\Delta_f H^\circ_m$(Fe_3O_4, cr, ~298 K) was also determined directly by oxygen combustion calorimetry.

Although reproducibility was quite good among the accepted Na_2O_2 fusion runs with Fe_2O_3, the number of runs deemed successful was quite low (3 of 7), and the value obtained, $\Delta_f H^\circ_m$(Fe_2O_3, α, ~298 K) = −804 kJ·mol^{-1}, is about 20 kJ·mol^{-1} less negative than typical current values. While the cumulative statistical uncertainty is only ± 4.2 kJ·mol^{-1}, there is a large uncertainty associated with the reduction of Na_2O_2(s) to Na_2O(s). Recalculation using Mixter’s thermochemical cycle and more recent enthalpy data for the sodium oxides yields a much more negative value, $\Delta_f H^\circ_m$(Fe_2O_3, α, ~ 298 K) = −(847 ± 20) kJ·mol^{-1}. It is also possible that different iron-containing starting materials did not yield the same final states (mixture of solid sodium oxides, sulfates and ferrates) upon reaction with the sodium peroxide-sulfur mixture. This would introduce an indeterminate, systematic error.

As with other attempts to measure $\Delta_f H^\circ_m$(Fe_3O_4, cr, ~298 K) directly, the combustion calorimetry is marred by incomplete conversion, relatively poor reproducibility, and the difficulty of correcting for wüstite impurity in the combustion product. The three runs yield $\Delta_f H^\circ_m$(Fe_3O_4, cr) = −(1111 ± 20) kJ·mol^{-1} (statistical uncertainty only, based on oxygen consumption and ignoring wüstite).

Because of the large uncertainties in the formation enthalpies for both hematite and magnetite, the results from this study were not included in the current assessment.

[1913ROL/ACC]

The authors reported average molar heat capacities for hydrated $FeSO_4 \cdot xH_2O$ (x = 4.89 to 7.04) for the temperature range 273.1 to 291 K. From these, values for the heat capacities of $FeSO_4 \cdot 4H_2O$(cr) and $FeSO_4 \cdot 7H_2O$(cr) (266.0 J·K^{-1}·mol^{-1} and 385.5 J·K^{-1}·mol^{-1}) were calculated. Recalculation using a linear least-squares treatment suggests 268 and 384 kJ·mol^{-1}. The value for $FeSO_4 \cdot 7H_2O$(cr) is approximately 8 J·K^{-1}·mol^{-1} less than the value based on Lyon and Giauque [1949LYO/GIA]. Also, there is no proof offered that the mixed hydrates contained $FeSO_4 \cdot 4H_2O$(cr) rather than $FeSO_4 \cdot H_2O$(cr), nor is there any proof that the composition-heat capacity relationship is linear (there are two compositions with an H_2O:Fe ratio within 0.04 of 7.00, and four compositions with an H_2O:Fe ratio within 0.12 of 5.00). The values reported for the zinc sulfate hydrates in the same paper [1913ROL/ACC] show discrepancies of a similar magnitude with respect to other literature values [1982WAG/EVA].

[1913RUF/GER]

This paper includes new measurements of the enthalpy of oxidation of wüstite (treated as FeO) to magnetite, which are then used to revise the authors' previous determination [1912RUF/GER] of $\Delta_f H_m^\circ$ (Fe_3O_4, cr) by combustion of metallic iron.

The authors also refer to a Russian measurement (Jarmilow, *Journal der Russischen Metallurgischen Gesellschaft*, (1911), 357-366), which is now difficult to obtain, but appears to be inaccurate, because it yielded the very negative value of $\Delta_f H_m^\circ$ (Fe_3O_4, cr) ≈ -1147 kJ·mol^{-1}.

The reported value of $\Delta_f H_m^\circ$ (Fe_3O_4, cr) at an unstated near-ambient temperature, corrected for modern atomic mass values, is $-(1118.6 \pm 0.9)$ kJ·mol^{-1}. The uncertainty is evidently over-optimistic; it is based on the small difference between two average values obtained with different iron specimens, each average being based on two measurements. When all four measurements are considered together, a much larger 95% uncertainty limit is obtained: $\Delta_f H_m^\circ$ (Fe_3O_4, cr) = $-(1118.6 \pm 11.2)$ kJ·mol^{-1}. This does not include any systematic errors from the treatment of wüstite impurity (from incomplete combustion) as stoichiometric FeO. Although the mean value agrees quite closely with more recent values for $\Delta_f H_m^\circ$ (Fe_3O_4, cr, 25 °C), it was not used in the current assessment because of the large uncertainty.

[1914FOR]

Values of the heats of solution of $FeSO_4 \cdot 7H_2O$ (18.09 kJ·mol^{-1}), $FeSO_4 \cdot 4H_2O$ ($-$ 6.69 kJ·mol^{-1}), $FeSO_4 \cdot H_2O$ ($-$ 31.54 kJ·mol^{-1}) and $FeSO_4$ ($-$ 62.35 kJ·mol^{-1}) were obtained by dissolution in water at 286.65 K (13.5 °C). The amount of water per mole of iron was not reported, but was probably similar for the dissolution of all four salts. An attempt (probably unsuccessful) was made to allow for the slight decomposition of the anhydrous solid during the synthesis. The enthalpy differences per mole of hydrated water for the heptahydrate, tetrahydrate and monohydrate are similar to those reported by Larson [1968LAR] at 298.15 K, but the details reported are inadequate to allow a direct quantitative comparison of the results with later work.

[1916SOS/HOS]

Composition– p_{O_2} isotherms for the Fe_3O_4-Fe_2O_3 system were measured at 1373 and 1473 K, but the interpretation in terms of a continuous solid solution series between magnetite and hematite is at odds with more recent phase equilibrium measurements (*e.g.*, [1961SAL], [1967KOM/OLE], and many others). If the results are reinterpreted in terms of a two-phase equilibrium between Fe_3O_{4+x} and Fe_2O_{3-y}, the equilibrium p_{O_2} values are ~0.13 Pa at 1373 K and ~2.5 Pa at 1473 K.

The authors state: "It would be too long a task to review completely the history of the many researches upon the iron oxides"... making the current review, 90 years later, all the more daunting!

A historically useful table mentions a number of mixed Fe(II), Fe(III) oxides, reported in the early literature, that are no longer accepted as distinct, stoichiometric phases: Fe_7O_{10}, $Fe_{13}O_{18}$, Fe_8O_{11}, $Fe_{11}O_{15}$, Fe_4O_5, Fe_5O_6, and Fe_6O_7.

Additional details of the dissociation of hematite in air at 1373 to 1573 K are provided in a companion paper, [1916HOS/SOS].

[1916TRE]

This pioneering cell-potential study predates the development of ZrO_2-based oxide ion-conducting electrolytes, which revolutionized high-temperature solid-state electrochemical studies on oxides, by about 40 years. Measurements were made relative to air, using an O-saturated Ag electrode and a complex porcelain/borax/silicate-glass electrolyte. Measurements were reported for 8 different oxide couples including Fe-"FeO", "FeO"-Fe_3O_4, and Fe_3O_4-Fe_2O_3 at temperatures near 1300 K, but the precision and accuracy were quite low and results are not included in the current review.

[1918SMI]

Crystalline $FeCO_3(s)$ was prepared in a steel bottle from equimolar quantities of iron(II) sulfate and sodium carbonate dissolved in water saturated with $CO_2(g)$. The bottle was pressurized to ~2.8 MPa and with $CO_2(g)$, kept at a temperature of 100 °C for "several" days, and the resulting crystalline precipitate (isomorphous with calcite and similar to siderite [1849SEN]) was washed with water saturated with $CO_2(g)$. No chemical analysis of the solid phase was given; and there was no check for a possible $Na_2SO_4(s)$ impurity in the precipitate. However, it seems reasonable that the washing procedure removed "most" of the impurities, provided that no mixed crystals were formed. Redox was not controlled.

Samples of the filtered, crystalline solid (50 to 100 g) were contacted with water containing carbon dioxide in a rotating sealed vessel for a one-week equilibration period. Fourteen individual experiments were done at 30 °C using carbon dioxide pressures between 0.5 MPa and 2.3 MPa (the pressures were measured but not reported). Aliquots were filtered, withdrawn into evacuated flasks and analyzed for total CO_2 (absorption on weighed soda-lime/phosphorus pentoxide mixtures) and total Fe (titration with permanganate after oxidation with nitric acid, precipitation as the hydroxide and re-reduction to Fe(II) by amalgamated Zn). The equilibrium iron(II) concentrations (0.00245 to 0.00434 $mol\cdot dm^{-3}$) at 30 °C were reported, as were the final concentrations of "$H_2CO_3(aq)$" (0.1868 to 0.7600 $mol\cdot dm^{-3}$), though actually it was the final total carbonate concentration in each solution that was measured. A rough conversion of the original data to molal units was done by assuming the densities of the dilute solutions at equilibrium to be equal to the density of water at 30 °C (995.65 $\text{g}\cdot\text{dm}^{-3}$ [1972KEL2]).

The measured values are consistent with those reported in later work [1969LAN], [1980REI], [1981REI/JOH], [1992GRE/TOM].

The original evaluation of the author used the law of mass action, and assumed that the formal $Fe(HCO_3)_2$ complex (according to the mass balance) is essentially completely dissociated. The author did not consider the presence of H^+ in his evaluation.

The reported iron and total carbonate concentrations were reanalysed using CODATA values for $CO_2(g)$, $CO_2(aq)$, HCO_3^-, CO_3^{2-} and $H_2O(l)$ at 298.15 K and the temperature dependence of the carbonate equilibria and ion-product of water from the equations of Nordstrom *et al.* [1990NOR/PLU]. Because the final solutions all had ionic strengths of less than 0.1 $\text{mol}\cdot\text{kg}^{-1}$, essentially no additional uncertainty is introduced by correction of these values to $I = 0$ using the standard TDB procedure, but neglecting interaction coefficients. If quantities of any iron(II) carbonate aqueous complex are assumed to be negligible, the average value for $\log_{10} {}^{*}K_{p,\text{s},0}$ (A.6) at 303.15 K is (7.495 ± 0.014) (this uncertainty represents the 95% confidence limit, not including uncertainties in the auxiliary data).

$$FeCO_3(cr) + 2\,H^+ \rightleftharpoons Fe^{2+} + CO_2(g) + H_2O(l) \qquad (A.6)$$

This is essentially the same as the values reported from recalculations in the papers of Langmuir [1969LAN] and Preis and Gamsjäger [2002PRE/GAM] (whereas the recalculated value in Nordstrom *et al.* [1990NOR/PLU] is smaller by ~ 0.3 in $\log_{10} {}^{*}K_{p,\text{s},0}$).

Another re-evaluation was done by assuming that the complex $FeHCO_3^+$ can form under the experimental conditions. In this calculation the species Fe^{2+}, $FeHCO_3^+$, H^+, $CO_2(aq)$ and HCO_3^- have been considered.

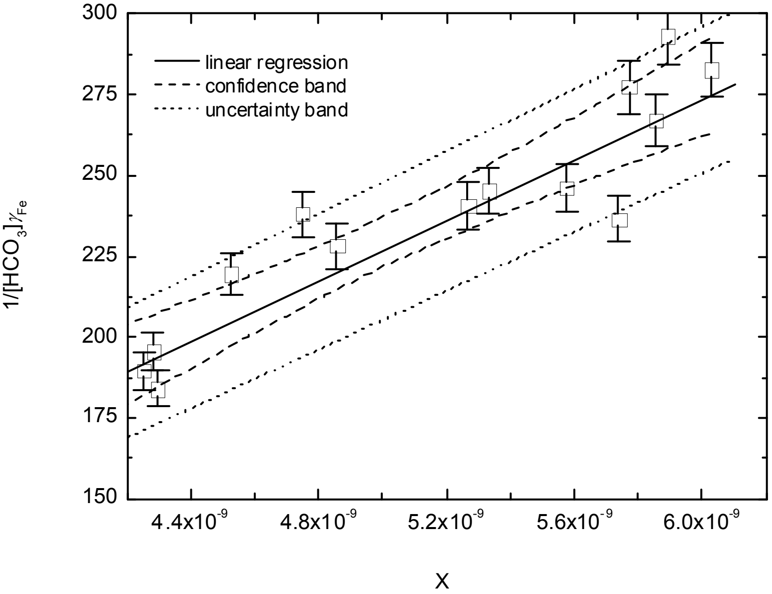
Values of $K(FeHCO_3^+)$ and $K_{\text{s},0}$ (*i.e.*, Eq. (X.7)) were determined using

$$\frac{1}{[HCO_3^-]\gamma^4} = -K_{FeHCO_3^+} + \frac{1}{K_{\text{s},0}}\left(\frac{K_2[\text{Fe}]_{\text{total}}\gamma^2[HCO_3^-]}{K_1([CO_2]_{\text{total}} - [HCO_3^-] - [FeHCO_3^+])}\right) \qquad (A.7)$$

(where K_1 is the first and K_2 the second deprotonation constant of $CO_2(aq)$) in an iterative process. The concentration of HCO_3^- can be calculated from the given mass balance equations, the known value of K_1 and an assumed value for $K(FeHCO_3^+)$. The procedure converges and leads to a unique value for $K(FeHCO_3^+)$, independent of the starting value. The low ionic strength (~0.007 to ~0.012 m) greatly simplifies the calculation of the activity coefficients because it can safely be assumed that only the

Debye-Hückel part contributes significantly to the activity coefficient. Hence the simplification $\gamma_{\mathrm{Fe}^{2+}} \approx \gamma^4_{\mathrm{FeHCO}_3^+} \approx \gamma^4_{\mathrm{H}^+} \approx \gamma^4_{\mathrm{HCO}_3^-} \approx \gamma^4$ holds.

Figure A-1: Evaluation of Eq. (A.7); X is the parenthetical expression (molal units) on the right hand side of the equation.



Assuming that the uncertainty in the calculated concentration of HCO_3^- is 3%, the regression converges to

$$K^{\circ}(\mathrm{FeHCO}_3^+, 303.15\ \mathrm{K}) = (8 \pm 15)$$

and

$$K^{\circ}_{s,0}(\mathrm{FeCO_3, cr, 303.15\ K}) = (2.11 \pm 0.13) \times 10^{-11}$$

$$(\log_{10} K^{\circ}_{s,0}(\mathrm{FeCO_3, cr, 303.15\ K}) = -(10.68 \pm 0.03)).$$

This calculated formation constant for FeHCO_3^+ is very small and from a statistical point of view is the same as zero, *i.e.*, the complex does not exist. With the same equations, but forcing the straight line of Eq. (A.7) to go through the origin, and assigning a more realistic uncertainty by increasing the assumed uncertainty in the concentration of HCO_3^- to 10%

$$\log_{10} K^{\circ}_{s,0}(\mathrm{FeCO_3, cr, 303.15\ K}) = -(10.65 \pm 0.01)$$

and the coefficient of determination R^2 is 0.997 (instead of 0.86). Hence, the data support the hypothesis that the complex $FeHCO_3^+$ is not a significant species under the conditions of Smith's experiments. This is almost exactly the same value as is obtained if a simple average is done using the individual results.

[1921CHA]

This paper describes a detailed study of equilibria in the Fe-H-O system at 360 to 1025 °C. Reactions examined were Fe(cr) + H_2O(g) $\rightleftharpoons$ "FeO"(cr) + H_2(g) [1] and 3"FeO"(cr) + H_2O(g) $\rightleftharpoons$ Fe_3O_4(cr) + H_2(g) [2] above the Fe-FeO-Fe_3O_4 eutectoid temperature, estimated to be 570 °C, and 3 Fe(cr) + 4 H_2O(g) $\rightleftharpoons$ Fe_3O_4(cr) + 4 H_2(g) [3] below the eutectoid. The corresponding equilibria in the Fe-C-O system, Fe(cr) + CO_2(g) $\rightleftharpoons$ "FeO"(cr) + CO(g) [4], 3 "FeO"(cr) + CO_2(g) $\rightleftharpoons$ Fe_3O_4(cr) + CO(g) [5], and 3 Fe(cr) + 4 CO_2(g) $\rightleftharpoons$ Fe_3O_4(cr) + 4 CO(g) [6] were also investigated, and results were combined to obtain the equilibrium constant of the water-gas reaction, CO(g) + H_2O(g) $\rightleftharpoons$ CO_2(g) + H_2(g) [7]. Measurements in both static and recirculating systems are described, and earlier work is well reviewed. The paper also includes studies of Co, Mo, and W oxide systems.

This paper is historically important for demonstrating the instability of "FeO"(cr) with respect to Fe(cr) + Fe_3O_4(cr) below about 570 °C. A contemporary reviewer [1922EAS] stated that "Little criticism can be made of Chaudron's methods", citing only minor probable errors in gas analyses (possibility of up to 4% N_2 in gas mixtures) and temperature measurements (uncertainties <5 °C). Ten measurements on Fe-Fe_3O_4 equilibrium in H_2-H_2O atmospheres, using a recirculating apparatus, appear to be reliable though relatively imprecise by modern standards. They yield $\Delta_f H_m^\circ$ (Fe_3O_4, cr, 298.15 K) = − (1113.65 ± 1.68) $kJ\cdot mol^{-1}$, excluding uncertainties in the thermal data 1used in the Third Law calculation.

Emmett and Shultz [1933EMM/SHU] and Darken and Gurry [1945DAR/GUR] have discussed thermal diffusion (partial separation of gas mixtures under a thermal gradient) as a probable source of error in early studies on the Fe-H-O system, including Chaudron's static-system measurements. Note that wüstite is treated as a stoichiometric compound, "FeO", since its true, non-stoichiometric nature was not described until 1927 [1927SCH/DIN].

[1921MAT]

This paper is difficult to obtain, except in German translation [1922MAT]; some of the key findings are summarized by Tigerschiöld [1923TIG]. The author generated equilibrium composition curves for Fe-O solids in contact with CO-CO_2 gas mixtures, and conducted additional tests approaching equilibrium from both the CO-rich and CO_2-rich sides. Altogether, 11 measurements were obtained for Fe-"FeO" equilibrium at 993 to 1448 K, and 12 measurements for "FeO"-Fe_3O_4 at 900 to 1448 K. These data are included among the representative measurements for wüstite equilibria, as used to obtain $\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\circ}$ (Fe_3O_4, cr, 298.15 K), in Section VII.2.7.2, but were not used in the final assessment.

[1922EAS]

This paper reviewed published data on equilibria between Fe(cr), "FeO"(cr) and Fe_3O_4(cr) in H_2O-H_2 and CO_2-CO atmospheres, performed prior to an experimental study [1924EAS/EVA] on the equilibria involving "FeO". The author attempted to resolve the "surprising degree of confusion" in the literature at that time. Important conclusions were drawn about solid solubility in the Fe-O system. The Fe-"FeO"-Fe_3O_4 eutectoid temperature was estimated to be 565 °C. The possible role of dissolved carbide in equilibria involving CO and CO_2 was discussed, but not completely resolved. Generally good agreement was found between investigations of univariant or divariant equilibria involving CO_2/CO atmospheres where the presence of "separate and definite" solid phases in large amounts was assured, but not in corresponding systems involving H_2O/H_2 atmospheres. The following smoothed values of equilibrium constants, $K = p_{CO_2} / p_{CO}$, were reported.

Table A-1: Smoothed values of equilibrium constants ($K = p_{CO_2}/p_{CO}$) from [1922EAS].

t/°C	K for Fe/"FeO"	K for "FeO"/Fe_3O_4
600	0.871	1.15
700	0.678	1.77
800	0.552	2.54
900	0.466	3.43
1000	0.403	4.42

This is a useful review of the early (pre-1922) literature on solid-gas equilibria involving iron oxides. While the assessed K values tabulated above are useful, the derived Gibbs energy values for "FeO" and Fe_3O_4 are not valid, because the non-stoichiometric, variable composition of "FeO" was not recognized at the time. Derivation of thermodynamic properties of Fe-O solids requires a knowledge of temperature-composition-activity relationships for the limiting compositions of wüstite at the Fe-"FeO" and "FeO"-Fe_3O_4 boundaries, as well as the corresponding gas-solid equilibrium constants (see Section VII.2.7.2.3).

The inconsistencies noted in data for the H_2O/H_2 systems may be at least partly due to thermal diffusion effects (partial separation of gas mixtures under a thermal gradient), as discussed by Emmett and Shultz [1933EMM/SHU] and Darken and Gurry [1945DAR/GUR].

[1922POS/MER]

This paper reports a careful study of the phases formed in the Fe_2O_3-SO_3-H_2O system from 50 to 200 °C. Crystal characteristics, stoichiometries and stability fields are discussed.

[1923SCH]

This is a careful study by Schumb of the water vapour pressure at 25.0 °C over a slightly dehydrated sample of $FeSO_4\cdot7H_2O$(cr) using a method involving saturation of dry, filtered, CO_2-free air flowing slowly through a tube containing the solid. An average value (6 measurements) of (14.56 ± 0.06) mm Hg (1.94 kPa) is reported (for weighting purposes an uncertainty of 0.2 mm Hg (27 Pa) was estimated). The author suggested that the dehydrated solid was $FeSO_4\cdot6H_2O$(cr), but it is likely that it was $FeSO_4\cdot4H_2O$(cr) [1964KOH/ZAS2].

[1923TIG]

This paper describes the assessment of $\Delta_f H_m^\circ$ (290 K) for crystalline wüstite ("FeO"), magnetite and hematite, using experimental data on the Fe-H-O and Fe-C-O systems from several sources. It is probably the most thorough such assessment of its time, but the accuracy is evidently limited by the available data.

Given the large volume of more recent data, this paper is of mainly historical interest.

[1923WOH/GUN]

Iron and tungsten oxide equilibria in H_2-H_2O atmospheres were measured in a static system. The following equilibrium measurements are tabulated: 12 values for Fe-Fe_3O_4 at 706 to 844 K, 29 for Fe-wüstite at 855 to 1282 K, and 19 for wüstite-Fe_3O_4 at 863 to 1335 K. According to [1933EMM/SHU], these data are in error because of thermal diffusion effects (partial separation of H_2 and H_2O gases in a thermal gradient), and were therefore not included in the current review.

[1924EAS/EVA]

This paper describes measurements of equilibrium constants between 951 and 1295 K for the reactions "FeO"(cr) + H_2(g) $\rightleftharpoons$ Fe(cr) + H_2O(g) [1] and Fe_3O_4(cr) + H_2(g) $\rightleftharpoons$ 3 "FeO"(cr) + H_2O(g) [2], and between 1091 and 1312 K for the reaction Fe_3O_4(cr) + CO(g) $\rightleftharpoons$ 3 "FeO"(cr) + CO_2(g) [3]. Care was taken to assure that measurements always referred to assemblages of two solid phases, and results were corrected for slow outgassing of solid and vitreous surfaces in the static system. Data were tabulated for individual runs, and "best values" for equilibrium constants, based on these and other published studies, were tabulated for the three equilibria and for the reaction "FeO"(cr) + CO(g) $\rightleftharpoons$ Fe(cr) + CO_2(g) [4], at 50 K intervals between 973 and 1273 K. Results were used to evaluate the water gas constant, *i.e.*, the equilibrium constant for the reaction CO_2(g) + H_2(g) $\rightleftharpoons$ CO(g) + H_2O(g) [5].

This experimental study has limited value because the static-gas procedure, developed from Deville's earlier work [1870DEV], is prone to significant errors from thermal diffusion, *i.e.*, partial separation of gas mixtures under a thermal gradient ([1933EMM/SHU], [1945DAR/GUR]). Wüstite is treated as a stoichiometric compound, "FeO", since its true, non-stoichiometric nature was not decribed until 1927 [1927SCH/DIN]. The authors' evidence for ~18 mol-% solubility of O in Fe(cr) at 1045 K appears to be erroneous [1967SWI/TUR].

[1925MAI]

This was a general scoping study of vapour pressures of a number metallic chlorides. For $FeCl_2$, static chlorine vapour-pressure measurements were carried out over the molten salt for temperatures between 972 and 1268 K. Also, vapour pressures (489.6 to 591.5 K) and dissociation pressures (at 564.6 and 574.9 K only) for $FeCl_3$ were reported. The equilibrium dissociation pressures for $FeCl_3$ were quite similar to those found in the later studies of Ringwald [1949RIN], [1953SCH/OEH], [1958WIL/GRE].

[1926BRO/FUR2]

Steady-state temperature measurements were made using 12 thermocouples at various radial positions in a hollow cylindrical drum (38 cm OD, 8.5 cm ID, 71.75 cm high), packed uniformly with about 216 kg of powdered crystalline Fe_2O_3 and heated by an electric element in an axial position within the cylinder. The Fe_2O_3 was 98.73% pure, the principal impurities being SiO_2, Mn (presumably present as either $(Mn,Fe)_2O_3$ or $MnFe_2O_4$), and Fe_3O_4.

As described in an accompanying paper [1926BRO/FUR], this experimental configuration permits the simultaneous determination of thermal conductivity and specific heat of the medium packing the cylinder, as well as the detection of any phase transitions and measurement of their heats of transition. The very large sample size is an obvious disadvantage for general application of this method, and the authors' estimated accuracy was ± 5%.

Three out of four steady-state runs yielded 38 specific-heat values at temperatures from 391 to 1051 K. The corresponding $C_{p,\mathrm{m}}$ values are generally higher than measurements obtained much more recently (and more conventionally) by Grønvold and Samuelsen [1975GRO/SAM]; the discrepancies increase from ~3% at 400 K to ~10% at 620 K and ~30% at 900 K. This variation is possibly linked to the sintering of material towards the centre of the sample, which may have perturbed the initially uniform packing density. A reported phase transition at 633 K has not been confirmed by more recent thermal studies of α-Fe_2O_3 [1951COU/KIN], [1962AHA/FRE], [1975GRO/SAM].

The paper is described here for historic interest, and the data are not used in the current review.

[1926HAM]

Hampton measured the potential of the cell without liquid junction: $Fe(s)|FeCl_2(m),HgCl|Hg(l)$ ($0.01 < m < 5.03$). Finely divided Fe metal was used, prepared by electrolytic reduction of $FeSO_4$ at mercury cathodes or from reduction of Fe oxide at 800 °C by H_2. The most stable potentials, 0.8088 V after 5 to 30 days, were obtained with solutions 0.1 m $FeCl_2$. Using the measured potential for the reference half cell with 0.01 m H^+ hydrogen electrode 0.510 V, and the activity coefficient of $BaCl_2$ in place of that of $FeCl_2$, a value of − 0.4413 V was calculated for $E^{\circ}(Fe^{2+}/Fe(0))$ *vs.* SHE. The value was later redetermined by Randall and Frandsen [1932RAN/FRA2] to be − 0.4387 V.

[1926PAR/KEL]

Heat capacities are reported for six oxides, including large crystals of "specular" natural hematite (α-Fe_2O_3; 12 measurements between 87.2 and 292.7 K), "Kahlbaum's" finely powdered Fe_2O_3 prepared from iron oxalate (11 measurements between 88.3 and 289.4 K), and "remarkably perfect, large crystals" of magnetite (Fe_3O_4) described by [1916SOS/HOS] (11 measurements between 90.0 and 295.0 K). The calorimetric procedure is described in detail, and results are reported with an estimated absolute error of < 1%. Analyzed purity of all samples was near 99%, the chief impurities being H_2O, SiO_2, and (in the magnetite), Fe_2O_3. Entropies were calculated using the Lewis-Gibson method (*J. Am. Chem. Soc.*, **39**, (1917), 2565): 90.0 $J \cdot K^{-1} \cdot mol^{-1}$ for α-Fe_2O_3 (specular crystals), and 146.9 $J \cdot K^{-1} \cdot mol^{-1}$ for Fe_3O_4. The latter value includes 5.9 $J \cdot K^{-1} \cdot mol^{-1}$ for a phase transition at 113 - 117 K, an early observation of the Verwey transition (see Section VII.2.7.1). Heat capacities and entropy for Kahlbaum's Fe_2O_3 were consistently higher (by 2.4 - 3.8%) than for the specular hematite; this was attributed to the "partly amorphous" [or poorly crystalline] nature of the powder, as indicated by XRD analysis.

The paper also included C_p data and entropy estimates for MgO, CaO, and α-Al_2O_3.

The entropy estimates are superseded by more recent values, based on C_p measurements to much lower temperatures. The C_p data for magnetite and specular hematite are discussed further in Sections VII.2.7.1 and VII.2.2.2, respectively.

[1927BAG]

Bagdasarian [1927BAG] carried out measurements to determine the equilibrium constant for the reaction

$$FeCl_2(l) + H_2(g) \rightleftharpoons Fe(cr) + 2\,HCl(g)$$

at temperatures from 975 to 1278 K. As discussed by the author, interpretation is complicated because of the λ-transition in the heat capacity of Fe(α) (near 1042 K) and the transition of Fe(α) to Fe(γ) at 1184 K. Also, extrapolation of thermodynamic quantities to 298.15 K requires good values for the heat of fusion of $FeCl_2$ (melting point 950 K), and the heat capacity of $FeCl_2$(l). Wagner ansd Stein [1943WAG/STE] and Schäfer and Krehl [1952SCH/KRE] have pointed out that the reported equilibrium constants also require correction to allow for the vaporisation of $FeCl_2$, especially at the higher temperatures [1925MAI]. The values from the paper of Bagdasarian [1927BAG] are not used further in the present review.

[1927GRE]

The gas pressures above (slightly decomposed) samples of $FeSO_4$(cr) were measured for temperatures between 524 and 929 K by a static method. The decomposition was not reversible at the higher temperatures (also see the discussion of Skeaff and Espelund [1973SKE/ESP]). From their results the authors estimated the enthalpy of dissociation between 589 and 827 K. However, as the solid was impure, and in the absence of a good entropy value for $FeSO_4$(cr) and heat-content data at higher temperatures, no attempt is made to use these results in the present review.

[1927SCH/DIN]

This paper is of historical interest for coining the mineral name wüstite and for demonstrating the variable, oxygen-rich composition of this phase, previously thought to be FeO.

The estimated compositional limits for wüstite were later shown by Darken and Gurry [1945DAR/GUR] to be rather inaccurate, and have been superseded by numerous other studies, notably [1945DAR/GUR] and other papers cited by Spencer and Kubaschewski [1978SPE/KUB] and Grønvold *et al.* [1993GRO/STO].

[1928GAR]

Previous literature on equilibria between Fe(cr), "FeO"(cr), Fe_3O_4(cr) and CO-CO_2 gas mixtures is reviewed, and the possibility of carbon deposition (or metastable equilibrium) below about 923 K for the "FeO"-Fe_3O_4 equilibrium and below about 983 K for the Fe-"FeO" equilibrium is discussed. A figure is presented with 44 new data for the equilibrium $Fe_3O_4\text{(cr)} + CO\text{(g)} \rightleftharpoons 3\,\text{“FeO”(cr)} + CO_2\text{(g)}$ and 60 data for the equilibrium $\text{“FeO”(cr)} + CO\text{(g)} \rightleftharpoons Fe\text{(cr)} + CO_2\text{(g)}$. Equilibration times ranged from 14 hours at ~920 K to 3.5 hours at ~1550 K.

Despite the use of relatively low-purity starting materials (2.6% siliceous impurity in Fe and 8.2% in Fe_3O_4), and an unusual experimental procedure in which Fe and Fe_3O_4 were placed in separate heaps in the reaction tube in a static apparatus, the precision of the results appears to be higher than in the earlier studies by Chaudron [1921CHA] and Matsubara [1922MAT], and agreement with later studies is quite good.

[1928JEL/RUD]

The equilibrium of the reaction

$$FeF_2(cr) + H_2(g) \rightleftharpoons Fe(cr) + 2\,HF(g) \tag{A.8}$$

was studied at 773, 873 and 973 K by passing hydrogen gas over the solid fluoride, and measuring the HF content of the gas that had passed over (and equilibrated with) the solid. The HF(g) volume per cent was found to vary with the flow rate. The authors extrapolated the HF(g) volume per cent to zero flow and calculated the equilibrium constants from the gas compositions. In the present review, the "zero flow" values were used with the selected thermal functions for FeF_2(cr) and Fe(cr), and CODATA values [1989COX/WAG] to calculate − 704, − 711 and − 713 $kJ\cdot mol^{-1}$ for $\Delta_f H^\circ_m$ (FeF_2, cr, 298.15 K). These derived values are consistent with those obtained from potential measurements (*e.g.*, [1966LOF/MCI], [1981SCH/GOK]). However, the procedure used to determine the equilibrium constants from measurements at different flow rates is not considered to be reliable [1959RIC/ALC], and in the present review the results of Jellinek and Rudat for FeF_2(cr) are used only for comparison purposes.

The authors also used a similar method to study the reaction

$$2\,FeF_3(cr) + H_2(g) \rightleftharpoons 2\,FeF_2(cr) + 2\,HF(g) \tag{A.9}$$

at 623, 723 and 823 K. In the present review the results are used with the values selected for FeF_2(cr) (Section VIII.3.1.1) and from CODATA [1989COX/WAG] to obtain values of $G(T)$ (− 1133, − 1151 and − 1169 $kJ\cdot mol^{-1}$).

[1928SCH]

The results of solubility measurements for hydrated $FeCl_2$ in water are reported. In contact with the saturated solutions, the solid-phase transitions from the hexahydrate to the tetrahydrate and from the tetrahydrate to the dihydrate were found to occur at 12.5 and 76.5 °C, respectively.

[1929POP/KUN]

The potential of the cell

$$Pt(s),H_2 \mid HCl(m) \parallel HCl\,(m\,), FeCl_2\,(x), FeCl_3\,(x) \mid Pt(s)$$

with a Lamb and Larson flowing H junction was measured at 25 °C. Double-linear extrapolations were carried out to x = 0 and zero ionic strength. Also see the Appendix A entry for [1934BRA/HER].

[1929HUT/GAR]

This is a lengthy study of the properties of hydrated iron(III) oxides as a function of different preparation methods and aging. For the current review, it is mainly of interest for the specific-heat measurements on 20 amorphous and microcrystalline specimens of "$Fe_2O_3\cdot xH_2O$" from 8 synthetic preparations, with values of x between 0.0858 and

3.791, plus one natural, near-stoichiometric goethite (α-FeOOH) specimen. These yield average $C^{\circ}_{p,\mathrm{m}}$ values over rather large, variable temperature intervals. A quadratic fit of $C^{\circ}_{p,\mathrm{m}}$ *vs.* x yields an estimate of $C^{\circ}_{p,\mathrm{m}}(\mathrm{Fe_2O_3{\cdot}3H_2O}) = (302 \pm 12)$ $\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$ and hence $C^{\circ}_{p,\mathrm{m}}$ (“$Fe(OH)_3$”, am) = (151 ± 6) $\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$. These are average values over the approximate temperature range 4 - 60 °C, which approximates the temperature range over which ferrihydrite might be expected to persist for significant periods of time. Ferrihydrite is the mineral that corresponds most closely to synthetic, amorphous “$Fe(OH)_3$”

Since there appear to be no “modern” C_p measurements for ferrihydrite, these values are included in the discussion of this phase.

[1929MIL]

This paper presents 48 C_p measurements for “FeO” between 70.7 and 301.8 K, and 32 for magnetite (Fe_3O_4) between 60.5 and 299.7 K, as well as data for Cu_2O and CuO. The synthetic “FeO” yielded the analysis: total Fe, 77.24%, Fe(II), 68.46%, free Fe(0), 0.80%, Fe(III) (by difference), 7.98%. The magnetite was a mineral specimen analysed by [1916SOS/HOS] as: Fe_3O_4, 99.0%, Fe_2O_3, 0.63%, SiO_2, 0.37%. The calorimeter was described earlier [1928MIL], and C_p data were corrected for the SiO_2 content (treated as quartz).

The non-stoichiometric nature of wüstite was not well understood at the time of this study. Millar recognized that his specimen was a solid solution, but “assumed that the specific heat of the sample was the same as that of pure ferrous oxide”, and the tabulated C_p values are thus based on a relative molecular mass of 71.84 for stoichiometric FeO. Grønvold *et al.* [1993GRO/STO] considered that Millar’s data for “FeO” are superseded by those of Todd and Bonnickson [1951TOD/BON] for a better-characterized wüstite specimen with the composition $Fe_{0.947}O$.

The data for magnetite below about 240 K agree well with other studies, but those obtained closer to ambient temperature are up to 6% lower than most reported values. The difference is attributed partly to the correction for SiO_2 content, and partly to “a correction for loss of heat during the measurements”. Insufficient information is given to evaluate or revise these corrections. Data from this paper are not included in the current assessment.

[1929ROT]

This paper describes calorimetric determinations of the heats of formation of solid magnetite (Fe_3O_4), hematite (α-Fe_2O_3), “FeO”, $FeCO_3$, and $Fe(CO)_5$, as well as several related Ni and Mn compounds. This synopsis is concerned primarily with the determinations for hematite. The researchers measured the heat of co-combustion of Fe with paraffin oil in an oxygen-bomb calorimeter to form a mixture of “FeO” and Fe_3O_4, and the heat of decomposition of α-Fe_2O_3 to Fe_3O_4 (also concomitant with paraffin combustion). They obtained the following heats of formation (presumably at or near 25 °C):

$\Delta_f H^\circ_m$ (“FeO”, cr) = – (64.3 ± 0.5) kcal·mol^{-1} (– (269.0 ± 2.1) kJ·mol^{-1}, based on 4.184 J·cal^{-1});

$\Delta_f H^\circ_m$ (Fe_3O_4, cr) = – (266.9 ± 0.5) kcal·mol^{-1} (– (1116.7 ± 2.1) kJ·mol^{-1});

$\Delta_f H^\circ_m$ (Fe_2O_3, α) = – (198.5 ± 0.8) kcal·mol^{-1} (– (830.5 ± 3.4) kJ·mol^{-1});

$\Delta_f H^\circ_m$ ($FeCO_3$, cr) = – (172.6 ± 0.9) kcal·mol^{-1} (– (722.2 ± 3.8) kJ·mol^{-1});

$\Delta_f H^\circ_m$ (Fe_3C, cr) = (5.4 ± 1.6) kcal·mol^{-1} ((22.6 ± 6.7) kJ·mol^{-1}).

This paper is mainly of historical interest, but a portion is reviewed here because it was cited recently in partial support of O’Neill’s cell-potential measurements on the magnetite-hematite equilibrium ([1988NEI], [1990HEM]). The latter authors cited the good agreement between the values for $\Delta_f H^\circ_m$ (Fe_2O_3, α) of −826.0 kJ·mol^{-1} obtained by [1988NEI] (adjusted to −826.23 kJ·mol^{-1} by [1990HEM]) and −826.8 kJ·mol^{-1} in [1929ROT]. The latter value, however, is a constant-volume value obtained directly from the calorimetric measurements, and the derived constant-pressure value (Table 3 of [1929ROT]) is −(830.5 ± 3.4) kJ·mol^{-1}. Furthermore, this value is based on separate determinations of the heats of reaction for formation of magnetite,

$$3\,Fe(cr) + 2\,O_2(g) \rightarrow Fe_3O_4(cr) \qquad (A.10)$$

and decomposition of hematite,

$$6\,Fe_2O_3(\alpha) \rightarrow 4\,Fe_3O_4(cr) + O_2(g) \qquad (A.11).$$

Both measurements were based on incomplete reactions, necessitating significant corrections. Furthermore, the heat effect for Reaction (A.11) was only about 3% of the total heat effect, which was dominated by paraffin combustion. In fact, the enthalpy value for Reaction (A.11) at constant pressure, based on Table 3 of [1929ROT], is 516.3 kJ·mol^{-1}, which is markedly different from O’Neill’s measurement of (494.46 ± 0.2) kJ·mol^{-1}. The latter value is undoubtedly more accurate, and the agreement between the enthalpies of formation for hematite appears to be due to a fortuitous cancellation of errors in [1929ROT]; the overall uncertainty estimates of [1929ROT] appear to be over-optimistic.

[1929ROT/BER]

Roth and Bertram carried out drop-calorimetry measurements (369 to 968 K) to determine the specific heat of a natural sample of fayalite (~ 0.98 weight fraction Fe_2SiO_4. with small amounts of iron, aluminium, manganese, calcium and silicon as oxides). The resulting values of $H^\circ_T - H^\circ_{298.15\,K}$ are systematically greater than values from later publications in which purer samples were used [1953ORR], [1984STE/CAR], and the measurements of Roth and Bertram were not considered further in the present review.

[1929SCH]

Schimmel identified a series of hydrates of $FeBr_2$ and reported the transition temperatures between $FeBr_2{\cdot}9H_2O$, $FeBr_2{\cdot}6H_2O$, $FeBr_2{\cdot}4H_2O$, $FeBr_2{\cdot}2H_2O$ in saturated aqueous solutions. In saturated solution $FeCl_3{\cdot}9H_2O$ is formed only below – 28 °C. $FeBr_2{\cdot}6H_2O$ is the stable solid between – 28 and 49 °C and $FeBr_2{\cdot}4H_2O$ between 49 and 83 °C. At higher temperatures (to the boiling point, 132 °C) $FeBr_2{\cdot}2H_2O$ is the equilibrium solid. At saturation at 25 °C the solution is ~ 5.6 m in $FeBr_2$.

[1930EMM/SHU]

This paper describes measurements of the equilibrium constants for the reactions "FeO"(cr) + H_2(g) $\rightleftharpoons$ Fe(cr) + H_2O(g) [1] and Fe_3O_4(cr) + H_2(g) $\rightleftharpoons$ 3 "FeO"(cr) + H_2O(g) [2]. A dynamic flow system was used in an attempt to eliminate errors due to "an abnormal consumption of hydrogen by the surface of the iron oxide specimens", thought to have been important in some earlier studies using static systems. A later, complementary paper by the same authors [1933EMM/SHU] showed that thermal diffusion (partial separation of H_2 and H_2O in a thermal gradient) is the principal source of error in static experiments; see also [1945DAR/GUR].

The paper presents 43 measurements for Equilibrium [1] at 854 to 1293 K, and 13 measurements for Equilibrium [2] at 970 to 1075.6 °C, *i.e.*, all measurements were above the Fe–"FeO"–Fe_3O_4 triple point of about 840 K. Uncertainties in temperature measurements were estimated to range from ±6 K to ±10 K (depending on the temperature and the type of thermocouple used), and the overall uncertainty in the equilibrium constant derived from the exit gas analysis (mass of H_2O and volume of H_2) was estimated to range from ±0.5% to ±1.9%, depending on the temperature and the specific equilibrium being measured. Measurements on each equilibrium were clustered at approximately 100 K intervals, and data were reduced to recommended equilibrium constants at exact 100 K intervals between 873 and 1273 K for Equilibrium [1] and at 973 and 1073 K for Equilibrium [2].

As with several contemporary studies of the Fe-H-O and Fe-C-O systems, one of the aims of this work was to refine values for the equilibrium constant for the industrially important water-gas shift reaction, CO_2(g) + H_2(g) $\rightleftharpoons$ CO(g) + H_2O(g).

Wüstite is treated as a stoichiometric compound, "FeO", since its true, non-stoichiometric nature was not yet well known (first described in [1927SCH/DIN]). The paper includes an excellent review of the earlier literature on these equilibria. While gas-solid data for these equilibria are largely superseded by solid-state cell-potential measurements, they are included in the discussion on the enthalpy of formation of magnetite, Section VII.2.7.2.3.

[1931POP/FLE]

The authors studied the equilibrium,

$$2\,Fe(ClO_4)_3(sln) + 2\,Hg(l) \rightleftharpoons 2\,Fe(ClO_4)_2(sln) + Hg_2(ClO_4)_2(sln) \qquad (A.12)$$

at 25 °C by chemical analysis rather than by making electrochemical potential-difference measurements. Equilibrium was approached from both sides by adjusting the temperature. The acid and iron(III) perchlorate concentrations were varied, from 0.002 to 0.02 $mol{\cdot}L^{-1}$ and from 0.001 to 0.008 $mol{\cdot}L^{-1}$, respectively, and hydrolysis of Fe^{3+} was regarded as being negligible.

For the acidities used by the authors this is not true, and large errors stemmed from neglecting Fe^{3+} hydrolysis. The standard potential $E^{o}(Fe^{3+}/Fe^{2+})$ found by the authors was 0.747 V, significantly different from 0.772 V, the value found by Bray *et al.* [1934BRA/HER] after they applied corrections for Fe^{3+} hydrolysis and used a more sophisticated method for the extrapolation to zero ionic strength. In the present review the results listed in Table II of the original paper have been treated using the SIT method after replacing the values of the Fe^{3+} concentrations by new values calculated taking hydrolysis into account.

The TDB constants for Fe^{3+} hydrolysis from this review were used to calculate the Fe^{3+} concentrations. Two hydrolytic species have been considered, $FeOH^{2+}$ and $Fe_2(OH)_2^{4+}$. The calculations results showed that the dimer is always a very minor species, less than 1%, of the total Fe(III), but the 1:1 species, $FeOH^{2+}$, can constitute 70% of the total Fe(III).

As the data cover only a narrow range of ionic strengths, the SIT plot of $\log_{10}K_m + 6D$ *vs.* I_m and the extrapolation to zero ionic strength by linear regression did not give satisfactory results. The data points form a cluster, and the value of the linear correlation coefficient r is − 0.074. In spite of that, the value of $\log_{10}K^{o}$ is reasonable and leads to a value of (0.7729 ± 0.0038) V for $E^{o}(Fe^{3+}/Fe^{2+})$, in line with most of the other results of the literature and with those given below.

A second SIT determination has been carried out by calculating 18 values of K^{o}

$$K^{o} = \{[Fe^{2+}]^2\,[Hg_2^{2+}]/[Fe^{3+}]^2\}\ \{(\gamma_{Fe^{2+}})^2\,(\gamma_{Hg_2^{2+}})/(\gamma_{Fe^{3+}})^2\}$$

by applying the SIT formula:

$$\log_{10}\gamma_M = -\,\Delta z^2 D + \varepsilon(M^{z+}, ClO_4^-)\,m_{ClO_4^-}\,. \qquad (A.13)$$

The γ_M values for $M^{z+} = Fe^{3+}$, Fe^{2+} and Hg_2^{2+} have been calculated using the following values of $\varepsilon(M^{z+}, ClO_4^-)$

$\varepsilon(Fe^{3+}, ClO_4^-) = (0.73 \pm 0.05)\ kg{\cdot}mol^{-1}$ (SIT_1 of this review)

$\varepsilon(\mathrm{Fe^{3+}, ClO_4^-}) = (0.78 \pm 0.05) - (0.41 \pm 0.05\ (\log_{10} I_m))\ \mathrm{kg{\cdot}mol^{-1}}$ (SIT$_2$ of this review)

$\varepsilon(\mathrm{Fe^{2+}, ClO_4^-}) = (0.37 \pm 0.04)\ \mathrm{kg{\cdot}mol^{-1}}$ (this review)

$\varepsilon(\mathrm{Hg_2^{2+}, ClO_4^-}) = (0.09 \pm 0.02)\ \mathrm{kg{\cdot}mol^{-1}}$ (Table B-4).

The unweighted average values of K° were found to be (0.161 ± 0.028) $\mathrm{mol{\cdot}kg^{-1}}$ using SIT$_1$ and (0.153 ± 0.030) $\mathrm{mol{\cdot}kg^{-1}}$ using SIT$_2$.

For this paper, the conversion factor from the molar scale to the molal one is very close to 1.000, and a factor of 1.003 was applied to all the data points.

The relation between K° and the $\mathrm{Hg_2^{2+}}$/Hg(l) and the $\mathrm{Fe^{3+}/Fe^{2+}}$ standard potentials is:

$$E^{\circ}(\mathrm{Hg_2^{2+}/Hg(l)}) - E^{\circ}(\mathrm{Fe^{3+}/Fe^{2+}}) = -(0.05916/2)\log_{10} K^{\circ} \qquad \text{(A.14)}$$

Using the TDB value

$$E^{\circ}(\mathrm{Hg_2^{2+}/Hg(l)}) = (0.7958 \pm 0.0036)\ \mathrm{V}$$

one obtains:

$$E^{\circ}(\mathrm{Fe^{3+}/Fe^{2+}}) = (0.7723 \pm 0.0044)\ \mathrm{V} \qquad \mathrm{SIT_1}$$

and

$$E^{\circ}(\mathrm{Fe^{3+}/Fe^{2+}}) = (0.7717 \pm 0.0042)\ \mathrm{V} \qquad \mathrm{SIT_2}$$

The weighted average of the values (0.7729 ± 0.0038), (0.7723 ± 0.0044) and (0.7717 ± 0.0042) V estimated using the three different SIT procedures is (0.7723 ± 0.0023) V, in very good agreement with the result of the paper of Bray and Hershey [1934BRA/HER] and also with other literature values.

[1932RAN/FRA]

The potential difference between Fe(s) + $\mathrm{Fe(OH)_2}$(s) and Hg(l) + HgO(s) couples, with 0.05 M $\mathrm{Ba(OH)_2}$ electrolyte, was monitored for periods up to 18 months at 25 °C with careful exclusion of air. This appears to be the only measurement of the stability of aged, rather than freshly precipitated $\mathrm{Fe(OH)_2}$. Some cells failed after a few months, but three cells stabilized at a potential of (0.973 ± 0.005) V, corresponding to $\Delta_{\mathrm{r}}G_{\mathrm{m}}^{\circ} = -(187.8 \pm 1.0)\ \mathrm{kJ{\cdot}mol^{-1}}$ for the reaction: Fe(s) + HgO(s) + $\mathrm{H_2O}$(l) $\rightleftharpoons$ Hg(l) + $\mathrm{Fe(OH)_2}$(s), whence $\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ}$ ($\mathrm{Fe(OH)_2}$, cr, 298.15 K) = $-(483.4 \pm 1.0)\ \mathrm{kJ{\cdot}mol^{-1}}$.

There was apparently no attempt to characterize the $\mathrm{Fe(OH)_2}$ or the Fe surfaces at the end of the experiments.

[1932RAN/FRA2]

This paper was mainly focused on reinterpretation of the data of Hampton [1926HAM]. A value of 0.2676 V was used for the potential for the reference half cell with a 1 m $\mathrm{H^+}$

hydrogen electrode (as measured by Randall and Young [1928RAN/YOU]). The revised value, $E^{\circ}(\mathrm{Fe^{2+}/Fe(0)})$ − 0.4387 V *vs.* SHE, was calculated using the potential difference of the cell: Fe(s)|$FeCl_2$(0.1 m)|HgCl,Hg(l). Activity coefficients for $FeCl_2$ solutions, measured after the publication of Hampton's results, were incorporated instead of the $BaCl_2$ activity coefficients used by Hampton.

[1932ROT/TRO]

The authors carried out measurements of the heat of solution of a natural sample of fayalite (analyses indicated 3.31% quartz, 3.72% magnetite) and quartz into an aqueous mixture of 240 g 20% hydrochloric acid and 50 g 20.6% hydrofluoric acid at 77 °C. Using measurements of the heat of solution of amorphous silica and "FeO", and the heats of solution of quartz and amorphous silica in 20% hydrofluoric acid, a value of − 43 $\mathrm{kJ \cdot mol^{-1}}$ was calculated for the enthalpy of formation of α-Fe_2SiO_4 (350 K) from "FeO" and quartz.

The "FeO" sample also was not pure wüstite (values for the heat of solution of the sample were corrected to (approximately) stoichiometric FeO by the authors). Moreover, the impurity amounts were large (~ 10%). The authors' calculated enthalpy of formation for α-Fe_2SiO_4 is not consistent with later measurements, and the experimental results are not used further in the present review.

[1932SCH/FRA]

The authors established the percentage CO_2 formed in a stream of CO brought to equilibrium with a mixture of iron and iron oxide with SiO_2 in an excess of SiO_2 at 1173 K, thus establishing the equilibrium conditions for formation of fayalite. The measured percentage carbon dioxide in the gas stream at each temperature is in good agreement with other measurements [1946CIR], [1962LEB/LEV]. In the present review, the CO_2 to CO ratios were calculated and combined with consistent auxiliary data for quartz ([1989COX/WAG], [1998CAR/SAL]) and carbon dioxide and carbon monoxide [1989GUR/VEY], and with the values selected in this review for the heat capacity and entropy of α-Fe_2SiO_4 (Section X.2.1.1.1) and Fe(cr) (Section V.2). These led to a value of $\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\circ}$ (Fe_2SiO_4, α, 298.15 K) of − 1476.7 $\mathrm{kJ \cdot mol^{-1}}$. This value, based on experiments at a single temperature, is used only for comparison purposes in the present review.

[1933EMM/SHU]

This paper complements [1930EMM/SHU]. The authors used a Deville-type apparatus [1870DEV], modified to permit gas circulation within a closed system, to help resolve the "puzzling and widely varying results" obtained in previous studies on equilibria in the Fe-H-O system. Three equilibria were examined: $\frac{1}{4}Fe_3O_4(cr) + H_2(g) \rightleftharpoons \frac{3}{4}Fe(cr) + H_2O(g)$ [1], "FeO"(cr) + $H_2(g) \rightleftharpoons Fe(cr) + H_2O(g)$ [2], and $Fe_3O_4(cr) + H_2(g) \rightleftharpoons$ 3 "FeO"(cr) + $H_2O(g)$ [3]. As with several contemporary studies of the Fe-H-O and Fe-C-O systems, one of the aims of this work was to refine values of the equilibrium constant for the industrially important water-gas shift reaction, $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$.

The paper presents: 35 measurements for Equilibrium [1] at 672 to 826 K, clustered near 673, 773, and 823 K; a summary of 73 measurements for Equilibrium [2] at ~873 to ~1273 K, the majority near 973 and 1073 K; and 17 measurements for Equilibrium [3] at 871.6 to 1075.6 K, clustered near 873, 973, and 1073 K.

Because it identifies and effectively avoids the thermal diffusion problem, this is probably the first reliable study of iron oxide equilibria in hydrogen–steam atmospheres. Previous values for equilibrium constants are shown to be in error by up to 40%.

Iron oxide sample purity was satisfactory (apparently >99% in most cases), and the stated accuracy of temperature and pressure measurements was good, yielding estimated uncertainties of ±0.003 to ±0.13 in the individual equilibrium constant measurements (depending on the temperature and the specific equilibrium). The tabulated data suggest a rather larger uncertainty than stated for measurements of Equilibrium [1]. Data for Equilibrium [2] agreed well with those obtained in earlier flow experiments by the same authors [1930EMM/SHU].

This paper is also significant as one of relatively few studies to include direct measurements on the $Fe(cr)$-$Fe_3O_4(cr)$ equilibrium below the wüstite eutectoid, and data are therefore included in the current assessment of the enthalpy of formation of magnetite (Section VII.2.7.2). As in most contemporary papers, however, wüstite continues to be treated as a stoichiometric compound, "FeO", though its true, non-stoichiometric nature was described in 1927 [1927SCH/DIN]).

[1933FLE]

This equilibrium study was similar to the work described by Popoff *et al.* [1931POP/FLE] on the equilibrium

$$2\,Fe^{3+} + 2\,Hg(l) \rightleftharpoons 2\,Fe^{2+} + Hg_2^{2+} \qquad (A.15)$$

but the measurements were done at 35 °C rather than 25 °C. A reanalysis was done by Bray and Hershey [1934BRA/HER], but no further reanalysis has been carried out in the present review.

[1933JET/FOO]

Preparative methods were devised for homogeneous wüstite specimens with different compositions, and the unit cell dimensions and densities were measured for a series of analysed specimens. The cell dimension, a_0, varied monotonically with composition, from 4.2816 Å for 47.68 at.% Fe ($Fe_{0.911}O$) to 4.3010 Å for 48.56 at.% Fe ($Fe_{0.944}O$); an extrapolated value of 4.332 Å was estimated for hypothetical, stoichiometric FeO. The authors deduced the structural nature of wüstite, nowadays denoted $Fe^{2+}{}_{1\text{-}3x}Fe^{3+}{}_{2x}\square_xO$, where □ represents a cation vacancy [1984HAZ/JEA].

[1933JET/FOO2]

Apparent boundaries for the wüstite phase field in the Fe-O system were obtained by XRD measurements on quenched samples. Comparison with later studies (*e.g.*, [1945DAR/GUR], [1993GRO/STO], and references therein) shows that quenching was not sufficiently rapid to prevent partial decomposition (precipitation of Fe_3O_4) with oxygen-rich compositions. The portion of the wüstite/Fe_3O_4 boundary above about 1200 K is therefore unreliable, with erroneous, low O/Fe values.

[1933KRI/AWS]

This is one of several early measurements of the solubility product of freshly precipitated "amorphous $Fe(OH)_3$". Both pH titrations monitoring the precipitation of $Fe(OH)_3$ and electrometric measurements on Fe^{2+} in equilibrium with $Fe(OH)_3$ are described. The titration experiments involving mixtures of iron(II) and iron(III) sulfate (> 0.001 molar) in a cell purged with nitrogen gas and containing platinum, glass and calomel electrodes were undertaken at 18 °C. The pH (on a molarity scale) was determined after calibration with six buffer solutions whose pH was previously obtained with a hydrogen electrode *vs*. presumably a calomel reference electrode. Titration curves are shown of Eh *vs*. pH (*ca*. 1.5 to 11) values (Eh as defined in Section II.1.7.5, pp. 20).

Results from this study were subsequently treated by Cooper [1937COO] who applied perhaps for the first time to this system, activity coefficient and simplistic hydrolysis corrections. These pioneering experiments were performed quite rapidly (5 to 7 minutes between additions) without knowledge of the complex nature of the solution speciation in regard to iron(III) in particular (hydrolyzed ions at high total concentrations, and the formation of iron(III) sulfato complexes) and to the nature of the amorphous iron hydroxide precipitates formed. Therefore, despite the precautions taken by these early investigators, no useful information can be extracted from this study.

[1934AND]

Heat-capacity measurements were carried out on a crushed, screened sample of natural siderite for temperatures between 54.1 and 296.3 K. The main impurities were $MnCO_3$, $MgCO_3$ and $CaCO_3$, and the purity of the sample with respect to $FeCO_3$ was reported as 88.29%. The authors reported values that were corrected for the impurities.

The heat-capacity values are within 1.5% of those reported in the later paper by Robie *et al.* [1984ROB/HAS], and extrapolation of the values of $C_p(T)$ from 211.9 to 296.3 K leads to a value of C_p ($FeCO_3$, cr, 298.15 K) of 82.1 $J\cdot K^{-1}\cdot mol^{-1}$.

The quantitative results from this study are not used in the present review because of the high amount of impurities in the experimental sample.

[1934BRA/HER]

The results of several earlier studies dealing with E° (Fe^{3+}/Fe^{2+}) were recalculated using common methods and auxiliary data. The potential-difference values of Popoff and Kunz [1929POP/KUN] were extrapolated to zero ionic strength (E° = 0.765 V), using the function $E^{\circ\prime} = f(I^{1/2})$. The use of a simplified activity coefficient model was undoubtedly facilitated by the low ionic strengths employed in the original investigations. When the partial hydrolysis of Fe^{3+} was taken into account, the value of E° was 0.767 V, and when the complex of Fe^{3+} with chloride was also considered ($15 < \beta_1^{\circ} < 25$) the calculated value of E° increased to 0.772 V.

Equilibrium constant data of Noyes and Brann [1912NOY/BRA] for

$$Fe^{3+} + Ag(s) \rightleftharpoons Fe^{2+} + Ag^{+} \text{ (in nitric acid medium)} \qquad (A.16)$$

were extrapolated to zero ionic strength ($K^{\circ} = (0.363 \pm 0.015)$), using the function $(\log_{10} K)/4 = f(I_m^{1/2})$.

Data of Popoff *et al.* [1931POP/FLE] and Fleharty [1933FLE] for

$$2\,Fe^{3+} + 2\,Hg(l) \rightleftharpoons 2\,Fe^{2+} + Hg_2^{2+} \text{ (in perchloric acid medium)} \qquad (A.17)$$

were extrapolated to zero ionic strength ($K^{\circ} = (0.137 \pm 0.010)$ at 25 °C using $E^{\circ}(Hg_2^{2+}/Hg(0)) = 0.7958$ V). That yields (0.7701 ± 0.0010) V for the E° (Fe^{3+}/Fe^{2+}) value. Also K°(308.15 K) = (0.55 ± 0.05) at 35 °C, using the function $(\log_{10} K)/6 = f(I^{1/2})$, and hence, $\Delta_r H = -(104.6 \pm 8.37)\ kJ\cdot mol^{-1}$ can be estimated for Reaction (A.17).

The recalculations of [1934BRA/HER] resolved apparent discrepancies in the older literature. As discussed in the main text, further recalculations using the SIT have been carried out in the present review using modern auxiliary data. These do not introduce significant changes in the values derived by Bray and Hershey [1934BRA/HER].

[1934FRI/ACK]

This paper presents chemical analyses (water content), particle size analyses (microcrystalline dimensions in the *a* and *c* directions by XRD), and heats of solution in 40.5% aqueous HF at 304 - 307 K for a series of nominally hematite (α-Fe_2O_3) specimens prepared by heating synthetic goethite (α-FeOOH) powder at five different temperatures between 493 and 873 K. A companion paper [1935FRI/KLE] deals with specimens prepared from an "amorphous ferric hydroxide" (probably ferrihydrite) precursor. The main aim of the work was to characterize active iron oxide powders of possible interest as catalysts.

Data from this paper and [1935FRI/KLE] have been treated by Diakonov *et al.* [1994DIA/KHO], who found a relatively poor correlation between the enthalpy of dissolution and the specific surface area (estimated from the hematite crystallite dimensions obtained by XRD). Given the relatively high water content of the "hematite" specimens (0.36 to 2.44 weight-%), they likely contained a significant quantity of "hydrohematite" or "protohematite", a metastable intermediate phase that occurs in the transformation of goethite to hematite (see, for example, [1991WAY] and [1999GUA/VEN]). Thus, the excess enthalpy of the active "hematite" specimens likely includes an internal structural component as well as a surface component. It is therefore difficult to extract meaningful information on either the surface energy or the ideal enthalpy of formation for hematite from these data. For further information on the surface energy of iron oxides, see Section VII.2.1 and references cited therein.

[1934HIE/APP]

The average heats of solution (two measurements) of $FeCl_2$(cr), 0.1 m in 1 M HCl(sln) (– 69.2 $kJ\cdot mol^{-1}$) and 2 M HCl (– 68.1 $kJ\cdot mol^{-1}$) at 0 °C are reported, as is the heat of solution of $FeBr_2$(cr) in 2 M HCl (– 72.9 $kJ\cdot mol^{-1}$). The heat of solution of FeI_2(cr) in 2 M HCl was reported as – 78.2 $kJ\cdot mol^{-1}$ at 20 °C. The heat of dissolution of $FeBr_2$(cr) in water at 20 °C (1660 moles water per mole of salt) was reported as – 85.2 $kJ\cdot mol^{-1}$.

[1934HIE/WOE]

Hieber and Woerner [1934HIE/WOE] measured the heats of solution of bromine, iodine, Fe(cr), $FeBr_2$(cr), and FeI_2(cr) into a 25% aqueous solutions KBr solution at 0 K. Only two measurements were carried out for each reaction, and the uncertainties are estimated here as twice the difference of the measured values. From appropriate cycles $\Delta_f H_m^\circ$ ($FeBr_2$, cr, 273.15 K) was found to be – 250.9 $kJ\cdot mol^{-1}$ and $\Delta_f H_m^\circ$ (FeI_2, cr, 273.15 K) was found to be – 125.9 $kJ\cdot mol^{-1}$. These were corrected to 298.15 K using the following heat-capacity values for 285.65 K) —the selected C_p equation for Fe(cr) (Section V.2), estimates (ex JANAF) of (80 ± 1) $J\cdot K^{-1}\cdot mol^{-1}$ for $FeBr_2$(cr) and (84 ± 1) $J\cdot K^{-1}\cdot mol^{-1}$ for FeI_2(cr) and the Pankratz [1982PAN] equations for Br_2(l) ((75.45 ± 0.50) $J\cdot K^{-1}\cdot mol^{-1}$) and I_2(s) ((57.4 ± 0.5) $J\cdot K^{-1}\cdot mol^{-1}$). Hence, $\Delta_f H_m^\circ$ ($FeBr_2$, cr, 298.15 K) = – (251.4 ± 3.2) $kJ\cdot mol^{-1}$ and $\Delta_f H_m^\circ$ (FeI_2, cr, 298.15 K) = – (125.9 ± 4.1) $kJ\cdot mol^{-1}$. Analyses of samples of the iron halides were not reported.

[1934ROT/WIE]

The authors reported measurements leading to enthalpy of formation values for iron oxides and for iron(III) chloride.

It also presents new data on the heat of reduction of α-Fe_2O_3 to Fe_3O_4, using the same bomb-calorimetric procedure as described in [1929ROT]. The authors concluded that their bomb-calorimetry data (*e.g.*, their Table 1) were not quantitatively useful because different solids (and solid mixtures) were formed in different runs (apparently at least partially a function of the amount of paraffin burned in any particular run (and the maximum temperature attained)).

A series of solution-calorimetry measurements were carried out at 20.7 °C using concentrated aqueous HCl (38.65%) as solvent. The heat of solution of iron metal and the heat of vaporisation of the solvent into the gas produced in that reaction and the heat of oxidation of an iron(II) chloride solution with 29.53 weight-% aqueous H_2O_2, were obtained. Samples of iron oxide solids were analyzed, and the heat of solution results for FeO(cr) and α-Fe_2O_3 were corrected for small amounts (3.6 to 6.7 weight-%) of Fe_3O_4 in the solid. Results for Fe_3O_4(cr) were corrected for small amounts (1.9 to 6.0%) of α-Fe_2O_3 in the samples. The results for α-Fe_2O_3 were also corrected for the heat of wetting of the solid. The heats of dissolution of the oxide samples led to heat-of-formation values of – (270.50 ± 0.50) $kJ\cdot mol^{-1}$, – (1116.12 ± 0.92) $kJ\cdot mol^{-1}$, – (816.67 ± 0.84) $kJ\cdot mol^{-1}$ for "FeO(cr)", Fe_3O_4(cr) and α-Fe_2O_3, respectively. Also, using an unpublished value for the heat of solution of $FeCl_3$(cr) into the same solvent, – (391.46 ± 0.96) $kJ\cdot mol^{-1}$ was reported as the value for the heat of formation of $FeCl_3$(cr). The value for the heat of solution of $FeCl_3$(cr) was later published by Kangro and Flügge [1935KAN/FLU], and is discussed in the Appendix A entry for that reference. All of the uncertainties reported in [1934ROT/WIE] are smaller than the 95% confidence limits, and are also smaller than the standard or average deviations.

The reported data were reanalyzed using the same basic cycles employed by the authors, but using current auxiliary data. Corrections were applied to allow for the amounts of minor oxides in the samples and for the reported moisture contents. Three experiments for which the authors' tabulated results contained minor calculation discrepancies were assumed to reflect typographical errors[1]. These experimental results were removed from the data sets used in the recalculations.

These led to heat of formation values of – (394.22 ± 2.19) $kJ\cdot mol^{-1}$, – (1116.42 ± 2.14) $kJ\cdot mol^{-1}$, and – (816.29 ± 1.74) $kJ\cdot mol^{-1}$ for $FeCl_3$(cr), Fe_3O_4(cr) and α-Fe_2O_3, respectively, all at 20.7 °C. Using heat-capacity values (for 296 K from the present review and from CODATA [1989COX/WAG]) the heat of formation values for $FeCl_3$(cr, 298.15 K) (– (394.14 ± 2.19) $kJ\cdot mol^{-1}$), Fe_3O_4(cr, 298.15 K) (– (1116.35 ± 2.14) $kJ\cdot mol^{-1}$), and α-Fe_2O_3(cr, 298.15 K) (– (816.25 ± 1.74) $kJ\cdot mol^{-1}$) were calculated.

The results for "FeO" pose a problem. The maximum Fe:O ratio normally encountered in wüstite is approximately 0.95. As the reported Fe:O ratio in the samples of "FeO" ranged from 0.980 to 0.989, the composition is not stoichiometrically compatible with any wüstite-magnetite mixture. This makes suspect the reported synthesis of the "FeO". An attempted data reanalysis assuming that the solid was a mixture of wüstite and iron metal (rather than FeO and Fe_3O_4) gave less scatter in the results, but the calculated value for the enthalpy of formation (– (252.0 ± 0.8) $kJ\cdot mol^{-1}$) is almost 20 $kJ\cdot mol^{-1}$ less negative than for FeO(cr) from a recalculation directly based on the assumptions in [1934ROT/WIE] (– (271.7 ± 1.3) $kJ\cdot mol^{-1}$). The synthesis of wüstite samples is best done by painstaking equilibration under H_2/H_2O or possibly CO/CO_2, followed by rapid quenching. Therefore, results for the heat of formation of "FeO" (or wüstite) from this study are not accepted in the present review.

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[1] These are the first-row entries in Tables 2 and 9, and the last-row entry in Table 10.

The recalculated enthalpy of formation for α-Fe_2O_3 is about 10 $kJ\cdot mol^{-1}$ less negative than typical recent experimental and assessed values, perhaps reflecting the difficulty of achieving complete dissolution of hematite in aqueous acid media (see, for example, [2005MAZ/NAV]). The results for α-Fe_2O_3 were "corrected" by the authors for a heat of wetting — an effect attributed to the finely divided state of the solid. Removing this "correction" leads to an even less negative enthalpy of formation value ($-(813.70 \pm 1.74)$ $kJ\cdot mol^{-1}$). If the solid samples did have an unusually large surface area, it would be expected that the measured enthalpy of formation would be *less* negative than values based on larger crystals of the solid. Also, the samples contained approximately one mole of water for every 10 moles of iron, and perhaps the sample should be treated as a goethite/α-Fe_2O_3 mixture rather than H_2O plus α-Fe_2O_3. However, by itself this still is insufficient to account for the difference. The enthalpy of formation for Fe_3O_4 is in excellent agreement with current values, as discussed in Section VII.2.7.2.

[1934TRA/SHU]

This is a preliminary note related to measurements of the specific heat of $FeCl_2$(cr) from ~ 18 to ~ 33 K. The results are presented in more detail in [1935TRA/SCH].

[1934WEL/BAU]

This is a review with 112 references on the precipitation and interconversion of iron oxyhydroxides. It includes a schematic diagram of the major synthetic and interconversion reactions — a precursor of those given by [1991SCH/COR], [1998JAM/DUT], and [2000SCH/COR]. It includes a discussion of the C_p data for "colloidal ferric hydroxide hydrates" of [1929HUT/GAR]. Otherwise it is of mainly historical interest as a source of references (mid-19th century to early 1930s) on low-temperature iron oxydroxides.

[1935BAS/CAM]

These researchers heated six concentrated sulfuric acid and iron(III) oxide mixtures on a water bath until the solid completely dissolved and then re-equilibrated them with agitation in a bath at 25 °C. Whenever necessary over a nine month period some solid materials were transferred from one bottle to another to act as seeds for further precipitation and finally, they were allowed to equilibrate for an additional four to five months at 25 °C. The mixtures were filtered through filter paper under pressure to obtain samples of the precipitates. It is postulated that a series of solid solutions exist involving hydrated iron(III) oxide as one end member and a compound with a composition approaching that of $Fe_2O_3\cdot 2.5SO_3\cdot 7H_2O$ as the other end member. XRD evidence is discussed that indicate these solid solutions fall into two categories or types.

One statement is made that the maximum solubility of Fe_2O_3 in sulfuric acid corresponds to 20.5 g in 26.4 g of sulfur trioxide. Clearly these extremely acidic conditions involving sulfuric acid are not pertinent to the scope of this review.

[1935BON/BUR]

This study by Bonnell and Burridge used a transpiration method to measure the equilibrium vapour pressure of water from 10 to 25 °C over a mixture of $FeSO_4{\cdot}7H_2O(cr)$ and a lower hydrate identified as the hexahydrate, but more likely $FeSO_4{\cdot}4H_2O(cr)$. Average values of (612.4 ± 6.7), (907.3 ± 5.0), (1352.7 ± 8.1) and (1939.5 ± 13.4) Pa were reported for 10, 15, 20 and 25 °C, respectively (1σ uncertainties, eight measurements for 10, 15 and 20 °C and seven measurements for 25 °C; for weighting purposes all values were estimated to have uncertainties of 27 Pa). If the measurements are assumed to be for dehydration to the tetrahydrate and $\Delta_r C_p$ is assumed to be zero for the reaction

$$FeSO_4{\cdot}7H_2O(cr) \rightleftharpoons FeSO_4{\cdot}4H_2O(cr) + 3\,H_2O(g) \qquad (A.18)$$

then $\Delta_r H^{o}_{m}$ (A.18) = (162.5 ± 2.9) $kJ{\cdot}mol^{-1}$.

[1935FRI/KLE]

This paper presents chemical analyses (water content), particle-size analyses (microcrystalline dimensions in the *a* and *c* directions by XRD), and heats of solution in 40.5% aqueous HF at 304-307 K for a series of nominally hematite (α-Fe_2O_3) specimens prepared by heating synthetic “amorphous ferric hydroxide” (probably ferrihydrite) powder at five different temperatures between 423 and 873 K. Only the specimens heated at 523 K or higher gave XRD patterns with a recognizable hematite component. A companion paper [1934FRI/ACK] deals with specimens prepared from a goethite (α-FeOOH) precursor. The main aim of the work was to characterize active iron oxide powders of possible interest as catalysts.

Data from this paper and [1934FRI/ACK] have been treated by Diakonov *et al.* [1994DIA/KHO], who found a relatively poor correlation between the enthalpy of dissolution and the specific surface area (estimated from the hematite crystallite dimensions obtained by XRD). Given the relatively high water content of the “hematite” specimens (0.50 to 4.54 weight-%), they likely contained a significant quantity of intermediate material, perhaps “hydrohematite” or “protohematite” (see, for example, [1991WAY] and [1999GUA/VEN]). Thus, the excess enthalpy of the active “hematite” specimens likely includes an internal structural component as well as a surface component. It is therefore difficult to extract meaningful information on either the surface energy or the ideal enthalpy of formation for hematite from these data. For further information on the surface energy of iron oxides, see Section VII.2.1 and references cited therein.

[1935KAN/FLU]

The authors measured the heat of solution of $FeCl_3(cr)$ at 20 °C in water and HCl(sln) as a function of the iron and acid concentrations. Differential heats of dilution were calculated. In water the iron molalities ranged (approximately) from 0.03 to 5.6 m. The enthalpy of solution of $FeCl_3(cr)$ to form a solution 0.05 m in $FeCl_3$ is reported as

– (132.26 ± 0.84) kJ·mol$^{–1}$. Heats of solution of $FeCl_3$(cr) in HCl(sln) were reported as a function of the acid content (0.31 to 37.5 weight-%, 0.03 m to 0.05 m $FeCl_3$(cr)). The experimental procedures are well described, and estimated uncertainties are reported, but details are lacking concerning exact sample sizes and reproducibility of specific measurements. There is a good discussion of earlier measurements.

The heat of solution of $FeCl_3$(cr) in concentrated HCl cited by Roth and Wienert [1934ROT/WIE] as Flügge, unpublished, likely is prepublication use of the value reported in this work [1935KAN/FLU]. In the present review, a quadratic function was fitted to the heats of solution of $FeCl_3$(cr) in the three HCl solutions of highest weight-% HCl [1935KAN/FLU], and a short extrapolation leads to – 8.332 kcal·mol$^{–1}$ (– 34.86 kJ·mol$^{–1}$) for dissolution of $FeCl_3$(cr) in 38.65 weight-% HCl at 20 °C. In Roth and Wienert [1934ROT/WIE], – 8.342 kcal·mol$^{–1}$ (– 34.90 J·K$^{–1}$·mol$^{–1}$) was used for the enthalpy of solution value at 20.7 °C.

[1935SCH/SWE]

Two series of batch experiments were performed at (25.00 ± 0.01) °C in which fine-grained Ag was reacted with iron(III) perchlorate overnight in rotating flasks. The approach to equilibrium was reversed by also heating the flask on about half the occasions to 40 - 50 °C for half an hour before returning it to the 25 °C bath. The iron(II) concentration was measured by titration of a filtered sample with permanganate and the corresponding iron(III) concentration was determined by difference. Silver(I) concentrations were measured by titration with thiocyanate.

The equilibrium to be considered is as follows: $Fe^{3+} + Ag(s) \rightleftharpoons Fe^{2+} + Ag^{+}$.

Neither the precision nor accuracy of the titration analyses was given and the number of significant figures tabulated is obviously excessive.

Table A-2: Raw experimental data from [1935SCH/SWE].

Series #1 Concentrations in mol·dm$^{–3}$			
$[Fe(ClO_4)_3]$	$[HClO_4]$	$[Fe^{2+}]$	$[Ag^{+}]$
0.1244	0.4673	0.07387	0.07363
0.09952	0.3738	0.06292	0.06256
0.08293	0.3115	0.05509	0.05496
0.08024	0.3014	0.05368	0.05363
0.06220	0.2336	0.04457	0.04450
0.04147	0.1558	0.03282	0.03256
0.02073	0.07788	0.01840	0.01824

(Continued on next page)

Table A-2 (continued)

Series #2 Concentrations in mol·dm^{-3}			
[Fe(ClO$_4$)$_3$]	[HClO$_4$]	[Fe^{2+}]	[Ag$^+$]
0.1045	0.9255	0.06529	0.06546
0.08360	0.7404	0.05504	0.05509
0.06270	0.5553	0.04420	0.04435
0.04180	0.3702	0.03223	0.03232
0.02090	0.1851	0.01811	0.01813
0.008360	0.07404	0.007976	0.007981

[1935TRA/SCH]

The authors reported measurements of the specific heat of FeCl$_2$(cr) between 16 and 127 K[1]. A maximum in the heat-capacity curve was found near 23.5 K, with what appears to be a poorly distinguished shoulder near 20 K. The accuracy of the results of measurements for other transition metal salts, as carried out by the same research group with the same apparatus (*e.g.*, [1936TRA/SCH]), has been questioned [1943KEL/MOO], [1952BUS/GIA2]. Although there is no reason to doubt the existence of the "anomaly", Busey and Giauque [1952BUS/GIA2] suggest that the thermometer used by Trapeznikowa *et al.* may not have attained thermal equilibrium, and consequently their specific heats tended to be greater than those reported by others (also see the much later results between 40 and 50 K from Lanuse *et al.* [1972LAN/CAR]). The results for the FeCl$_2$(cr) are more scattered than might be hoped (by as much as 4%), but are considerably less discrepant with other measurements [1943KEL/MOO], [1961STO], [1964KOS] than the measurements for CrCl$_3$, MnCl$_2$ or NiCl$_2$. For the purposes of fitting a single function to all the calorimetry results, the uncertainties in the individual values for the heat capacities were estimated in the present review as ± 1.0 J·K^{-1}·mol^{-1} for $T = 28$ K, and ± 0.5 J·K^{-1}·mol^{-1} at lower temperatures.

[1936KRE/KAR]

Krestovnikov and Karetnikov reported specific heats for FeCl$_2$(cr) based on drop-calorimetry measurements (reference temperature 288 K) from 473 to 913 K. The enthalpy differences are about 15% lower than those found by Moore [1943MOO] near 500 K, and a few per cent higher than Moore's values at the high end of the range (see Figure 1 of [1943MOO]). Also, the specific-heat values are not concordant with the results of Oetting and Gregory [1960OET], [1961OET/GRE], nor with values of $C^{\circ}_{p,\mathrm{m}}$ (FeCl$_2$, cr, 298.15 K) based on low-temperature adiabatic calorimetry

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[1] There is a value reported for 221.60 K. This temperature value is assumed to be a simple typographical error, as the reported heat capacity is consistent with a temperature of 121.60 K.

[1943KEL/MOO]. The results of Krestovnikov and Karetnikov have not been used further in the present review.

[1937COO]

This is of historical interest as the first "modern" estimate of the solubility product of amorphous "$Fe(OH)_3$", in the sense that an activity, rather than concentration, product was calculated while taking account of the partial hydrolysis of Fe^{3+} to $FeOH^{2+}$. The following values for the activity product $a_{Fe3+}\cdot(a_{OH-})^3$ were recalculated from data of [1933KRI/AWS]: $10^{-37.2}$ from titration data, and $10^{-39.2}$ from electrometric data (potential measurements on Fe^{2+} in equilibrium with "$Fe(OH)_3$") with an assumed activity coefficient of 0.2 for Fe^{2+}. The "$Fe(OH)_3$" of [1933KRI/AWS] was freshly precipitated, and likely corresponded to a 2-line ferrihydrite.

The paper includes a brief discussion about the solubility product of $Fe(OH)_2$. The author cites an earlier study [1935COO] of the solubility of iron(II) hydroxide as being 1.8×10^{-14}, presumably at ambient conditions.

The aim of this work was to establish "iron" levels in seawater and to estimate the likely speciation of iron (claimed to be principally $FeOH^{2+}$ and Fe^{2+}) based on earlier work. Due to the weakness of the existing database at that time and the well documented problems associated with studies of the solubility of amorphous iron hydroxides, no useful quantitative thermodynamic data can be extracted from this article.

[1937DOM]

The equilibrium of the reaction

$$2\,FeF_3(cr) + 3\,H_2O(g) \rightleftharpoons Fe_2O_3(cr) + 6\,HF(g) \qquad (A.19)$$

was studied from 573 to 723 K. The measured equilibrium constants showed only a small variation with flow. In the present review the results were used with the values selected for $Fe_2O_3(cr)$ (Section VII.2.2) and from CODATA [1989COX/WAG] to obtain values of $G(T)$, − 1066, − 1074, − 1083 and − 1092 $kJ\cdot mol^{-1}$, at 573.15, 623.15, 673.15 and 723.15 K, respectively.

[1937FRI/ZER]

This paper deals mainly with the experimental heats of solution of various iron oxides and oxyhydroxides in 40% aqueous HF at (20.5 ± 0.5) °C. The specimens included: both natural and synthetic lepidocrocite (γ-FeOOH); synthetic maghemite (γ-Fe_2O_3), including materials prepared both by low-temperature air oxidation of magnetite and by dehydration of lepidocrocite; synthetic magnetite (nominally Fe_3O_4); synthetic hematite (α-Fe_2O_3, obtained by heating γ-Fe_2O_3 at 500 °C); synthetic goethite (α-FeOOH); and amorphous hydrated iron(III) oxide (probably ferrihydrite). The material characterization included analysis of excess water content for all specimens and measurement of crystallite size by X-ray diffraction for representative specimens of maghemite and lepidocrocite.

This paper does not appear to contain any data likely to improve estimates of the thermodynamic properties of hematite, goethite, or magnetite, and the review therefore focuses on lepidocrocite and maghemite.

Majzlan *et al.* [2003MAJ/GRE] suggest that these measurements are "perhaps only of historical interest", because the solution enthalpies for natural and synthetic lepidocrocite differ by about 25 $\mathrm{kJ \cdot mol^{-1}}$; however, this difference refers to heats of solution expressed per mol Fe_2O_3 [2FeOOH is equivalent to $Fe_2O_3 \cdot H_2O$]. The heats of solution per mol FeOOH for six synthetic lepidocrocite specimens were 10.8 to 14.1 $\mathrm{kJ \cdot mol^{-1}}$ (average 12.5 $\mathrm{kJ \cdot mol^{-1}}$) more negative than for one natural mineral specimen. This is comparable to the variation in enthalpy for synthetic goethite with different specific surface areas ([2005MAZ/NAV] and references therein).

Diakonov ([1998DIA], [1998DIA2]) reviewed data for maghemite and lepidocrocite from this paper, and attempted to extract self-consistent thermodynamic values. While Diakonov showed that the difference in heats of solution between the natural and synthetic lepidocrocites is not inconsistent with estimated surface area and surface-energy values, the uncertainties in these estimates are large for the very fine-grained (< 5 nm) synthetic lepidocrocite, making it difficult to estimate the enthalpy of formation for well-crystallized material. Diakonov's best estimate based on the synthetic lepidocrocite [1998DIA2] is:

$$\Delta_f H_m^\circ (\mathrm{FeOOH}, \gamma, 298.15\ \mathrm{K}) = -(550.1 \pm 2.5)\ \mathrm{kJ \cdot mol^{-1}}$$

Based on data for synthetic maghemite and goethite (including measurements from [1934FRI/ACK]), plus the single measurement for natural lepidocrocite, Diakonov ([1998DIA], [1998DIA2]) also calculated:

$$\Delta_f H_m^\circ (\mathrm{Fe_2O_3}, \gamma, \text{disordered}, 298.15\ \mathrm{K}) = -(805.8 \pm 5.7)\ \mathrm{kJ \cdot mol^{-1}} \text{ and}$$

$$\Delta_f H_m^\circ (\mathrm{FeOOH}, \gamma, 298.15\ \mathrm{K}) = -(556.4 \pm 2.0)\ \mathrm{kJ \cdot mol^{-1}}.$$

Note that the value for γ-FeOOH is significantly different from the one based on synthetic material; the uncertainty in the latter value is probably underestimated, given the stated difficulty of estimating surface area and surface energy.

These values are discussed further in Sections VII.2.4.2 and VII.2.11.2.

[1937MER/POS]

This paper mainly used results from an earlier study [1922POS/MER] to propose a phase diagram for mineral formation in the Fe_2O_3-H_2O-SO_3 system. A reinterpretation of some of the results of Baskerville and Cameron [1935BAS/CAM] was also provided.

[1937MOL]

This paper reported measurements of the electrochemical potential difference of cells of the type

$$\text{Pt} \mid \text{equimolar solutions of } Fe^{3+}\text{-}Fe^{2+}, Cl^{-} \vdots\vdots\ 3.5\ \text{M KCl} \mid Hg_2Cl_2 \mid \text{Hg(0)}.$$

Equimolar solutions of Fe(III) and Fe(II) chlorides were used, the acid concentration (HCl(sln)) was maintained at 0.1 M, and the molar concentration of KCl(sln) was varied from 0.0 to 3.0 M. The effects of the changes in supporting electrolyte were found to be small, and an average value, K_1 = 4.1 $mol^{-1}\cdot dm^{3}$, the formation constant for $FeCl^{2+}$ at 25 °C, was reported. No hydrolysis correction was applied. The results of this work were not reported in sufficient detail to be used further in the present review.

[1937NEU/HEI]

The gas pressures above samples of anhydrous iron sulfates were measured by a static method. The decomposition of $FeSO_4$ was found to be irreversible, and it was proposed that the decomposition is not a single-step reaction. In the absence of a good entropy value for $FeSO_4$(cr) and heat-content data at higher temperatures, no attempt is made to use these results in the present review. The measurements over $Fe_2(SO_4)_3$(cr) were compared to those from earlier work [1908KEP/ANS], [1908WOH/PLU], [1910BOD/SUZ], [1913GRU] (and partial tables of values were listed from those references[1]). In Kellogg's review [1964KEL], the results of Neumann and Heintke were found to be consistent with those from later studies (also see the Appendix A entry for [1964KEL]). Decomposition pressures were reported for a solid with a composition close to $Fe_3(SO_4)_4$. At temperatures from 686 to 889 K, this solid appeared to decompose without first being converted to the simple iron(III) sulfate.

[1937SCH/SHE]

This was one of the first detailed investigations that was used to establish the value of E° (Fe^{3+}/Fe^{2+}) as (0.770 ± 0.002) V, a value that was adopted by almost all the Tables and continues to appear as a reference value today. The cell used at 25 °C was:

$$\text{Pt},H_2 \mid HClO_4\,(c_1) \vdots HClO_4\,(c_1), Fe(ClO_4)_3\,(c_3), Fe(ClO_4)_2\,(c_2) \mid \text{Pt}.$$

The ratios c_3/c_2 were maintained constant close to 1 with various concentrations of Fe. Four solutions with different values of c_1 were investigated. The authors used the activity coefficient equation

$$\log_{10} \gamma_A = -\,0.505\, z_A^2 \left(\sqrt{I_m} \,/\left(1+\sqrt{I_m}\right)\right) \tag{A.20}$$

for extrapolation to an ionic strength I_m of zero.

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[1] There appears to have been a number of fairly insignificant typographical errors in the transcription of values from the earlier publications.

These results were reanalysed using the SIT method for the extrapolation of the $E^{o\prime}$ values to zero ionic strength with the constants accepted by the TDB for other quantities such as the hydrolysis constants for Fe^{3+}. For convenience, we define a potential $E^{\ddagger} = E^{o\prime} + (RT / F)\ln\gamma_{H^+}$ so that in Eq. (A.21)

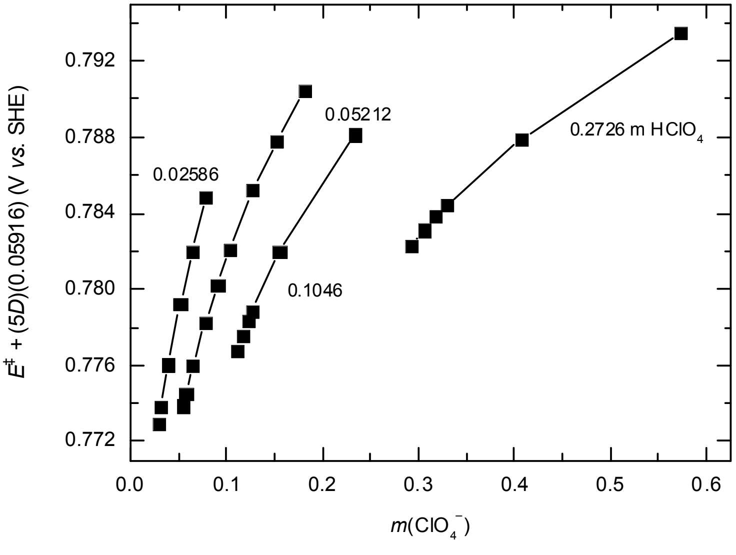
$$E^{\ddagger} + (5D)\,0.05916 = E^{o} - (0.05916\,\Delta\varepsilon m_{ClO_4^-}) \qquad \text{(A.21)}$$

the term $\Delta\varepsilon$ is the diffrence ($\varepsilon(Fe^{2+}, ClO_4^-) - \varepsilon(Fe^{3+}, ClO_4^-)$).

In the present analysis, two hydrolysis species were taken into account, $FeOH^{2+}$ and $Fe_2(OH)_2^{4+}$; only $FeOH^{2+}$ was considered in the original paper.

The SIT formalism has been applied to the four series of measurements made by Schumb *et al.* ([1937SCH/SHE], Figure A-2). The uncertainties in the measurements of Schumb *et al.* are estimated here as ± 0.002 V. It was not possible to treat all the data together for the four acidities employed because the experimental points form a cluster, which does not give a clear-cut E^{o} value for $I = 0$.

Figure A-2: Function $E^{\ddagger}$ + $(5D)(RT(\ln(10))/F)$ *vs.* $m_{ClO_4^-}$ from the experimental data of [1937SCH/SHE], for 298.15 K. The numbers indicate the acid molal concentrations at which the series of potential-difference measurements have been done. The concentration of total iron varies along each series with a constant Fe^{3+}/Fe^{2+} ratio.



As shown by the curves of Figure A-2 it is possible to fit the four curves separately, but it is obvious that the slopes, which are supposed to give the value of $\Delta\varepsilon$, are different, and increase with the decrease of the ionic strength. One contributing factor to the observed multiple lines with different curvatures may be the junction potentials, which will differ with changes in iron(II) and iron(III) concentrations at each acid molality. These junction potentials are likely to be more important for solutions containing the higher iron:$HClO_4$ concentration ratios. If all the data points are used, the calculated value of $\Delta\varepsilon$ varies from 3.7 to 0.29 kg·mol^{-1} for the solutions with added $HClO_4$ concentrations of 0.02586 to 0.2726 m, and the data of Schumb *et al.* cannot be used with the rest of the literature data to get a unique value of E° (Fe^{3+}/Fe^{2+}) according to the SIT method. To overcome this difficulty we eliminated the data points for which the ratio of Fe:$HClO_4$ was greater than 0.1. In doing so, we selected the data for which the junction potentials are estimated to be sufficiently small to be neglected. This selection eliminated 12 of the authors' 25 data points, but allowed treatment of the remaining data using the SIT formalism. Hence the important low ionic strength points could be used in the extrapolation of $E^{\ddagger}$ to zero ionic strength. This is well illustrated by comparison of Figures VI-2 and VI-3 of the main text. The curvature in the line in Figure VI-3 justified the introduction of a second ionic-strength dependent SIT coefficient (SIT_2, Section VI.1.2.1.1.1). As discussed in the main text (Section VI.1.2.1.1), the selected points from this work, together with values from several other sources, were used in the present review in the determination of the value of E° (Fe^{3+}/Fe^{2+}) and the values of $\varepsilon(Fe^{3+}, ClO_4^-)$ (SIT_1) and $\varepsilon_1(Fe^{3+}, ClO_4^-)$, $\varepsilon_2(Fe^{3+}, ClO_4^-)$ (SIT_2). The results of Schumb *et al.* make an important contribution to the final assessed values.

[1938LAM/JAC]

This study was carried out using a home-made glass-electrode assembly in conjunction with an Ag/AgCl reference electrode at 25 °C and using conductivity cells, which are not described. Much of this paper is given over to following the kinetics of Fe(III) hydrolysis-induced precipitation of colloidal iron(III) chlorides and/or hydroxides, analogous to the results reported in [1896GOO]. From the two experiments reported with HCl added (Table VI), values of $\log_{10} {}^{*}K_{1,1}$ of -2.75 and -2.73 are calculated under the assumption of no further hydrolysis occuring at low ionic strengths of 0.0017 and 0.0019, respectively. These values are much lower than those reported later by other authors despite the relatively high measured pH values, 3.335 and 3.189, respectively, where other hydrolysis equilibria should take place leading to higher apparent values of $\log_{10} {}^{*}K_{1,1}$. Other measurements without added HCl are therefore even more suspect, noting that all of these measurements were reported by extrapolating the changing cell potential back to zero time.

These results also warn of problems of rapid colloid formation in mildly acidic Fe(III) solutions such that the results obtained here cannot be considered to be representative of simple homogeneous hydrolysis equilibria.

[1938SAN]

Sano studied the reaction

$$\mathrm{FeCl_2(cr) + H_2(g) \rightleftharpoons Fe(cr) + 2\,HCl(g)}$$

at nine temperatures between 769 and 868 K. The $\log_{10} K_p$ values from the author's table were converted to equilibrium constants expressed in bars, and values for the enthalpy of reaction at 298.15 K were obtained from a third-law calculation using the selected values for the entropies and heat-capacity functions for Fe(α) and $FeCl_2$(cr) (Sections V.2 and VIII.3.2.1.1) and for H_2(g) and HCl(g) [1989COX/WAG]. Internal agreement is unusually good (154.36 ± 0.53) $kJ\cdot mol^{-1}$, although agreement with values from other studies (*e.g.*, [1950KAN/PET], [1960NOV/MAK]) is not within the combined uncertainty limits (Parker and Khodakovskii [1995PAR/KHO] assigned an unceratinty of ± 1.7 $kJ\cdot mol^{-1}$).

[1940CHI/MAR]

This paper describes a careful study of the Fe(cr)-"FeO"(wüstite, cr) and Fe(cr)-"FeO"(l) equilibria in water-saturated hydrogen atmospheres. In 22 measurements at temperatures from 1165 to 1514 °C, equilibrium was approached from both the reducing and oxidizing side, as determined thermogravimetrically on $>$99.9% pure Fe-foil-based specimens, at each temperature. Special care was necessary because oxidation of the iron was delayed to varying degrees (up to 32 minutes) in some tests. In addition, the melting points of wüstite (in equilibrium with Fe metal), and of pure and oxygen-saturated Fe, were determined to be 1369, 1524, and 1535 °C, respectively.

Results on the iron-wüstite equilibrium were combined by the authors with those of Emmett and Shultz [1933EMM/SHU], yielding the following thermodynamic values for wüstite with the composition $Fe_{0.95}O$:

$$\Delta_f H^\circ_m(\mathrm{Fe_{0.95}O, cr, 298\ K}) = -63.38\ \mathrm{kcal\cdot mol^{-1}} = -265.2\ \mathrm{kJ\cdot mol^{-1}}$$

$$S^\circ_m(\mathrm{Fe_{0.95}O, cr, 298\ K}) = 14.06\ \mathrm{cal\cdot K^{-1}\cdot mol^{-1}} = 58.8\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

This is based on the following expression, obtained by graphical methods, with corrections for the heats of transition (α → β → γ) of Fe(cr).

$$\mathrm{Fe_{0.95}O(cr) + H_2(g) \rightleftharpoons 0.95Fe(cr) + H_2O(g)}$$

$$\Delta_f G^\circ_m(T)/\mathrm{kcal\cdot mol^{-1}} = 7457 + 7.24T\cdot\ln(T/\mathrm{K}) - 0.00321(T/\mathrm{K})^2 - 52.628(T/\mathrm{K})\,.$$

These values are not reviewed further, because of the very high experimental temperature range, and the limited treatment of wustite in the current review.

[1940MIL/NAC]

Heat-capacity values from 193 calorimetric measurements between 12 and 110 K were reported for a sample of anhydrous $FeBr_2$. The result of an iron analysis for the sample

(26.61%) was slightly higher than calculated (25.9%) for a stoichiometric sample of $FeBr_2$. A heat-capacity maximum was reported for 14.1 K, and integration of $C^{o}_{p,m} / T$ from 12 to 20 K indicates ~ 5.5 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ for the difference between S^{o}_{m} ($FeBr_2$, 20 K) and S^{o}_{m} ($FeBr_2$, 12 K). This maximum and the approximate size of the entropy contribution were later confirmed [1972LAN/CAR] (6.3 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ for the same entropy difference). A second, smaller maximum was found near 21.8 K. However, this was not confirmed in the later study of Lanusse *et al.* [1972LAN/CAR].

[1940MIL/PAR]

Heat-capacity values from 156 calorimetric measurements from 11.5 to 129.2 K were reported for a sample of anhydrous FeI_2. The result of an iron analysis for the sample (18.5%) was slightly higher than calculated (18.0%) for a stoichiometric sample of FeI_2. No sharp heat-capacity maximum was found in this range of temperatures, although the results show a broad plateau between 90 and 100 K (perhaps better described as a broad peak with a maximum near 90 K).

[1941BEL/SHP]

Belopolskii and Shpunt carried out an extensive solubility study for the $FeSO_4$-H_2SO_4-H_2O system at 50, 60, 70 and 90 °C. There is a limited amount of new data for the $FeSO_4$-H_2O binary system, and the authors contend that they provide support for the existence of $FeSO_4{\cdot}4H_2O$ over a limited temperature range near 60 °C. They also suggest that the tetrahydrate is stable in the saturated ternary system at 50 °C over a very small region near 8 weight-% H_2SO_4 and at 60 °C for compositions < 1.24 weight-% H_2SO_4. Much of the study was focused on the dehydration of $FeSO_4{\cdot}H_2O$ to $FeSO_4$(cr), which occurs at weight fractions of H_2SO_4 above 0.83 (solution weight fractions of $FeSO_4$ < 0.01). The equilibrium solution concentration of iron(II) was found to increase slightly as the weight fraction of sulfuric acid approached the composition at which $FeSO_4{\cdot}H_2O$(cr) is dehydrated to $FeSO_4$(cr). The weight fractions were used to estimate the water vapour pressures (~ 50 to 500 Pa) for the dehydration reaction as a function of temperature. The results at these low “equilibrium” vapour pressures are too scattered to provide good values for the thermodynamic quantities related to the dehydration reaction.

[1941BEN/FRE]

This early spectroscopic study (at 500 nm) measured the effect of added chloride on formation of $FeSCN^{2+}$, and a dissociation constant for $FeCl^{2+}$ was also determined. The ionic strength was maintained at 0.665 M ($NaClO_4$ + NaCl (0.022 to 0.655 M)) in the presence of 0.00011 M NaSCN and 0.011 M HCl. The temperature of the measurements was not specified. The reported value for the dissociation constant of $FeCl^{2+}$ was (0.78 ± 0.10) M. As noted by Lister and Rivington [1955LIS/RIV3], this rather high value probably resulted, at least in part, from omission of the mixed complex $FeClSCN^{+}$ in the data analysis. The result was not used further in the present review.

[1941BRO]

The speciation of iron in iron(III)/iron(II) chloride solutions used in this study was assumed *a priori* to consist of Fe^{3+}, $FeOH^{2+}$, $FeCl^{2+}$ and Fe^{2+} with millimolar HCl concentrations at a fixed ionic strength of *ca*. 0.53 M (KNO_3) at 25 °C. However, the chloride ion concentration reached that of the ionic strength so that the supporting indifferent electrolyte condition was certainly not met. A cell was used fitted with Hg,HgCl and platinum electrodes, and possessing a liquid junction (although there was no mention of liquid-junction potentials). Total iron concentrations were $< 1.7 \times 10^{-3}$ M and $[H^+]_{calc} < 6.2 \times 10^{-3}$ M. Values were reported of the first hydrolysis constant of Fe^{3+}, $(1.73 \pm 0.01) \times 10^{-3}$ M and of the dissociation constant of the monochloridoiron(II) complex, (0.44 ± 0.02) M for the purported ionic strength of 0.53 M.

In view of the assumptions made as to the speciation of the solutions, the absence of any liquid-junction potential treatment and the violation of the supporting electrolyte medium approach, as well as the insignificantly low association constant for a 3:1 electrolyte, these results are not considered reliable by this reviewer.

[1941DEM/FED]

This paper describes conductance and polarographic studies for several sulfates, mixtures of sulfates and double sulfates. A sample of hydrated iron(II) sulfate was analyzed, and a series of solutions was prepared by weight (0.0002 to 2.0 $mol \cdot dm^{-3}$). The experimental method is described in more detail in a companion paper [1941FED]. Fedoroff indicated that a precision (high frequency) AC conductance bridge was unavailable for carrying out these experiments. For the purposes of the authors, this was not a problem, because their primary interest was in doing comparative measurements.

In the present review, using a modified version of the Lee-Wheaton approach (*cf.* the Appendix A entry for [1988KUB/MOC]), reanalysis was carried out with the 25 °C conductance results for the solutions with concentrations from 0.0002 to 0.005 $mol \cdot dm^{-3}$. From this, $\Lambda°$ is 272.5 $S \cdot cm^2 \cdot mol^{-1}$, and the ion association constant K_1° is (148 ± 81) (*i.e.,* $\log_{10} K_1^{\circ}$ is 2.2). The experimental molar conductances are generally greater than those found later by Kubota *et al.* [1988KUB/MOC], and the slope of the plot of molar conductances *vs.* concentration is less. The conductances reported by Fedoroff for $NiSO_4$ solutions [1941FED] show similar differences relative to values from other studies of $NiSO_4$ solutions [2005GAM/BUG] (even the 1895 work of Franke [1895FRA]). It appears that the conductance values from the paper of Demassieux and Fedoroff are not very accurate, and the value of the association constant for Fe^{2+} with SO_4^{2-} as calculated from these data is not used further in the present review.

[1941FRI/WAL]

The influence of Fe particle size and prior heat treatment on Fe-Fe_3O_4 equilibrium in H_2-H_2O atmospheres was examined. Since even the “inactive” Fe specimens were extremely fine-grained (mean particle size 470 Å), the data are not used in the current review.

[1941KEL]

The heat capacity of a synthetic "ferrous silicate" sample was determined by adiabatic calorimetry for temperatures from 52.2 to 295.2 K. A sharp maximum was found near 65 K. The Fe:Si ratio in the sample was 1.99 by analysis. For the purposes of fitting a single function to all the relevant calorimetry results, the uncertainties in the individual values for the heat capacities were estimated in the present review as $\pm 0.3\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ for temperatures below 270 K, and as $\pm 0.5\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ for temperatures closer to room temperature.

[1941MAS]

Isopiestic measurements of $\mathrm{SmCl_3}$ and $\mathrm{EuCl_3}$ were made at 25 °C using sodium and potassium chloride reference solutions whose osmotic coefficients were apparently derived from a plot by Scatchard *et al.* [1938SCA/HAM]. These authors tabulate the osmotic coefficients for other lanthanides and $\mathrm{AlCl_3}$ that they fitted using the Scatchard method, but do not give the source of these data.

These osmotic coefficients were treated and are shown in the plot in [1949ROB/STO] who also used pre-existing isopiestic data to form a table of smoothed values using different osmotic coefficients for the reference solution. At the present time, it is not clear what the source of either data set is, although it is likely that the same original data were in fact used. Therefore, these auxiliary data must be used with some caution in seeking out surrogate systems in the evaluation of the elusive $\varepsilon(\mathrm{Fe^{3+}},\mathrm{X^-})$ interaction coefficients that exhibit weak interactions between the triply charged metal cation and $\mathrm{X^-}$ where $\mathrm{X^-}$ represents a halide or pseudohalide anion. The small aluminium cation appears to be the best choice for this evaluation. More $\mathrm{AlCl_3(sln)}$ osmotic-coefficient data were presented by Robinson and Stokes [1949ROB/STO].

Table A-3: Smoothed osmotic coefficients for $\mathrm{AlCl_3(sln)}$ at 25 °C from an unknown source (Scatchard [1936SCA]).

m, molal	ϕ			m, molal	ϕ
0.05	0.823	0.7	1.141	1.4	1.751
0.1	0.819	0.8	1.214	1.5	1.855
0.2	0.841	0.9	1.292	1.6	1.966
0.3	0.890	1.0	1.376	1.7	2.081
0.4	0.948	1.1	1.469	1.8	2.203
0.5	1.009	1.2	1.558		
0.6	1.073	1.3	1.653		

[1941PER]

Perreu reported the results of heats of solution of $FeCl_2 \cdot 4H_2O$ in water at 12.5 °C (final salt to water molar ratios between 400 and 1105.5), and also heats of dilution of iron(II) chloride solutions from high concentrations to 0.0009 mole fraction salt.

[1941PER2]

Heats of solution of $FeSO_4 \cdot 7H_2O$ were measured at 19 - 21 °C for $Fe:H_2O$ ratios of 1500 to 32.7 (saturation). The values for the lowest final salt molalities were 18.24 $kJ \cdot mol^{-1}$ (0.0907 m $FeSO_4$), 18.20 $kJ \cdot mol^{-1}$ (0.0597 m $FeSO_4$), and 18.08 $kJ \cdot mol^{-1}$ (0.0358 m $FeSO_4$). These are consistent with values reported in other studies [1908THO], [1914FOR]. Measurements were also done to generate an equation for $C^{\circ}_{p,\mathrm{m}}(T)$ for the solutions, but only for $m \geq 0.118$ (and therefore not particularly useful for calculation of the partial molar heat capacity for $FeSO_4$(sln)).

[1941STO/ROB]

These pioneering isopiestic studies of Stokes and Robinson using glass desiccators fitted with a copper block were extended to iron(II) chloride solutions with KCl standards. They modified their technique to allow the $FeCl_2$ solutions to be added to two empty silver cups sealed inside the desiccator which had been thoroughly purged with hydrogen. After removing and weighing the cups containing the equilibrated solutions, the iron(II) concentrations were determined gravimetrically. By this laborious technique the osmotic coefficients of nine solutions were measured from 0.3132 to 2.050 $mol \cdot kg^{-1}$ at 25 °C.

The osmotic coefficients of Stokes and Robinson were recalculated in [2004MOO/HAG] using a more recent compilation of osmotic coefficient data [1999ARC2] for aqueous KCl and were found to be in excellent agreement with their results. Therefore, the data from [1941STO/ROB] are included in the determination of $\varepsilon(Fe^{2+},Cl^{-})$ in this review.

[1941VER/HAA]

Although this paper does not include any thermodynamic data, it is important as an early, detailed reference on the low-temperature (~ 120 K) phase transition in magnetite, now commonly known as the Verwey transition (see Section VII.2.7.2). It includes several references to prior studies on various aspects of the phase transition, including electrical conductivity and magnetic effects but not to its detection by the heat-capacity measurements of Parkes and Kelley [1926PAR/KEL] and Millar [1929MIL]. It explains the phase transition in terms of order/disorder of divalent and trivalent Fe on the octahedral sites in the spinel structure of magnetite, and includes the effects of changing stoichiometry by partial oxidation, which was subsequently examined in more detail, *e.g.*, by Shepherd *et al.* ([1991SHE/KOE] and references therein).

[1942JOH/WEI]

The vapour pressures of pure $FeCl_3$ and three mixtures of $FeCl_3$ and NaCl were measured under anhydrous conditions from 232 °C to a maximum of 332 °C. A eutectic was observed with a composition of 46 mole per cent NaCl and 56 mole per cent iron(III) chloride at 158 °C.

No relevant thermodynamic information could be gleaned from this paper.

[1942MOO/KEL]

Moore and Kelley [1942MOO/KEL] carried out adiabatic calorimetry measurements of the heat capacity of $FeSO_4$(cr) for temperatures between 53.0 and 294.9 K. No thermal anomalies were found within this temperature range. The authors encountered difficulty in preparing a pure sample of $FeSO_4$(cr), and the sample used contained one to two per cent of an iron(III) solid (probably Fe_2O_3 [1973SKE/ESP]). The value of 100.78 $J\cdot K^{-1}\cdot mol^{-1}$ is calculated for $C^{o}_{p,m}$ ($FeSO_4$, cr, 298.15 K) based on extrapolation from a simple second-order polynomial fit to the values reported for temperatures between 236.6 and 294.9 K. The polynomial fits the data very well (within 0.3 $J\cdot K^{-1}\cdot mol^{-1}$). As the calorimetry results near room temperatures are subject to greater possible systematic errors, and the sample was impure, the uncertainty in $C^{o}_{p,m}$ for 298.15 K is estimated in the present review as $\pm$ 2.00 $J\cdot K^{-1}\cdot mol^{-1}$.

[1942RAB/STO]

This early paper reported on a very complete investigation of the Fe^{3+} aqueous inner-sphere complexes $FeCl^{2+}$, $FeCl_2^+$ and $FeCl_3$(aq) by spectrophotometry. The maximum of the main Fe^{3+} peak occurs at *ca.* 240 nm where the molar absorption coefficient $\varepsilon_{Fe^{3+}}$ $\approx$ 500 $m^2\cdot mol^{-1}$ in acidic perchlorate solutions.The strong charge-transfer absorption bands of the Fe^{3+} chlorido complexes in the UV-visible region were used to determine the speciation and the values of the formation constants. The absorption due to the first hydrolysis species, $FeOH^{2+}$ and the absorption of the Fe^{3+} aqueous ion, were taken into account. Absorption from $FeOH^{2+}$ (charge-transfer band) was observed even in 0.5 M $HClO_4$ solutions.

The absence of spectral variation for Fe(III) in perchlorate solutions up to 3 molar indicated that no significant quantities of Fe^{3+} perchlorato complexes were formed. To avoid interference from higher chloride associates of Fe^{3+}, the determination of the formation constant of $FeCl^{2+}$ was carried out in dilute chloride solutions with rather high Fe^{3+}/Cl^- ratios. The formation constant of $FeCl^{2+}$ as a function of the ionic strength from 0.13 to 2.17 molar was measured and yielded the following relationship:

$$\log_{10} K_1 = 1.51 - (3I_c^{½}/(1 + 1.5\, I_c^{½})) + 0.295 I_c$$

The reported value for $I_c = 0$ was K_1^{o} = 30 $mol^{-1}\cdot dm^3$ which gives $\Delta_r G^{o}$ = – (8.36 $\pm$ 0.83) $kJ\cdot mol^{-1}$, a number close to values from later studies.

The formation constant as a function of temperature (~ 20 to 50 °C) at an ionic strength $I_c = 0.61$ M, indicated $\Delta_rH(I_c = 0.61\text{ M}) = (35.56 \pm 0.83)\text{ kJ·mol}^{-1}$. The value of $\Delta_rC_p^o$ was assumed to be zero. The enthalpy value and derived entropy value, 130.86 $\text{J·K}^{-1}\text{·mol}^{-1}$ ($I_c = 0.61$ M), are quite different from those found in later studies.

The complexes $FeCl_2^+$, and $FeCl_3(aq)$ were introduced to interpret the UV-visible absorption curves at higher Cl^-/Fe^{3+} ratios. The concentrations of $FeCl_4^-$ were negligible in the range of Cl^- concentrations, 0 to 1 M, used in this investigation. However, there were indications that $FeCl_4^-$ is formed in more concentrated chloride solutions, between 6 and 12 M HCl. Solutions of this species are less highly coloured than the 1:1 to 3:1 complexes. The molar absorption coefficients for $FeCl_4^-$ are lower than for $FeCl_3(aq)$.

In the equation ($\varepsilon_{\text{exp}} = f(Cl^-)$), which expresses the mean molar Fe(III) absorption coefficient as a function of chloride concentration, there are seven unknown parameters. These were determined step-by-step. K_1 and molar absorption coefficients ε_1 and ε_0 were known from the investigation of the 1:1 complex described above. K_2 and ε_2 were determined by using the first part of the curve ($\varepsilon_{\text{exp}} = f(Cl^-)$); K_3 and ε_3 were determined by using the last part of the curve ($\varepsilon_{\text{exp}} = f(Cl^-)$) and the values of K_2 and ε_2. It has been found at 26.7 °C and for an ionic strength of 1 M, $K_1 = (4.2 \pm 0.2)\text{ mol}^{-1}\text{·dm}^3$, $K_2 = (1.3 \pm 0.4)\text{ mol}^{-2}\text{·dm}^6$ and $K_3 = (0.04 \pm 0.02)\text{ mol}^{-3}\text{·dm}^9$. The last two values must be considered only as estimates. The corresponding Δ_rG values are $\Delta_{r2}G = -0.65\text{ kJ·mol}^{-1}$ and $\Delta_{r3}G = 7.98\text{ kJ·mol}^{-1}$. Extrapolation to zero ionic strength and 25 °C gave $K_1^o = (30 \pm 5)\text{ mol}^{-1}\text{·dm}^3$; $K_2^o = (4.5 \pm 2.0)\text{ mol}^{-2}\text{·dm}^6$ and $K_3^o = (0.10 \pm 0.05)\text{ mol}^{-3}\text{·dm}^9$.

The results were based on absorption measurements at several wavelengths. There are overlaps of the absorption bands of the different complexes, and the quality of the derived constants depends considerably on the sophistication of the calculations. Computer analysis is necessary, and the required computers and programs were not available in 1942.

In the present review the molar concentrations and formation constants were converted to molal values by using values from Table II-5. A polynomial fit to the values was carried out, and the coefficients were used to calculate the conversion factors for any concentration of $NaClO_4$ or $HClO_4$. For mixed $NaClO_4$, $HClO_4$ solutions a weighted average has been used.

The original paper of Rabinowitch and Stockmayer [1942RAB/STO] does not contain the exact compositions of the solutions used for the determination of the association constants as a function of ionic strength. The ratio Na^+/H^+ in the mixed perchlorate solutions used for that investigation is missing. We assumed that it was 1.0 and carried out the SIT treatment of the data plotted in Fig. 8 of the original paper. Values of (1.55 ± 0.04) for $\log_{10} K_1^o$ and $-(0.29 \pm 0.03)\text{ kg·mol}^{-1}$ for the interaction coefficient difference were found

$$\Delta\varepsilon = \varepsilon(\mathrm{FeCl^{2+}, ClO_4^-}) - \varepsilon(\mathrm{Fe^{3+}, ClO_4^-}) - \varepsilon(\mathrm{H^+,Cl^-}).$$

Some results from this paper have been used in the determination of the values of $K^{\mathrm{o}}_{1\mathrm{m}}$ and $K^{\mathrm{o}}_{2\mathrm{m}}$ as well as $\varepsilon(\mathrm{FeCl^{2+}, ClO_4^-})$. We used the original values K_1 = (4.2 ± 0.2) $\mathrm{mol^{-1}\cdot dm^3}$ and K_2 = (1.3 ± 0.4) $\mathrm{mol^{-1}\cdot dm^3}$ obtained in 1 M ionic strength solution at 26.7 °C. After conversion to the molal scale, the values of these constants at 25 °C then were calculated using the van't Hoff formula with the value of $\Delta_{\mathrm{r}}H_1$ given by [1967VAS/LOB2] and an estimated value of 20 $\mathrm{kJ\cdot mol^{-1}}$ for $\Delta_{\mathrm{r}}H_2$.

[1943KEL/MOO]

The authors used adiabatic calorimetry to measure the heat capacity of $\mathrm{FeCl_2(cr)}$ from 53.2 to 295.0 K. The smooth curve shows no heat-capacity anomalies over that temperature range. A value of (76.30 ± 0.20) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ can be estimated for $C^{\mathrm{o}}_{p,\mathrm{m}}$ ($\mathrm{FeCl_2}$, cr, 298.15 K) using these results (a similar unpublished value, 76.8 $\mathrm{kJ\cdot mol^{-1}}$, was reported [1960OET] to have been obtained by Westrum). The authors estimated a total entropy contribution of 98.1 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ between 50.12 and 298.16 K, and a further contribution of 21.7 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ between 0 and 50.12 K based on a theoretical extrapolation to 0 K and the work of Trapeznikowa and Schubnikow [1935TRA/SCH]. For the purposes of fitting a single function to all the calorimetry results, the uncertainties in the individual values for the heat capacities were estimated in the present review as ± 0.2 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$.

[1943MOO]

The author reported drop-calorimetry measurements for $\mathrm{FeCl_2(cr)}$ based on experiments in which the capsule containing the sample was heated to temperatures between 386 and 1080 K. From these, the author derived an expression for ($H^{\mathrm{o}}_{\mathrm{m}}(T) - H^{\mathrm{o}}_{\mathrm{m}}(298.15\ \mathrm{K})$) for $\mathrm{FeCl_2(cr)}$ as a function of temperature, which on adjusting to current atomic mass values and reconversion of the units from cal to J, becomes:

$$H^{\mathrm{o}}_{\mathrm{m}}(T) - H^{\mathrm{o}}_{\mathrm{m}}(298.15\ \mathrm{K})/\mathrm{J\cdot mol^{-1}} = 79.226\,(T/\mathrm{K}) + 4.35\times10^{-3}\,(T/\mathrm{K})^2 - 4.894\times10^{5}\,(T/\mathrm{K})^{-2} - 25659.$$

This function reproduces the experimental values to better than 0.3% for temperatures above 500 K. At lower temperatures the calculated enthalpy differences are 1 to 3% less than the measured values, and differentiation of the equation generates a value of 76.30 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ for $C^{\mathrm{o}}_{p,\mathrm{m}}$ ($\mathrm{FeCl_2}$, cr, 298.15 K), identical to the value reported by Kelley and Moore [1943KEL/MOO]. It would appear from this minor disagreement in enthalpy differences for temperatures below 500 K, and from the wording in the text of the paper, that the equation was specifically chosen to mesh with the heat-capacity results of Kelley and Moore [1943KEL/MOO]. For the purposes of fitting a single function to all the calorimetry results, the individual values for the enthalpy differences are estimated in the present review to have uncertainties of 1%.

The authors also used their results to calculate the enthalpy of fusion (950 K) as (43.0 ± 0.2) $\mathrm{kJ\cdot mol^{-1}}$ (assumed to represent a 1σ uncertainty). The drop-calorimetry results from 978.7 to 1079.7 K would lead to an average value for $C^{\circ}_{p,\mathrm{m}}$ ($FeCl_2$, l) of (102.1 ± 2.0) $J\cdot K^{-1}\cdot mol^{-1}$ (2σ statistical uncertainty). The assumption of a constant value for $C^{\circ}_{p,\mathrm{m}}$ ($FeCl_2$, l) introduces some additonal uncertainty, and could lead to incorrect extrapolation of thermodynamic quantities for temperatures above 1100 K.

[1943WAG/STE]

Although Parker and Khodakovskii [1995PAR/KHO] indicate that this paper provides independent data for the equilibrium constant for the reaction

$$FeCl_2(cr) + H_2(g) \rightleftharpoons Fe(cr) + 2\,HCl(g)$$

at 1152 K and 1203 K[1], the values at the two temperatures appear to have been based on an interpolation of the measurements of Bagdasarian [1927BAG], followed by correction for the vapour pressure of $FeCl_2$ [1925MAI]. Also, the value used for the enthalpy of fusion of $FeCl_2$ in the Parker and Khodakovskii recalculation [1995PAR/KHO] also is not specified. The results are not used further in the present review.

[1944LIN]

The author studied the kinetics of hydrolysis of "Epichlorhydrin" or (chloromethyl)-oxirane, $ClCH_2CHOCH_2 + H_2O \rightleftharpoons ClCH_2CH(OH)CH_2(OH)_2$, that were followed with a dilatometer over a range of $HClO_4$ and Fe(III) concentrations at 25 °C. For example, in the presence of 0.1 M $HClO_4$ and 0.1 M $Fe(ClO_4)_3$, the observed rate constant, k_{obs}, for the hydrolysis reaction was 0.00384 and 0.00381 min^{-1} with the rate law predicted to be: $k_{\mathrm{obs}} = k_{\mathrm{o}} + k_{\mathrm{h}}[H^+]$, whereby $k_{\mathrm{h}} = k_{\mathrm{h0}} + k'[\mathrm{salt}]$. By extracting the value of k' at constant [Fe] and [$HClO_4$], the deviation of the k_{obs} *vs.* [$HClO_4$] at constant [Fe] from linearity gave a measure of the [H^+] caused by hydrolysis of Fe^{3+} after correction for k' with the intercept giving k_{o}. Thus, $[FeOH^{2+}] = [H^+] - [HClO_4]$ and $[Fe^{3+}] = [Fe] - [FeOH^{2+}]$. From the six tabulated molar concentrations of [$HClO_4$], [H^+], [$FeOH^{2+}$] and [Fe^{3+}], molal hydrolysis constants for Fe^{3+} can be calculated as a function of ionic strength that are only 0.3 log units higher than those obtained by conventional equilibrium measurements. No consideration was made for the presence of other Fe(III) species in solution, such as dimers which should in fact be present at [Fe] = 0.01 M.

Although this kinetic study is very innovative and the resulting hydrolysis constants for iron(III) are within a factor of *ca.* 2 from those reported much more

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[1] Parker and Khodakovskii [1995PAR/KHO] indicate in their reaction catalogue that based on [1943WAG/STE] $\Delta_r H$ for the equilibrium with respect to $FeCl_2$(cr) is (157.66 ± 2.0) $kJ\cdot mol^{-1}$, but show (157.10 ± 1.0) $kJ\cdot mol^{-1}$ in their Table 1, and assign this value the highest weight. Actually, the value from the reaction catalogue and its uncertainty seem to have been properly incorporated in the [1995PAR/KHO] average at the bottom of their Table 1, and the value listed under [1943WAG/STE] in the [1995PAR/KHO] Table 1 is a typographical error.

recently by conventional thermodynamic measurements, these data cannot be used in this evaluation.

[1944OLE]

This was a spectrophotometric study (366 nm) carried out at 20 °C using solutions with total Fe(III) concentrations between 0.00105 and 0.00310 M (C_{Fe}), always lower than the chloride concentrations (C_{Cl}), 0.005 to 0.120 M HCl(sln). The supporting medium was perchloric acid at a molarity of ($2 - 6C_{Fe} - C_{Cl}$). The $FeCl_x^{3-x}$ stability constants evaluated from spectrophotometric measurements in accordance with potential-difference measurements were: β_1($FeCl^{2+}$, 20 °C) = 5.7 $dm^3 \cdot mol^{-1}$ (also see [1943OLE]), β_2($FeCl_2^+$, 20 °C) = 11.5 $dm^6 \cdot mol^{-2}$ and β_3($FeCl_3$, aq, 20 °C) = 10 $dm^9 \cdot mol^{-3}$. The conversion factor for 2 M $HClO_4$ to mass-based units at 20 °C ([1985SOH/NOV]) is 1.0989 $dm^3 \cdot kg_{H2O}^{-1}$. Hence, the stability constants in the molal scale are 5.2 $kg \cdot mol^{-1}$ for β_1($FeCl^{2+}$, 2.2 $mol \cdot kg^{-1}$ $HClO_4$, 20 °C), 9.5 $kg^2 \cdot mol^{-2}$ for β_2($FeCl_2^+$, 2.2 $mol \cdot kg^{-1}$ $HClO_4$, 20 °C) and 7.5 $kg^3 \cdot mol^{-3}$ for β_3($FeCl_3$, aq, 2.2 $mol \cdot kg^{-1}$ $HClO_4$, 20 °C).

The approximate extrapolation of the β_1 value to 25 °C was done by applying the van't Hoff formula with $\Delta_r H_1^\circ$ = (22.5 ± 2.5) $kJ \cdot mol^{-1}$. That yields: $\ln K_1$(25 °C) = 0.1548 + $\ln K_1$(20 °C) and K_{1m}(25 °C) = (6.1 ± 1.0) $kg \cdot mol^{-1}$. The value of $\Delta_r H_2^\circ$ is not well established, but if we use the value indicated by the results of Liu *et al.* [2006LIU/ETS], $\Delta_r H_2^\circ$ = (19.4 ± 7.3) $kJ \cdot mol^{-1}$ one gets K_{2m} = (2.1 ± 0.5) $kg \cdot mol^{-1}$. The resulting values have been used as part of the determination of standard values of the formation constants of $FeCl^{2+}$ and $FeCl_2^+$ using the SIT formalism, and in the concomitant calculations of $\varepsilon(FeCl^{2+}, ClO_4^-)$ and $\varepsilon(FeCl_2^+, ClO_4^-)$. The reported $FeCl_3$(aq) stability constant is much greater than other published values, and has not been used further in the present review.

The author did not give uncertainties, but from the scatter of the points used to perform the evaluation it is estimated that an uncertainty of ± 1 $dm^3 \cdot mol^{-1}$ for β_1(Fe(III)) (and for β_1(Fe(II)), see below) seems appropriate. Again, by considering the scatter of the values in the literature, the uncertainty for the second formation constant β_2(Fe(III)) is at least ± 3.7 $dm^6 \cdot mol^{-2}$.

Combining β_1($Fe(III)Cl^{2+}$, 20 °C) = 5.7 $dm^3 \cdot mol^{-1}$ with potential-difference measurements in Fe(II)/Fe(III) – $HCl/HClO_4$ solutions the author estimated the values of β_1($Fe(II)Cl^+$, 20 °C) and β_2($Fe(II)Cl_2$(aq), 20 °C) as 2.3 $dm^3 \cdot mol^{-1}$ and 2.5 $dm^6 \cdot mol^{-2}$, respectively. As outlined above, the uncertainty in β_1($Fe(II)Cl^+$, 20 °) is estimated as ± 1 $dm^3 \cdot mol^{-1}$. Conversion to the molality scale (see above) gives β_1($Fe(II)Cl^+$, 2.2 $mol \cdot kg^{-1}$ $HClO_4$, 20 °C) = 2.1 $kg \cdot mol^{-1}$ and β_2($Fe(II)Cl_2$(aq), 2.2 $mol \cdot kg^{-1}$ $HClO_4$, 20 °C) = 2.1 $kg^2 \cdot mol^{-2}$. The formation constants of the Fe(II) chlorido complexes were a by-product of the work on the Fe(III) chlorido complexes and are not considered further in the present review.

[1945DAR/GUR]

This paper describes a detailed investigation of the wüstite phase field at 1311 to 1682 K. The results consist of 8 measurements on CO/CO_2 equilibrium gas compositions at the γ-Fe–wüstite phase boundary at 1311 to 1638 K (their Table II) and 5 of equilibrium $H_2/H_2O/CO/CO_2$ or CO/CO_2 compositions at the wüstite-magnetite boundary at 1369 to 1661 K (their Table III), plus 118 measurements of equilibrium gas and single-phase wüstite compositions at 1373 to 1682 K (their Tables V and VI). Phase boundaries at lower temperatures were estimated by extrapolation, down to the eutectoid point (their Figures 6 and 9), and represent a substantial improvement on previous estimates (see below).

Phase-boundary determinations were conducted in a vertical tube furnace, employing the temperature gradient to pinpoint equilibrium temperatures for given gas compositions. In this way, sharp Fe-wüstite boundaries were obtained. Wüstite compositions near the magnetite boundary are extremely difficult to quench, but the boundary between single-phase magnetite and two-phase (wüstite + magnetite) zones in cooled samples indicated the position of the wüstite-magnetite boundary at temperature. This quenching difficulty was responsible for previous, erroneous measurements of the magnetite-wüstite boundary by XRD of quenched specimens ([1933JET/FOO], [1933JET/FOO2]).

Experiments were conducted with pure materials (~99.86% Fe, ~99.92% and ~99.99% Fe_2O_3, metal basis), and the influence of key impurities (Ni, Cu) on the phase-boundary determinations is discussed. The authors also noted the need to minimize silica contamination, which leads to a surface silicate film on the specimens. They also observed that the atmospheres used were mildly carburizing, with 0.03 weight-% C in the Fe phase at 1273 K; uptake of carbon in the cooler parts of the specimens ceased to influence gas composition after an hour. The linear gaseous flow rate ($0.9\ \mathrm{cm \cdot s^{-1}}$) was selected to be high enough for minimal perturbation of the gas composition by thermal diffusion effects but low enough not to compromise temperature measurements. Thermal diffusion effects are discussed further in an appendix.

The thermodynamic discussion focuses mainly on the activities and partial molar enthalpies of solution of Fe and O in wüstite, as a function of temperature and composition. While this is beyond the scope of the current review, it is interesting to note that the enthalpy of formation of wüstite per mole of oxygen is almost constant over the entire phase field (values for six compositions between $FeO_{1.055}$ and $FeO_{1.16}$ at 1523 K vary between −263.88 and −264.14 $\mathrm{kJ \cdot mol^{-1}}$). The authors derived values of $\Delta_f H_m^\circ$ (Fe_3O_4, cr, 1523 K) = −1091.7 $\mathrm{kJ \cdot mol^{-1}}$ and $\Delta_f H_m^\circ$ (Fe_3O_4, cr, 298 K) ~ −1118.0 $\mathrm{kJ \cdot mol^{-1}}$. While the latter value is in good agreement with that derived in the current assessment, it is not included in the assessment because of the high experimental temperature and relatively complex derivation (compared with direct measurement of the Fe-Fe_3O_4 equilibrium in the small experimental window below the eutectoid point).

This paper is a classic, one of the most frequently cited studies of wüstite phase limits; however, the high experimental temperatures limit its value for the current review. The experimental description is very detailed and appears to reflect a meticulous and thoughtful approach to all aspects of the study, with careful attention to minimizing sources of experimental error. While subsequent research has refined understanding of wüstite, this work is still highly regarded. For example, Grønvold *et al.* [1993GRO/STO] state that "the thermodynamic characterization of the wüstite phase was advanced considerably through [this] work". Spencer and Kubaschewski [1978SPE/KUB] noted that "The phase limits tabulated by Darken and Gurry… were self-consistent both with regard to their directly-observed phase boundaries and to the thermodynamic values determined…".

[1946CIR]

The author established the percentage CO_2 formed in a stream of CO brought to equilibrium with a mixture of iron and iron oxide in an excess of SiO_2 at 1173, 1273 and 1373 K, thus establishing the equilibrium conditions for formation of fayalite. The measured percentage carbon dioxide in the gas stream at each temperature is in good agreement with other measurements [1932SCH/FRA], [1962LEB/LEV]. In the present review, the CO_2 to CO ratios were calculated and combined with consistent auxiliary data for quartz ([1989COX/WAG], [1998CAR/SAL]) and carbon dioxide and carbon monoxide [1989GUR/VEY], and with the values selected in this review for the heat capacity and entropy of α-Fe_2SiO_4 (Section X.2.1.1.1) and Fe(cr) (Section V.2). These led to a value of $\Delta_f H_m^\circ$ (Fe_2SiO_4, α, 298.15 K) of $-(1478.3 \pm 2.31)$ $kJ\cdot mol^{-1}$ (2σ). The reported values for p_{O_2} from the paper lead to values of approximately -1469 $kJ\cdot mol^{-1}$. The author attempted to characterize the solids using magnetic susceptibility measurements, but better characterization would have been useful.

[1946DAR/GUR]

This is a companion paper to the same authors' study of wüstite [1945DAR/GUR]. Because it deals primarily with phase equilibria and thermodynamic properties at temperatures above 1500 K, with particular attention to Fe-O liquids, it does not appear to be relevant to the current assessment.

[1948RIC/JEF]

The main purpose of this review was the selection of thermodynamic data for constructing Ellingham diagrams of possible interest in iron and steel making; many oxide systems are briefly discussed.

The review does not contain any original experimental data of value for the current (OECD/NEA) assessment of iron oxides. It indicates rather poor accuracy for the then-available data on the hematite–magnetite equilibrium. Wüstite is approximated as stoichiometric FeO.

[1948STO]

The paper presents smoothed osmotic and activity coefficients based on previous isopiestic measurements using the then newer values for the osmotic coefficients of the isopiestic standards. Values for iron(III) chloride are listed up to 2.0 mol·kg^{-1} at 25 °C.

These calculations have been superseded by new measurements of the standard solutions and the data for $FeCl_2$(sln) in particular have been augmented by other studies. Therefore, these smoothed results were not considered further in this review.

[1949DOD/ROL]

The authors actually carried out an investigation of complex formation of the Fe^{3+} ion with fluoride by measurement of the potential of the iron(II)-iron(III) half-cell potential as a function of the hydrofluoric and perchloric acid in the system, and interpreted their results quantitatively by assuming the formation of the complexes Fe(III)F^{2+}, Fe(III)F_2^+, and Fe(III)F_3(aq) in solution. In their analysis the authors explicitly assumed that the complex Fe(II)F^+ was not formed, and in their discussion they estimated the extent to which formation of the Fe(II)F^+ complex could have had a possible effect on the measured electrochemical potentials. Based on freezing point depression data presented by Peters [1898PET] the authors estimated that the constant for the equilibrium Fe^{2+} + $F^- \rightleftharpoons FeF^+$ is less than 30 dm^3·mol^{-1}, and concluded that formation of FeF^+ did not influence their experimental results.

[1949EVA/BAX]

The experiments involved addition of 20 mL of a slightly acidified 1.4 mol·L^{-1} solution of iron(II) sulfate to 230 mL of a 1 mol·L^{-1} perchloric acid solution, 0.05 mol·L^{-1} in hydrogen peroxide. The final iron concentration was quite high (0.1 mol·L^{-1}). The extent of the reaction was apparently limited by the amount of peroxide used, and the uncertainty in the concentration is not clearly stated. The authors claimed an uncertainty of 3% (probably 1 σ). The results from this study are not used in the present review except for making a rough comparison with results from other studies.

[1949EVA/PRY]

A solubility product of $10^{-35.5}$ is reported for “freshly precipitated ‘gelatinous’ ferric hydroxide” of “admittedly undefined” structure, based on electrometric titrations of acidic iron(III) ammonium sulfate solutions against NaOH.

The solubility product seems to be based on a naïve calculation of “free Fe^{3+}” at the point of formation of a “gelatinous ferric hydroxide” precipitate from a “colloidal solution” produced in the initial stages of the titration. The rather high value for the solubility product is due partly to the absence of corrections for either ionic activities or the hydrolysis of Fe^{3+} to $FeOH^{2+}$. There do not appear to be sufficient data to recalculate an ionic activity product for the purposes of the current (OECD/NEA) review.

[1949LYO/GIA]

Lyon and Giauque [1949LYO/GIA] measured the heat capacity for $FeSO_4 \cdot 7H_2O$(cr) between 13.1 and 307.7 K using a copper adiabatic calorimeter, and a separate calorimeter/magnetic-susceptibility apparatus was used for measurements between 0.9 and 20 K. The sample of the heptahydrate was carefully prepared, and was found to be slightly hyperstoichiometric with respect to water ($FeSO_4 \cdot 7.0254H_2O$), and appropriate corrections were applied. Heat capacities from the two sets of calorimetry measurements agree well within the small experimental scatter. A small maximum found in the heat-capacity curve at 2.3 K was discussed, and for 0 to 1 K, a contribution of 0.8 $J \cdot K^{-1} \cdot mol^{-1}$ (0.2 $cal \cdot K^{-1} \cdot mol^{-1}$) to S^{o}_{m} ($FeSO_4 \cdot 7H_2O$, cr) was estimated. At 1 K, the value of $C^{o}_{p,m}\,T^{-1}$ is already greater than 1.5 $J \cdot K^{-2} \cdot mol^{-1}$, and $C^{o}_{p,m}\,T^{-1}$ decreases with increasing temperature to approximately 4 K. The value of (409.1 ± 1.3) $J \cdot K^{-1} \cdot mol^{-1}$ from this work is accepted in the present review for S^{o}_{m} ($FeSO_4 \cdot 7H_2O$, cr, 298.15 K). The value of 394.4 $J \cdot K^{-1} \cdot mol^{-1}$ is calculated for $C^{o}_{p,m}$ ($FeSO_4 \cdot 7H_2O$, cr, 298.15 K) based on a linear fit to the eight values reported for $C^{o}_{p,m}$ ($FeSO_4 \cdot 7H_2O$, cr, 298.15 K) for temperatures between 269 and 308 K. There is a fair bit of scatter between the results from calorimetry Series A and B, (of the order of 1 - 2 $J \cdot K^{-1} \cdot mol^{-1}$) and in the present review the uncertainty in $C^{o}_{p,m}$ for 298.15 K is estimated as ± 2.0 $J \cdot K^{-1} \cdot mol^{-1}$.

$[C^{o}_{p,m}]^{308\,K}_{269\,K}$ ($FeSO_4 \cdot 7H_2O$, cr, T)/$J \cdot K^{-1} \cdot mol^{-1}$ = 76.055 + 1.0677(T/K) for temperatures between 269 and 308 K.

[1949OLS/SIM]

Three 4.70×10^{-4} M iron(III) perchlorate solutions were investigated by spectrophotometry at (25.0 ± 0.1) °C at three $HClO_4$ concentrations with $[ClO_4^-]$ = 0.046 M. No experimental data are tabulated and the authors quote a mean $\log_{10} {}^{*}\beta^{o}_{1}$ value of − 2.553 at an average ionic strength of 0.0469 (± 0.0001) M $NaClO_4$.

The first hydrolysis constant based on the limited data is within the uncertainty range of the more recent results [1955MIL/VOS] and [2000BYR/LUO], although no uncertainly limits were given or can be assigned *a priori*.

[1949ROB/STO]

Also see the entry for the work of Mason [1941MAS] in this Appendix.

No new experimental data are presented in this summary paper, although earlier osmotic coefficient data are recalculated using the experimental results available at that time for the reference solutions. As a result, only smoothed values are presented for a wide range of acids, bases and salts at 25 °C. Table A-4 lists those for $AlCl_3$.

If these results are to be used to generate auxiliary data, the source of the raw experimental results should be traced and the osmotic coefficients of the reference solutions should be recalculated using the most recent accepted values.

Table A-4: Smoothed osmotic coefficients for $AlCl_3$(sln) at 25 °C.

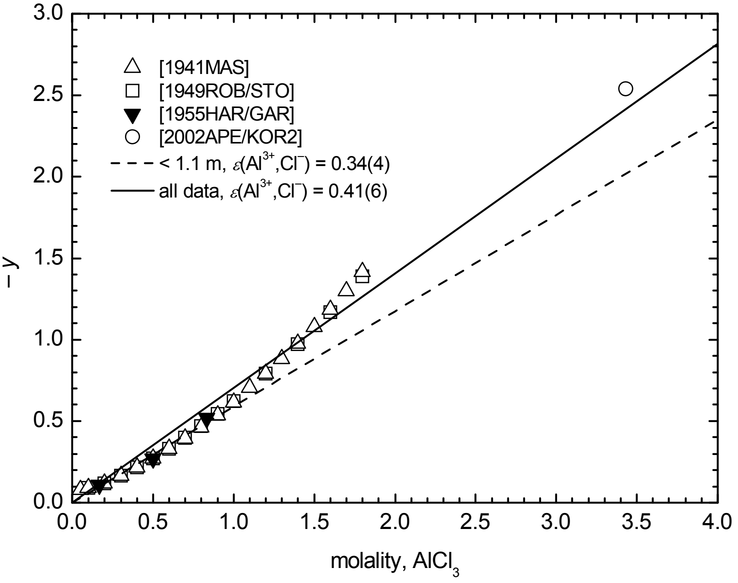
m, molal	ϕ	m, molal	ϕ
0.1	*0.819*	0.8	1.220
0.2	0.841	0.9	1.299
0.3	0.889	1.0	1.382
0.4	0.947	1.2	1.560
0.5	1.008	1.4	1.749
0.6	1.074	1.6	1.951
0.7	1.145	1.8	2.175

The following provisional plot is based on the equation:

$$1-\phi-\frac{3.516}{I_m(3.375)}\left[1+1.5\sqrt{I_m}-2\ln(1+1.5\sqrt{I_m})-\frac{1}{(1+1.5\sqrt{I_m})}\right]=$$
$$-1.727\varepsilon(\mathrm{Al}^{3+},\mathrm{Cl}^-)m_{\mathrm{AlCl_3}}$$

and includes not only the smoothed data of [1949ROB/STO] but also those of [1941MAS], which in fact were recalculated by Robinson and Stokes and more recent very limited osmotic coefficient data as well. Although a further update of the osmotic coefficient standards could be performed, this will not improve the overall fit appreciably. The reason for this curvature, which was not observed for the analogous iron(III) chloride data where complexation is much more significant, is not clear. Linear regression of all the data (unweighted) yielded a slope of (0.704 ± 0.011) which gives a $\varepsilon(\mathrm{Al}^{3+},\mathrm{Cl}^-)$ = (0.41 ± 0.02) $\mathrm{kg\cdot mol^{-1}}$. A regression of the data at $\leq$ 1 $\mathrm{mol\cdot kg^{-1}}$, chosen virtually at random, yielded a slope = (0.588 ± 0.008) or $\varepsilon(\mathrm{Al}^{3+},\mathrm{Cl}^-)$ = (0.34 ± 0.04) $\mathrm{kg\cdot mol^{-1}}$. Note that for the analogous iron(III) chloride data, which showed excellent linearity up to at least 1.7 $\mathrm{mol\cdot kg^{-1}}$, $\varepsilon(\mathrm{Fe}^{3+},\mathrm{Cl}^-)$= (0.133 ± 0.007) (1σ) without any consideration of specific chloride complexation and hydrolysis. Also see the entry for the work of Mason [1941MAS] in this Appendix.

Figure A-3: Plot of the LHS of the above equation *vs*. the molality of $AlCl_3$.



[1949SCH]

Schäfer reported measurements of the vapour pressure of water above appropriate mixtures of $FeCl_2{\cdot}4H_2O$(cr), $FeCl_2{\cdot}2H_2O$(cr), $FeCl_2{\cdot}H_2O$(cr) and $FeCl_2$(cr). Both static and transpiration methods were used, and the results showed good agreement. The results were reported graphically, but were not tabulated. The author reported equations of $\log_{10} p\,(H_2O)$ in mm of Hg as functions of the (inverse) kelvin temperature. Parker and Khodakovskii [1995PAR/KHO] accepted these equations, assigned uncertainties, and made minor corrections for the estimated heat capacities of reaction to correct the thermodynamic quantities to a standard temperature of 298.15 K. In the present review, the equations and the author's fit to the measurements were rechecked by digitizing the pressure-temperature points from the figures in the original paper. If the data were weighted assuming a constant uncertainty in p_{H_2O}, and $\Delta_r C^o_{p,m}$ equal to zero, the least squares fits were identical to those of the author within the statistical uncertainties.

Functions incorporating different constant values of $\Delta_r C^o_{p,m}$ were also fitted to the data. Parker and Khodakovskii estimated $\Delta_r C^o_{p,m}$ to be $-4\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ for the dehydration of $FeCl_2{\cdot}2H_2O$(cr) to $FeCl_2{\cdot}H_2O$(cr) (325 to 383 K) and $FeCl_2{\cdot}H_2O$(cr) to $FeCl_2$(cr) (383 to 443 K), and assumed that the measurements for the dehydration of $FeCl_2{\cdot}4H_2O$(cr) to $FeCl_2{\cdot}2H_2O$(cr) were carried out at temperatures sufficiently close to 298.15 K (294 to 338 K) that no heat-capacity correction was necessary. Inclusion of reasonable values tends to increase the values of both $\Delta_{\mathrm{r}}S_{\mathrm{m}}^{\mathrm{o}}$ and $\Delta_{\mathrm{r}}H_{\mathrm{m}}^{\mathrm{o}}$. However, for example, for the dehydration of the dihydrate to the monohydrate, the "best fit" value of $\Delta_{\mathrm{r}}G_{\mathrm{m}}^{\mathrm{o}}$ (298 K) changed only from 18.79 $\mathrm{kJ\cdot mol^{-1}}$ to 18.85 $\mathrm{kJ\cdot mol^{-1}}$ as $\Delta_{\mathrm{r}}C_{p,\mathrm{avg}}$ was varied from 0 to – 10 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$.

Parker and Khodakovskii noted that the entropy of dehydration of the monohydrate (approximately 130 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$) was less than is normal for such reactions (~ 145 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$), and on that basis they retained the value for $\Delta_{\mathrm{r}}G_{\mathrm{m}}^{\mathrm{o}}$ (298 K), but rejected the value of $\Delta_{\mathrm{r}}H_{\mathrm{m}}^{\mathrm{o}}$ (298 K). However, there are only five experimental data points for the reaction, and rejection of no single data point results in a substantially more "reasonable" entropy value. Inclusion of the data points from the early work of Lescoeur [1894LES] leads to an even lower value for the calculated entropy of dehydration.

Of course, Schäfer fitted his functions using the original numerical data, which were unavailable to the current reviewers (except from the plots). On that basis, the equations in the original paper were accepted. The resulting values of $\Delta_{\mathrm{r}}G_{\mathrm{m}}$, $\Delta_{\mathrm{r}}H_{\mathrm{m}}$ and $\Delta_{\mathrm{r}}S_{\mathrm{m}}$ were then corrected to 298.15 K on the basis of the calculations done in this review using different average values of $\Delta_{\mathrm{r}}C_p$.

The value of $C_{p,\mathrm{m}}^{\mathrm{o}}$ (H_2O, g) is ~ 34 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ from 300 to 400 K. Each additional water of hydration seems to increase the value of $C_{p,\mathrm{m}}^{\mathrm{o}}$ of a salt by between 35 and 55 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ (*e.g.*, [1986MEI/GRO], though there are surprisingly few other firm data on which to base this estimate [1982WAG/EVA]). For these calculations, it has been assumed in the present review that $\Delta_{\mathrm{r}}C_{p,\mathrm{avg}}$ is – 10 $\mathrm{J\cdot K^{-1}}$ per mole of water removed in a dehydration reaction (*i.e.*, – 20 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ for dehydration of $FeCl_2\cdot 4H_2O$(cr) to $FeCl_2\cdot 2H_2O$(cr), and – 10 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ for each of the other dehydration steps).

Table A-5: Thermodynamics of the dehydration reactions for Fe(II) chlorides.

Reaction	$\log_{10} p_{H_2O}$ [1]	$\Delta_{\mathrm{r}}C_{p,\mathrm{avg}}$ / $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	$\Delta_{\mathrm{r}}G$ (298 K)/ $\mathrm{kJ\cdot mol^{-1}}$	$\Delta_{\mathrm{r}}H$ (298 K)/ $\mathrm{kJ\cdot mol^{-1}}$	$\Delta_{\mathrm{r}}S$ (298 K)/ $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$
$FeCl_2\cdot 4H_2O(cr) \rightleftharpoons FeCl_2\cdot 2H_2O(cr) + 2H_2O(g)$	$7.3949 - 2820(T/K)^{-1}$	– 20	23.58 ± 1.50	108.55 ± 2.00	285.0
$FeCl_2\cdot 2H_2O(cr) \rightleftharpoons FeCl_2\cdot H_2O(cr) + H_2O(g)$	$7.7099 - 3286(T/K)^{-1}$	– 10	18.97 ± 3.00	63.62 ± 4.00	149.7
$FeCl_2\cdot H_2O(cr) \rightleftharpoons FeCl_2(cr) + H_2O(g)$	$9.497 - 3270(T/K)^{-1}$	– 10	25.00 ± 2.00	63.86 ± 3.00	130.3

[1] These are directly from the equations provided by Schäfer, but modified such that the water vapour pressure is with respect to the 1 bar standard state.

The values for the uncertainties of the different thermodynamic quantities are highly correlated, and the uncertainties themselves are estimates. The scatter in the results is greatest for dehydration of the dihydrate to the monohydrate. However, there are fewest results for the dehydration of the monohydrate.

Solubility measurements for iron(II) chloride at 20 °C in water and in aqueous HCl solutions are also reported. The value for $FeCl_2$ in water (3.04 mmoles $FeCl_2$ per g solution) appears to be completely consistent with those reported by Schimmel [1928SCH], [1952SCH3].

[1949SMI/KID]

This paper describes a study on the relative stability of goethite and hematite, and concludes that goethite (α-FeOOH) decomposes to hematite (α-Fe_2O_3) in neutral solutions above (125 ± 15) °C, and in alkaline solutions above (165 ± 5) °C.

Unfortunately, there are two serious flaws in this study. First, four experiments purporting to show conversion of hematite to goethite near 100 °C (Runs 1, 31, 32, and 33) used a precipitated gel, not well-crystallized hematite, as starting material. Second, the authors suggest that an iron(III) oxyhydroxide should be more stable, relative to iron(III) oxide, in alkaline than in acidic solution, whereas the phase change is in fact dependent only on water activity:

$$2\,\mathrm{FeOOH(cr)} \rightleftharpoons \mathrm{Fe_2O_3(cr)} + \mathrm{H_2O(g\ or\ l)}$$

Thus, the results are better interpreted in terms of competitive crystallization kinetics of goethite and hematite from metastable precursors, rather than thermodynamic stability relationships. Berner [1969BER] has made similar critical comments on this paper, which is therefore rejected in the current (OECD/NEA) assessment.

[1950ARD]

The following solubility (concentration) products of white $Fe(OH)_2$ and dark olive-green "$Fe_3(OH)_8$" or "$Fe_4(OH)_{10}$" were reported on the basis of potentiometric titration of acidic iron sulfate solutions with NaOH:

$$\mathrm{Fe(OH)_2(am)} \rightleftharpoons \mathrm{Fe^{2+}} + 2\,\mathrm{OH^-},\ K = [\mathrm{Fe^{2+}}]\cdot[\mathrm{OH^-}]^2 = 2.4 \times 10^{-14}$$

(mean of 7 measurements, starting with iron(II) sulfate solution);

$$2\,\mathrm{Fe(OH)_3(am)} \rightleftharpoons \mathrm{Fe_3(OH)_8(am)} + \mathrm{Fe^{2+}} + 2\,\mathrm{OH^-},\ K = [\mathrm{Fe^{2+}}]\cdot[\mathrm{OH^-}]^2 = 6.4 \times 10^{-18}$$

(mean of 3 measurements, starting with a mixed solution of iron(II) and iron(III) sulfates).

No activity correction was made for these measurements, which were performed at ionic strengths near 0.1 M. This appears to be the only solubility measurement for the ill-defined "ferrosic hydroxide", and the author notes that the solubility product value “applies only to the compound produced from mixed ferric and ferrous solutions under conditions of rising pH”. It was the third solid formed in the titration, following basic “ferric sulphate” (between pH 2.5 and 3.5, no formula given) and “$Fe(OH)_3$” (between pH 3.5 and 6.5). The authors suggested that the final product was $Fe_4(OH)_{10}$.

Given the uncertain nature of the precipitates on which these measurements are based, these data are not used in the current assessment.

[1950BOB/LAR]

As part of a study on the behaviour of electrolytes and non-electrolytes in ethanol water mixtures, heats of solution of $FeCl_3(cr)$ ($-(130.96 \pm 0.27)$ kJ·mol^{-1} (1 mole per 600 moles of H_2O, 24 °C)) and $FeCl_3 \cdot 6H_2O$ ($-(21.42 \pm 0.28)$ kJ·mol^{-1} (1 mole per 429 moles of H_2O, 22 °C)) were measured using a twin calorimeter system. If the fairly minor differences in dilution, the difference in temperature, and possible differences in the extent of hydrolysis are neglected, the difference between the two heats of solution is in reasonable agreement (within 2 kJ·mol^{-1}) with the result of Novikov *et al.* [1984NOV/BEL].

[1950GRE/THA]

Gregory and Thackrey reported results of a study of the equilibrium

$$FeBr_3(cr) \rightleftharpoons FeBr_2(cr) + \tfrac{1}{2}Br_2(g) \qquad (A.22)$$

from 340 to 411 K. Equilibrium bromine pressures were obtained primarily from decomposition of two samples of $FeBr_3(cr)$, though the results were checked against those from the much slower recombination reaction. In the absence of well-established values for the entropy, enthalpy of formation or heat capacity of $FeBr_3(cr)$, the authors assumed $\Delta_r C^o_{p,m}$(A.22) to be zero, and derived best-fit values (~ 376 K) of 33.5 kJ·mol^{-1} for $\Delta_r H^o_m$(A.22) and 81.6 kJ·mol^{-1} for $\Delta_r S^o_m$(A.22). Using our selected values for $FeBr_2(cr)$ these would lead to S^o_m($FeBr_3$, cr, 298.15 K) = 181.6 J·K^{-1}·mol^{-1} and $\Delta_f H^o_m$($FeBr_3$, cr, 298.15 K) = $-$ 263.7 kJ·mol^{-1}.[1]

A least squares treatment was used to try to determine “best-fit” values for S^o_m($FeBr_3$, cr. 298.15 K) and $\Delta_f H^o_m$($FeBr_3$, cr, 298.15 K) using the reported Gregory and Thackrey pressure values, heat-capacity functions for $FeBr_2$ (Section VIII.3.3.1.1), $Br_2(g)$ [1989COX/WAG] and estimates for the heat capacity of $FeBr_3(cr)$. The difficulty in assigning both $\Delta_r H^o_m$(A.22) and $\Delta_r S^o_m$(A.22) from the same data set arises because the two numbers are strongly correlated. If the assumed value of S^o_m($FeBr_3$, cr, 298.15 K) is fixed close to the least-squares value, a change of only 6 J·K^{-1}·mol^{-1}, alters

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[1] The source of the rather strange recalculated $\Delta_f H^o_m$ value reported by Gregory and MacLaren [1955GRE/MAC] is not clear. Possibly it is a typographical error ($-$ 74 kcal·mol^{-1} rather than $-$ 64 kcal·mol^{-1}).

the calculated value of $\Delta_f H^\circ_m$ (FeCl$_3$, cr, 298.15 K) by more than 2 kJ·mol^{-1}. Thus, a small systematic measurement error would change the estimated values substantially. For example, if the heat capacity of the solid is estimated at 104 J·K^{-1}·mol^{-1}, the best-fit values of S°_m (FeBr$_3$, cr. 298.15 K) and $\Delta_f H^\circ_m$ (FeBr$_3$, cr, 298.15 K) are 180.2 J·K^{-1}·mol^{-1} and −263.4 kJ·mol^{-1}, respectively. However, with S°_m (FeBr$_3$, cr, 298.15 K) as 175 J·K^{-1}·mol^{-1} (still somewhat greater than the Latimer-type estimate [1971NAU/RYZ] to be consistent with the value selected for FeCl$_3$(cr)), a value of – 265.4 kJ·mol^{-1} for $\Delta_f H^\circ_m$ is calculated (this does introduce a very slight drift in the differences between the calculated and experimental pressures as a function of temperature). If the value of $\Delta_f H^\circ_m$ (FeBr$_3$, cr, 298.15 K) is fixed at −262.63 kJ·mol^{-1} [1989EFI/EVD], the value of S°_m (FeBr$_3$, cr, 298.15 K) is calculated to be 182.2 J·K^{-1}·mol^{-1}. The uncertainties in the "best-fit" values (also considering the uncertainties in the values used for FeBr$_2$(cr)) are estimated here as ± 10.0 J·K^{-1}·mol^{-1} in S°_m (FeBr$_3$, cr, 298.15 K) and ± 5.0 kJ·mol^{-1} in $\Delta_f H^\circ_m$ (FeBr$_3$, cr, 298.15 K). Changes in the weighting used for the pressure data can introduce changes of 3 to 4 J·K^{-1}·mol^{-1} in S°_m (FeBr$_3$, cr. 298.15 K), but reasonable changes in the heat-capacity function for FeBr$_3$(cr) introduce changes of less than 2 J·K^{-1}·mol^{-1}.

[1950KAN/PET]

The authors studied the reaction

$$\mathrm{FeCl_2(cr) + H_2(g) \rightleftharpoons Fe(cr) + 2\,HCl(g)}$$

at eighteen temperatures between 737 and 935 K. The $\log_{10} K_p$ values from the authors' table were converted to equilibrium constants expressed in bars, and values for the enthalpy of reaction at 298.15 K were obtained from a third-law calculation using the selected values for the entropies and heat-capacity functions for Fe(α) and FeCl$_2$(cr) (Sections V.2 and VIII.3.2.1.1) and for H$_2$(g) and HCl(g) [1989COX/WAG]. Internal agreement is reasonable (159.55 ± 1.79) kJ·mol^{-1}, although agreement with values from other studies (*e.g.*, [1938SAN], [1952NOV/ORA]) is not within the combined uncertainty limits (Parker and Khodakovskii [1995PAR/KHO] assigned an uncertainty of ± 1.5 kJ·mol^{-1}). The third-law $\Delta_r H$ values, corrected to 298.15 K, drift very slightly to more positive values when the equilibrium data from the higher-temperature measurements are used.

The value of the equilibrium constant, when extrapolated to the melting point of FeCl$_2$ (~ 950 K) was found to be consistent with the values from other studies [1952SCH/KRE].

The authors also reported a reanalysis of the results of Stirnemann [1925STI], and values for the equilibrium constant for the reaction:

$$\mathrm{FeCl_3(cr) \rightleftharpoons FeCl_2(cr) + \tfrac{1}{2}Cl_2(g)}\ (526\text{ to }574\text{ K}).$$

These would lead to $\Delta_r H_m^o$(298.15 K) = (108.0 ± 0.2) kJ·mol^{-1} for the reaction. The reanalysis has been criticized by Schäfer [1951SCH] (also see [1953SCH/OEH]). Rustad and Gregory [1983RUS/GRE] suggest that the equilibrium between Fe_2Cl_6(g) and $FeCl_2$(cr) plus Cl_2(g) is established only slowly at lower temperatures. The results of this reanalysis of Stirnemann's data are not used in the present review.

[1950MCC/DAV]

This spectrophotometric study is confined to strongly acidic chloride solutions (5 to 12 mol·L^{-1}) presumably at ambient temperatures of concentrated iron(III) and iron(II) solutions (> 0.1 mol·L^{-1}) as well as those of Mg(II), Mn(II) and Zn(II). Chlorido complexes of Fe^{3+} were rightly thought to dominate the spectra of the pure iron(III) and iron(II) mixtures along with chloride-bridged dimers of Fe(III) and Fe(II).

No quantitative data were presented in this paper.

[1951CON/MCV]

Potentials were measured for the cell

$$\mathrm{Pt,H_2(g)\mid HClO_4(sln) \,\vdots\vdots\, HClO_4(sln), Fe(ClO_4)_2(sln), Fe(ClO_4)_3(sln)\mid Au}$$

with the following solute concentrations: 0.5036 M $HClO_4$, 0.002658 M $Fe(ClO_4)_2$, 0.006545 M $Fe(ClO_4)_3$, at temperatures from 10 to 35 °C. From these, a potential-difference value of 0.7394 V "corrected to unit concentration of H^+" at 25 °C and 1 atm H_2(g) pressure, was reported for

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

In the present review, the uncertainties in the measurements are estimated to be ± 0.002 V. No value for $I = 0$ was reported, but the measured value and the formal potential are consistent with those obtained by other groups [1937SCH/SHE], [1953MAG/HUI], [1972WHI/LAN], [2000TAG/DIA], and have been incorporated in the analysis shown in the main text (FigureVI-2).

The value of the slope, dE/dt, of the straight line representing $E^{o\prime}(t) = \mathrm{f}(t)$ at a single ionic strength (0.5 M) is 0.00121 V, and is similar to that found from other work at constant ionic strength (see Figures VI-7 and VI-8 in Chapter VI).

[1951COU/KIN]

Heat-content and derived entropy increments above 25 °C are presented for synthetic specimens of "ferrous oxide" (composition $Fe_{0.947}O$, which is near the Fe-rich limit for the wüstite stability field), magnetite (Fe_3O_4), and iron(III) oxide (hematite, α-Fe_2O_3). Molar quantities are based on 1949 "atomic weights" (55.85 for Fe and 16.00 for O), but the resulting bias is less than the rounding errors in the heat measurements and in the parameters reproduced below. Two references by other authors are given for the drop-calorimetry apparatus used for the enthalpy measurements. Samples were held in welded, He-backfilled Pt-Rh alloy capsules. Temperatures were calibrated at the melting point of Au and, less frequently, that of Pt. Overall calorimetry was checked with high-purity corundum (α-Al_2O_3) as reference material. For measurements on $Fe_{0.947}O$ between 890 and 1270 K, the specimen was pre-heated for at least 0.5 hour at 1270 K to assure homogeneity. Some decomposition of the $Fe_{0.947}O$ was detected following the four measurements at 521.1 to 708.1 K; in each case, the sample was regenerated by heating for 0.5 hour at 1270 K before further measurements were made.

Ninety-one individual enthalpy measurements are tabulated: 30 values for $Fe_{0.947}O$ at 339.8 to 1784 K, including 4 above the melting point of ~ 1650 K; 29 values for Fe_3O_4 at 351.6 to 1825 K, including 13 between 821.1 and 1044.8 K; 32 values for Fe_2O_3 at 374.8 to 1757 K, including 12 between 924.5 and 1203.4 K.

The tabulated parameters were obtained for the following relationship (H in cal·mol^{-1}): ($H^\circ(T) - H^\circ(298.15\,\mathrm{K})$, substance, $T_1 < T < T_2$) = A + BT + CT^2 + DT^{-1} ± z%.

substance	T_1/K	T_2/K	A	B	C	D	z
$Fe_{0.947}O$, cr	298	1650	-3790	11.66	0.00100	67000	0.3
$Fe_{0.947}O$, l	1650	1800	-1200	16.30	0	0	0.1
Fe_3O_4, cr	298	900	-8666	21.88	0.0241	0	0.6
Fe_3O_4, cr	900	1800	-12650	48.00	0	0	0.2
Fe_2O_3, cr	298	950	-9021	23.49	0.0093	355000	0.1
Fe_2O_3, cr	950	1050	-11980	36.00	0	0	0.1
Fe_2O_3, cr	1050	1750	-8446	31.71	0	0	0.1

The measured heat of fusion of $Fe_{0.947}O$ was 7.49 kcal·mol^{-1}. Presumed magnetic anomalies were detected for Fe_3O_4 near 880 K and for Fe_2O_3 near 950 and 1050 K. Note that the authors use Greek letters α, β and γ to define the phases above and below the various transitions; *this does not correspond to the normal usage for describing different polymorphs.*

These appear to be reliable measurements on carefully prepared and characterized materials. The only analysed impurity was 0.22% SiO_2 in the Fe_3O_4 (and presumably an equivalent amount in the wüstite, and possibly also in the Fe_2O_3, which were a product and a precursor, respectively, of the magnetite).

While the measurements below ~ 1000 K have been largely superseded by more detailed heat-capacity measurements for all three phases, the data presented here appear to remain the only reliable measurements of the thermal properties of wüstite above 999 K, magnetite above 1044 K, and hematite above 1054 K. This is important for evaluation of magnetite-hematite equilibrium above ~ 1050 K (see Section VII.2.2.1) and hence the standard enthalpy of formation of hematite.

[1951SID/VOS]

Spectrophotometric measurements were made of the first hydrolysis step at constant iron(III) concentrations (1.5×10^{-4} and 4.5×10^{-4} M) and ionic strengths apparently to 0.1 M with perchloric acid concentrations between *ca*. 0.001 and 0.016 M, but with no real temperature control (ranged between 24.8 and 30.3 °C). Only some of the experimental data are shown in figure form with one summary graph that is difficult to reconcile with the figures.

The authors give a $\log_{10} {}^{*}\beta^{\circ}_{1,1}$ value of $-(2.19 \pm 0.003)$ at *ca*. 25 °C, which is in good agreement with more recent values, and appears to be extracted from an ionic strength dependence up to 0.1 M ($NaClO_4$), but this value is not included in the final analysis by this review.

[1951TOD/BON]

Forty $C^{\circ}_{p,\mathrm{m}}$ measurements were performed at 54.37 to 296.46 K on a 312.89-g specimen of wüstite with the composition $Fe_{0.947}O$. The material, which was also used for high-temperature enthalpy measurements in the same laboratory [1951COU/KIN], was much better defined than the "FeO" studied by Millar [1929MIL], making these the most reliable heat-capacity data for wüstite prior to [1993GRO/STO]. The only measured impurity was 0.17 wt.% SiO_2.

The authors obtained $C^{\circ}_{p,\mathrm{m}}$ ($Fe_{0.947}O$, cr, 298.15 K) = 48.1 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ and S°_{m} ($Fe_{0.947}O$, cr, 298.15 K) = (59.4 ± 0.8) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$. The latter value includes a calculated contribution of 2.9 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ for $[\Delta S^{\circ}_{\mathrm{m}}]^{52\,\mathrm{K}}_{0\,\mathrm{K}}$ and a configurational entropy of 1.72 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ based on a random distribution of iron vacancies in the wüstite structure.

Similar measurements and entropy calculations are also presented for MnO and VO.

[1951TOD/COU]

In this paper heat-capacity measurements are reported for temperatures from 52.9 to 296.8 K, as are drop-calorimetry results from 339.6 to 560.9 K. The drop-calorimetry results for 549.1 and 560.9 K were affected by "premelting effects", and are not considered further here. The rest of the sparse drop-calorimetry results are rather scattered, and do not mesh particularly well with the low-temperature results near 300 K. Todd and Coughlin [1951TOD/COU] provided an equation that can be re-expressed as $C^{\circ}_{p,\mathrm{m}}$ ($FeCl_3$, cr, T)/$\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ = $123.66 - 2.556 \times 10^{6}(T/\mathrm{K})^{-2}$. This leads to 94.91 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ at 298.15 K, but the curve diverges downwards from the experimental results by almost 2 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ at 285 K. A smooth extrapolation only through the adiabatic calorimetry results leads to $C^{\circ}_{p,\mathrm{m}}$ ($FeCl_3$, cr, 298.15 K) = 95.00 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$. The JANAF tables also supplies smoothed values (and an estimate of $C^{\circ}_{p,\mathrm{m}}$ ($FeCl_3$, cr, 298.15 K) = 96.65 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$), and the JANAF values better match most of the full set of experimental results, but show an unexplained upward inflection in the $C^{\circ}_{p,\mathrm{m}}(T)$ curve above 300 K. The entropy contribution from 51 to 298.15 K was estimated by the authors to be (115.84 ± 0.38) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$.

[1952BUL/CAN]

The solubilities of iron(II) sulfate hydrates were measured in water and aqueous mixtures with sulfuric acid for temperatures from 0 to 100 °C. Dissolution of both the monohydrate and heptahydrate was examined, and in some cases (*e.g.*, dissolution and transformation of the heptahydrate at 70 °C) several weeks were required for the system to approach equilibrium. No evidence was found that the tetrahydrate formed as a stable phase, even in water near 60 °C. It was concluded that the equilibrium solubilities are lower than those reported previously by Fraenckel [1907FRA] for temperatures above 56.7 °C. Except at the lower acid concentrations, good agreement was found with the work of Belopolskii and Shpunt [1941BEL/SHP]. No evidence was found for the dihydrate reported by Cameron [1930CAM].

[1952KIN]

King measured the heats of dissolution of α-$\mathrm{Fe_2SiO_4}$, α-$\mathrm{SiO_2}$, $\mathrm{FeCl_2}$(cr), $\mathrm{H_2O}$(l) and $\mathrm{HCl{\cdot}5.806H_2O}$(l) in 20.1% aqueous HF at 333.15 K. Using then-current values for $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($\mathrm{SiO_2}$, α), $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($\mathrm{FeCl_2}$, cr), $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($\mathrm{H_2O}$, l) and $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ (HCl, aq) for 298.15 K, the reported value of $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($\mathrm{Fe_2SiO_4}$, α) was − 1447.7 $\mathrm{kJ{\cdot}mol^{-1}}$.

In the present review, using the value selected for $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($\mathrm{FeCl_2}$, cr, 298.15 K) and CODATA values for the other three quantities, a value of −(1478.77 ± 2.61) $\mathrm{kJ{\cdot}mol^{-1}}$ is calculated for $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($\mathrm{Fe_2SiO_4}$, α, 298.15 K). The large difference results primarily from a change in the accepted value for $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($\mathrm{SiO_2}$, α, 298.15 K).

There have been several previous attempts to re-evaluate King's measurements. The US-NBS Tables [1969WAG/EVA] and Robie and Waldbaum [1968ROB/WAL] reported − 1479.9 $\mathrm{kJ{\cdot}mol^{-1}}$ (− 353.7 $\mathrm{kcal{\cdot}mol^{-1}}$), and − 1479.2 $\mathrm{kJ{\cdot}mol^{-1}}$ (− 353.54 $\mathrm{kcal{\cdot}mol^{-1}}$), respectively, presumably based at least in part on King's results. Hemingway and Robie [1977HEM/ROB] carried out measurements of the heat of solution of quartz into HF(sln) (and also reviewed literature values as functions of temperature and the percentage HF in the solution). They contended that because the quartz samples used by King were composed of very small particles, King's reported enthalpy of solution was ~ 1.3 $\mathrm{kJ{\cdot}mol^{-1}}$ more negative than if particles > 10 μm had been used [1977HEM/ROB]. They also carried out new measurements of the heat of solution of HCl(sln) and $\mathrm{H_2O}$(l) into 20.1% HF(sln) at 60 °C, but a direct comparison with King's results is difficult because no measurements were carried out on the concentration dependence. The change in the heat of dissolution for $\mathrm{SiO_2}$ would mean that any recalculated enthalpy of formation for α-$\mathrm{Fe_2SiO_4}$ should have been less negative. Nevertheless, the procedure used by Hemingway and Robie to recalculate an almost unchanged value for the enthalpy of formation (reported as −(1479.4 ± 2.4) $\mathrm{kJ{\cdot}mol^{-1}}$) was not clearly described.

The Hemingway and Robie value also probably incorporated third-law results from some high-temperature equilibrium measurements (*e.g.*, [1964TAY/SCH]). However, it is somewhat puzzling that over a decade later Haas and Hemingway [1992HAA/HEM] reported $-(1479.7 \pm 1.9)$ $kJ\cdot mol^{-1}$ based *solely* on recalculation of King's results—again, the values used for auxiliary data were not provided.

The arguments of Hemingway and Robie [1977HEM/ROB] concerning the heat of dissolution of quartz are quite convincing, and in the present review, it is accepted that the SiO_2 used by King [1952KIN] was (1.26 ± 0.80) $kJ\cdot mol^{-1}$ less stable that the α-SiO_2 tabulated in the CODATA tables [1989COX/WAG]. From this, King's other measured values, and the auxiliary data discussed above, the recalculated value of $\Delta_f H_m^\circ$ (Fe_2SiO_4, α, 298.15 K) is $-(1476.73 \pm 2.68)$ $kJ\cdot mol^{-1}$.

[1952LI/GRE]

The average heat of solution of $FeCl_2$ in water at 298.15 K (five measurements, final concentrations 0.00139 to 0.0117 m $FeCl_2$) was reported as -81.84 $kJ\cdot mol^{-1}$, and the value at the lowest concentration was -81.59 $kJ\cdot mol^{-1}$. The measurements for $FeBr_2$ (0.00247 to 0.00828 m $FeBr_2$ final) appear to show a more definite concentration dependence, and the value at the lowest concentration was -85.36 $kJ\cdot mol^{-1}$.

Use of heats of dilution calculated using Eqs. (IX.70) and (IX.71) from Grenthe *et al.* [1997GRE/PLY2] (also see the discussion of the paper by Cerutti and Hepler [1977CER/HEP] in Appendix A of the present review) leads to $-(82.4 \pm 0.7)$ $kJ\cdot mol^{-1}$ for the average heat of solution for $FeCl_2(cr)$ in water, corrected to $I = 0$. The set of results for $FeCl_2$ appear to be less internally consistent than those from later studies [1977CER/HEP], [1982COB/MUR], and possible reasons for this have been discussed by Cerutti and Hepler [1977CER/HEP].

For $FeBr_2(cr)$ in water, use of the SIT limiting-law heat of dilution equations from Grenthe *et al.* results in an average heat of solution of $-(85.05 \pm 1.30)$ $kJ\cdot mol^{-1}$. Use of the equation of Silvester and Pitzer [1978SIL/PIT] with the $FeBr_2$ measurements leads to $-(85.09 \pm 1.28)$ $kJ\cdot mol^{-1}$, essentially the same result. Whereas the corrected results for $FeCl_2$ are scattered, those for $FeBr_2$ show a distinct trend to a more negative molar heat of solution for "corrected" results from solutions at lower final molalities. Therefore, the uncertainty in the heat of solution of $FeBr_2(cr)$ at $I = 0$ is estimated as ± 1.5 $kJ\cdot mol^{-1}$.

For $FeCl_3$ (0.000766 to 0.00318 m $FeCl_3$ final) the heats of solution were -116.31 to -130.12 $kJ\cdot mol^{-1}$; for $FeBr_3$ (0.00098 to 0.00736 m $FeBr_3$ final) the heats of solution were -101.67 to -121.34 $kJ\cdot mol^{-1}$. The authors attempted to correct the heats of solution of the trihalides for complexation and hydrolysis. This appeared to remove the systematic drift in the values as functions of final concentration, and resulted in $-(159.2 \pm 1.2)$ $kJ\cdot mol^{-1}$ for $\Delta_{sln}H$ ($FeCl_3$, cr, 298.15 K). For $FeBr_3$, the authors reported an average value of -147.7 $kJ\cdot mol^{-1}$ ($-(35.3 \pm 1.0)$ $kcal\cdot mol^{-1}$) based on "four independent samples". Results for seven $FeBr_3$ measurements were listed (including the corrections applied), and there is no indication as to which four might have been from different samples of $FeBr_3$(cr) (and then used in obtaining the average). Recalculation considering all seven "corrected" measurements leads to – (146.7 ± 4.5) $kJ\cdot mol^{-1}$ for $\Delta_{sln}H$ ($FeBr_3$, cr, 298.15 K).

[1952NOV/ORA]

Novikov *et al.* measured the equilibrium amount of HCl(g) in a stream of H_2(g) and HCl(g) equilibrated over $FeCl_2$(cr) and Fe(cr) at three temperatures, 696, 746 and 796 K. At each temperature the equilibrium measurements were done using both gas mixtures initially deficient in HCl(g) and mixtures with HCl(g) in excess of the equilibrium gas fraction. Values for the enthalpy of reaction at 298.15 K are obtained from a third-law calculation using the selected values for the entropies and heat-capacity functions for Fe(α) and $FeCl_2$(cr) (Sections V.2 and VIII.3.2.1.1) and for H_2(g) and HCl(g) [1989COX/WAG]. An average value of $\Delta_r H^\circ_m$((A.23), 298.15 K) = (154.4 ± 2.3) $kJ\cdot mol^{-1}$ is obtained.

$$FeCl_2(cr,l) + H_2(g) \rightleftharpoons Fe(cr) + 2\,HCl(g). \quad (A.23)$$

$$FeBr_2(cr) + H_2(g) \rightleftharpoons Fe(cr) + 2\,HBr(g) \quad (A.24)$$

Similar measurements were done for the bromide system at 726, 796, 826 and 896 K (although the data at 896 K were not reported in detail, and the authors regarded the values for that temperature as tentative). The analysis in the original paper assumes the same temperature function for the chloride and bromide reactions, and obtained a calculated value of – 290 $kJ\cdot mol^{-1}$ for $\Delta_f H^\circ_m$ ($FeBr_2$, cr, 298.15 K), 40 to 50 $kJ\cdot mol^{-1}$ more negative than the calorimetric results [1934HIE/WOE], [1989EVD/EFI2]. In the present review a third-law reanalysis was attempted using TDB auxiliary data and the $FeBr_2$ heat-capacity values from O'Neal [1957NEA]. First, Westrum's entropy value for $FeBr_2$(cr, 298.15 K) [1967CHR/GRE] was used to calculate $\Delta_r H^\circ_m$ (A.24) from 158 to 167 $kJ\cdot mol^{-1}$ (and values of $\Delta_f H^\circ_m$ ($FeBr_2$, cr, 298.15 K) from – 231 to – 239 $kJ\cdot mol^{-1}$). Then, the enthalpy of formation values based on Hiebert and Woener [1934HIE/WOE] can be used to calculate (129 ± 4) $J\cdot K^{-1}\cdot mol^{-1}$ for S°_m ($FeBr_2$, cr, 298.15 K) and the enthalpy of formation value based on Evdokimova and Efimov [1989EVD/EFI2] can be used to calculate (137 ± 5) $J\cdot K^{-1}\cdot mol^{-1}$ for S°_m ($FeBr_2$, cr, 298.15 K). The entropy value of (129 ± 4) $J\cdot K^{-1}\cdot mol^{-1}$ is almost certainly too low (only 11 $J\cdot K^{-1}\cdot mol^{-1}$ more positive than the value for $FeCl_2$(cr)). Thus, these calculations suggest that the results of the high-temperature equilibrium measurements are incompatible with the results of Hieber and Woerner [1934HIE/WOE], and only marginally consistent with the combined results of Evdokimova and Efimov [1989EVD/EFI2] and Westrum.

[1952SCH3]

The results of solubility measurements for hydrated $FeCl_2$ in water and aqueous HCl solutions are reported. In contact with the saturated solutions, the solid-phase transitions from the hexahydrate to the tetrahydrate and from the tetrahydrate to the dihydrate were found to occur at lower temperatures as the concentration of HCl was increased. It is not clear whether the results for the solubilities in water are from the same measurements reported earlier by the same author [1928SCH]. Measurements were also reported for the $FeCl_2$-$FeCl_3$-H_2O system. At 25 °C the only two solid phases that exist in contact with the saturated solutions are $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$.

[1952SYK]

The retardation of the reaction of Fe(III) with I^- was studied as a function of added sulfate concentration at a constant ionic strength of 0.066 M. The reagents used were iron(III) nitrate (0.00167 M), nitric acid (0.006 M), a mixture of SO_4^{2-}/HSO_4^-, and sodium (or potassium) perchlorate to reach the desired ionic strength. Corrections for hydrolysis and protonation of sulfate ion were applied. The reported value of the formation constant for $FeSO_4^+$ was 1040 M^{-1} (I = 0.066 M, 18 °C). A Davies-type extrapolation was used to estimate 1.5×10^4 as the value for K_1^o at 18 °C.

After conversion to the molal scale and temperature correction of the K_1 constant value, this value was included in the calculation of the optimised K_1^o value and interaction coefficients using the SIT formalism. The van't Hoff formula is used with $\Delta_r H_m^o$ = (26.0 ± 6.3) $kJ \cdot mol^{-1}$, for the temperature correction from 18 to 25 °C. This is the value of $\Delta_r H_1$ determined by taking the unweighted average of literature values [1960KUM], [1962DAV/SMI] and [1963WIL] (see the main text). The uncertainty is estimated in the present review from the scatter of the literature values, hence:

$$K_{1m}(298.15\ K) = (1330 \pm 300)\ mol^{-1} \cdot kg.$$

[1953GAM/JOR]

This paper describes an investigation of the iron(III) chlorido complexes over the entire range of possible aqueous chloride concentrations. The goal was to study the higher-order complexes of iron(III), which exist only in concentrated aqueous chloride solutions. The limiting species is the tetrahedral $FeCl_4^-$, as shown spectroscopically by comparison with the spectrum characterized earlier by Friedman [1952FRI]. All the individual spectra for $FeCl^{2+}$, $FeCl_2^+$, $FeCl_3$(aq) and $FeCl_4^-$ were deduced from the data.

This paper did not contain tables of numerical values of absorption at constant ionic strength, which would have permitted recalculation of the equilibrium constants and application of the SIT formalism. However, the numerical values contained in this paper are one of the few sources of values for formation of the $FeCl_3$(aq) and $FeCl_4^-$ complexes. Therefore, they are presented below, and were used in the calculation of the average values of K_3^o and K_4^o.

Using absorption at different wavelengths and extrapolating roughly to I = 0 the authors found: K'^o_3 = 0.73 $mol^{-1} \cdot dm^3$ and K'^o_4 = 0.0105 $mol^{-1} \cdot dm^3$. K'^o_3 and K'^o_4 are constants defined as

$K'^{\mathrm{o}}_3 = [\mathrm{FeCl_3(aq)}]/([\mathrm{FeCl_2^+}]\,[\mathrm{Cl^-}]\,\mathrm{f_{HCl}})$ $K'^{\mathrm{o}}_4 = [\mathrm{FeCl_4^-}]/([\mathrm{FeCl_3(aq)}]\,[\mathrm{Cl^-}]\,\mathrm{f_{HCl}})$

and $\mathrm{f_{HCl}}$ is the mean activity coefficient of HCl (assumed equal to $\mathrm{f_{Cl^-}}$), which was used in place of $\mathrm{f_{FeCl_4^-}}/(\mathrm{f_{FeCl_3(aq)}}\cdot\mathrm{f_{Cl^-}})$ for K'^{o}_4 and $\mathrm{f_{FeCl_3(aq)}}/(\mathrm{f_{FeCl_2^+}}\cdot\mathrm{f_{Cl^-}})$ for K'^{o}_3. This also required use of the extra thermodynamic assumption: $\mathrm{f_{FeCl_3(aq)}}/\mathrm{f_{FeCl_2^+}} = \mathrm{f_{FeCl_4^-}}/\mathrm{f_{FeCl_3(aq)}} = 1$. The stability constants K'^{o}_3 and K'^{o}_4 given in Table VI-4 of the main text are molar concentration constants, and no attempt has been made to convert them to the molal scale. The equilibria $\mathrm{FeCl_2^+} + \mathrm{Cl^-} \rightleftharpoons \mathrm{FeCl_3(aq)}$ and $\mathrm{FeCl_3(aq)} + \mathrm{Cl^-} \rightleftharpoons \mathrm{FeCl_4^-}$ were observed only in highly concentrated HCl solutions, far beyond the range of applicability of the SIT model.

The values of K'^{o}_3 and K'^{o}_4 were assumed to be approximately equal to the values of K^{o}_3 and K^{o}_4, and correspond, respectively, to values of 0.78 and 11.30 $\mathrm{kJ\cdot mol^{-1}}$ for $\Delta_{\mathrm{r}}G^{\mathrm{o}}_3$ and $\Delta_{\mathrm{r}}G^{\mathrm{o}}_4$. The uncertainties are estimated here as $\pm$ 4 $\mathrm{kJ\cdot mol^{-1}}$.

The value of $\Delta_{\mathrm{r}}G^{\mathrm{o}}_3$ is not in good agreement with the average of the few other literature values, 5.19 $\mathrm{kJ\cdot mol^{-1}}$, as recommended in the present review. Nevertheless, the $\Delta_{\mathrm{r}}G^{\mathrm{o}}_4$ value is very close to the average value recommended in this review.

[1953HED]

Potentiometric titrations were performed at 25 °C in 1 M $\mathrm{NaClO_4}$ at three Fe(II) concentrations with a cell fitted with a calomel reference electrode and a glass pH probe. The standard potential was measured empirically, the liquid-junction potential was assumed to be negligible due to the presence of the swamping electrolyte and a second burette was used cleverly to maintain a constant Fe(II) concentration. Interestingly, stable redox potentials could not be obtained with an iron electrode. Similar to comparable studies of magnesium hydrolysis, only very small values of $\bar{n}$ (defined as the number of ligands per metal centre in a complex) = $(h - H)/c_{\Sigma\mathrm{Fe}}$, were attained before precipitation occurred (*viz.*, < 0.008), such that only the first hydrolysis constant was considered; polynuclear species were rejected due to the insensitivity of $\bar{n}$ to $c_{\Sigma\mathrm{Fe}}$. A mean value for $\log_{10}{}^{*}K_{1,1}$ of $-$ (9.5 ± 0.2) with K_{11} in molar units was reported.

Although the liquid-junction potentials were neglected for I = 1 ($\mathrm{NaClO_4}$, M) containing concentrations of $\mathrm{Fe^{2+}}$ as high as 0.054 M, these careful titrations where < 1% hydrolysis could be monitored, appear to be very reliable. Experience shows that more emphasis on titrations at lower Fe(II) concentrations would have produced more precise K_{11} values. The large uncertainty obviates the need to convert to molal units, *i.e.*, $\log_{10}{}^{*}K_{1,1}$ of $-$ (9.4$_8$ ± 0.2) at 1.052 $\mathrm{mol\cdot kg^{-1}(H_2O)}$, 25 °C.

[1953HED2]

Electrochemical potential-difference measurements of iron(III) solutions were made at 25 °C in 3 M $\mathrm{NaClO_4}$ with a cell with Pt *vs.* a calomel electrode, CE. The liquid-junction potential was estimated as $-$ 0.018 h, where h is the hydrogen-ion concentration added [1953BIE/SIL]. The results were interpreted in terms of the generalized equilibrium:

$$p\,\mathrm{M}^{z+} + q\,\mathrm{H_2O(l)} \rightleftharpoons \mathrm{M}_p(\mathrm{OH})_q^{pz-q} + q\mathrm{H}^+ .$$

The $[\mathrm{H}^+]$ was measured with a glass electrode *vs.* CE. Interestingly, aqueous $\mathrm{NaHCO_3}$ was used as base titrant to prevent localized precipitation of iron hydroxides. One reverse titration with acidic titrant was performed with "identical" results. Three hydrolysis constants were derived, *viz.*, ${}^*\beta_{1,1}$, ${}^*\beta_{2,1}$ and ${}^*\beta_{2,2}$. The reported $\log_{10}{}^*\beta_{q,p}$ values are: − (2.98 ± 0.05), − (6.18 ± 0.09) and − (2.85 ± 0.04) converted to molal units. The authors used a wide range of $c_{\mathrm{Fe_{total}}}$, $(0.1 - 50) \times 10^{-3}$ mol·L^{-1}, but at the two lowest concentrations at which titrations were performed in duplicate, *viz.*, (1 and 2) $\times 10^{-4}$ mol·L^{-1}, where the mononuclear species dominate and the $\bar{n}$ (or *Z*, defined as the number of ligands per metal centre in a complex) are not shown and even for the 1×10^{-3} mol·L^{-1} titration curve, which is shown, the data appear very scattered.

Although these titrations appear to have been carefully carried out, the value of $\log_{10}{}^*\beta_{1,1}$ of − 2.98 is *ca.* 1.2 units lower than reported by [1955MIL/VOS] and [2000BYR/LUO] who employed spectrophotometry. Extracting two hydrolysis constants from these data may have been overfitting the data, especially as we can not be sure that *Z* values greater than 1 were obtained. On the other hand, it would be expected that the constant for the dimer would be more reliable.

[1953HIL/SMI]

Calorimetric measurements of the specific heat of $\mathrm{(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O}$ were carried out at temperatures from ~ 2 to 30 K, and compared with measurements for the corresponding zinc salt. The results were presented graphically and in a table of "smoothed" values from 2.5 to 30 K. There are two maxima in the difference curves, at 3.8 and 20.5 K.

[1953LEU/KOL]

Solubility measurements are presented for $\mathrm{Fe(OH)_2}$, based on iron analysis and pH measurements (made using a glass electrode calibrated with a single buffer solution) for supernatant solutions associated with $\mathrm{Fe(OH)_2}$ suspensions prepared from deaerated NaOH and Fe(III)-free $\mathrm{FeCl_2}$ solutions. The precipitate was shown to be free of chloride (by analysis) and of iron(III) (by its white colour), but as with other studies of this era or earlier, it was not characterized by XRD, microscopy, or surface area measurements. The $\mathrm{FeCl_2}$ stock solutions were prepared from HCl and a slight excess of Fe metal; in some cases, the solutions contained a small quantity of unreacted HCl, the quantity of which is not always given. Three initial solubility measurements were used to estimate the value $K^\circ = 4 \times 10^{-10}$ for Reaction (A.25).

$$\mathrm{Fe(OH)_2(s)} \rightleftharpoons \mathrm{FeOH^+} + \mathrm{OH^-} \qquad \text{(A.25)}$$

$$K^\circ\,\text{(A.25)} = a_{\mathrm{FeOH^+}}\,a_{\mathrm{OH^-}}$$

A total of 19 measurements then yielded $K^{\circ} = (8 \pm 3) \times 10^{-16}$ for Reaction (A.26).

$$\mathrm{Fe(OH)_2(s)} \rightleftharpoons \mathrm{Fe^{2+}} + 2\,\mathrm{OH^-} \qquad \text{(A.26)}$$

$$K^{\circ}\ (\text{A.26}) = a_{\mathrm{Fe^{2+}}}\, a^{2}_{\mathrm{OH^-}}$$

The paper includes a brief critical review of previous solubility and solubility product values from 11 different publications, in comparison with the values reported in the current paper. There is also a short discussion of the apparent stability of the $\mathrm{Fe(NH_3)_4^{2+}}$ complex.

Table A-6: Solubility data for precipitated $Fe(OH)_2(s)$, aged for up to 14 days at 25 °C, from Table III of [1953LEU/KOL].

[NaOH] $^{(a)}$/M	V $FeCl_2$ $^{(b)}$	pH	[Fe] $^{(c)}$/M	[NaOH] $^{(a)}$/M	V $FeCl_2$ $^{(b)}$	pH	[Fe] $^{(c)}$/M
0.0241	5	7.63	0.0095	0.0514	15	7.42	0.0373
0.0241	5	7.60	0.0109	0.01	6	7.40	0.0203
0.0241	5	7.60	0.0116	0.01	7.5	7.37	0.0256
0.0495	10	7.57	0.0215	0.01	6	7.35	0.0205
0.01	3	7.55	0.0091	0.0495	25	7.33	0.0765
0.01	4	7.52	0.0113	0.0514	18	7.26	0.0541
0.01	4	7.46	0.0112	0.0099	8.3	7.23	0.0338
0.0514	10	7.46	0.0234	0.0514	25	7.15	0.0827
0.01	5	7.45	0.0183	0.0099	22.5	7.05	0.0895
0.01	10	7.42	0.0377				

(a) Initial concentration of NaOH (M), 100 mL.

(b) Volume (mL) of nominally 0.5 M $FeCl_2$.

(c) Total dissolved iron, analysed by titration with cerium(IV) sulfate, in supernatant solution.

Although the solid phase is not very well characterized, this appears to be one of the better solubility studies on $Fe(OH)_2$. Cation hydrolysis is taken into account, and activity corrections are made. Sufficient data (tabulated above) are provided, in principle, for a self-consistent recalculation of the solubility product by correcting the solution composition for the quantity of $Fe(OH)_2$ precipitated, then using a current, iterative procedure for the activity correction and current (OECD/NEA assessed) data for the first hydrolysis constant of Fe^{2+}. Two (probably minor) corrections can not be made with the available data: (i) excess HCl in the starting solution; (ii) loss of H_2O from the NaOH solution when the solutions were “deaerated by vigorously bubbling nitrogen through them for one-half hour”. The results, however, show a residual variation with pH (possibly linked to the single-point calibration), and it is unlikely that a modern treatment of the activity correction will provide a more reliable estimate for the solubility product K°(A.26) than the authors' value of $(8 \pm 3) \times 10^{-16}$, which is similar to the value obtained by application of the Davies equation.

In order to estimate the allusive first hydrolysis constant of the Fe^{2+}, recalculation of the results of the three experiments carried out with HCl initially present, gave $\log_{10} {}^{*}K^{\circ}_{11}$ values between -7.6 and -7.1, which is *ca.* two orders of magnitude higher than reported from the more direct potentiometric studies. Indeed, the choice of values for the equivalent total iron(II) concentration based on either the actual volumes added of $FeCl_2$(sln) to the NaOH solutions or the measured total chloride concentration led to markedly different estimations of the $FeOH^{+}$ concentration. Clearly, with the latter representing only 1% of the concentration of dissolved iron(II) before iron(II) hydroxide precipitates, this type of batch experiment is useless for the determination of $\log_{10} {}^{*}K^{\circ}_{11}$. In fairness to the authors, they did not even attempt to report this value.

The value of $K^{\circ}(\text{A.26}) = (8 \pm 3) \times 10^{-16}$ can be compared with $K^{\circ}(\text{A.27}) = (1.2 \pm 0.4) \times 10^{-15}$ for Reaction (A.27), based on the OECD/NEA assessed $\Delta_{f}G^{\circ}_{m}$(298.15 K) values of $-1012.719\ \text{kJ}\cdot\text{mol}^{-1}$ for Fe_3O_4(cr) and $-90.719\ \text{kJ}\cdot\text{mol}^{-1}$ for Fe^{2+}.

$$0.25\,Fe_3O_4(cr) + 0.25\,Fe(cr) + H_2O(l) \rightleftharpoons Fe^{2+} + 2\,OH^{-} \qquad (A.27)$$

This suggests that $Fe(OH)_2$(s) is only marginally stable, if at all, with respect to Fe(cr) + Fe_3O_4(cr) + H_2O(l) (*i.e.*, disproportionation to magnetite and metallic iron) at 298.15 K.

[1953MAG/HUI]

Mid-point potentials were measured for the cell

$$Pt,H_2(g)\ |\ HClO_4(sln)\ ⁝⁝\ HClO_4(sln),\ Fe(ClO_4)_2(sln),\ Fe(ClO_4)_3(sln)\ |\ Pt$$

by potentiometric titration of Fe^{2+} with $K_2Cr_2O_7$(sln) at 288.38, 298.19 and 308.53 K. The acid concentration was 0.985 M $HClO_4$, and the total iron concentration was 0.01 M. From these measurements, a potential-difference value of 0.738 V corrected to unit molar concentration of H^{+} at 25°C and 1 atmosphere H_2(g) pressure, was reported for

$$Fe^{3+} + \tfrac{1}{2}H_2(g) \rightleftharpoons Fe^{2+} + H^{+}.$$

No value for $I = 0$ was reported, but the measured value at 0.985 M $HClO_4$ and the formal potential are consistent with those obtained by other groups [1937SCH/SHE], [1951CON/MCV], [1972WHI/LAN], [2000TAG/DIA] (see Figure VI-3). The values of $E^{\ddagger} + (5D)(RT(\ln(10))/F)$ from experiments done using $NaClO_4$, rather than $HClO_4$, as the supporting electrolyte to maintain constant ionic strength are off the curve for 298.15 K (Figure VI-2), and are not shown in Figure VI-3 (Section VI.1.2.1.1.1). Only the single value obtained from the experiment at 298.19 K in $HClO_4$

was incorporated into the calculations in the present review, and the uncertainty in the measured potential is estimated as ± 0.002 V.

The three values of $E^{\ddagger}(t)$ as a function of temperature obtained at 1 M ionic strength fall perfectly on the straight line yielded by the work of Connick and MacVey [1951CON/MCV] as shown in Figure VI-8 of the main text.

[1953ORR]

A portion of the same sample prepared by Kelley [1941KEL] was used to carry out drop-calorimetry measurements of the heat content of α-Fe_2SiO_4. Measurements were done with initial sample temperatures from 395.1 to 1452.4 K, and the calorimeter at 298.15 K. Stebbins and Carmichael [1984STE/CAR] showed that the experiments near the melting point were subject to incongruent melting, and noted that interaction of Orr's platinum-rhodium capsules with molten α-Fe_2SiO_4 likely affected the results at higher temperatures. The results of the measurements in which premelting was reported, and from the measurement at 1288.7 K, made after the sample had been melted, are not used in the present review. For the purposes of fitting a single function to all the calorimetry results, the individual values for the enthalpy differences were estimated (in the present review) to have uncertainties of 0.5%. This is slightly greater than the author's estimate of 0.2%.

[1953PAT/THO]

This paper is an attempt to determine the value of $E^{\circ}(Fe^{2+}/Fe(0))$ by cell-potential measurements using three cells without liquid junctions.

(A) $Fe(s) \mid FeCl_2(sln) \mid HgCl,Hg(l)$

(B) $Fe(s) \mid FeSO_4(sln) \mid Hg_2SO_4,Hg(l)$

(C) $Fe(s) \mid FeSO_4(sln) \mid PbSO_4,Pb(s)$

The iron was prepared by decomposition of iron carbonyl under vacuum (powder electrode) or as a massive iron electrode obtained by melting the powder under vacuum. These preparations led to Fe electrodes with low H_2 or O_2 contents. The $FeCl_2$ or $FeSO_4$ in solution was in the range of 0.01 to 0.1 m. Various stable potentials were obtained after 20 days.

In their calculations, the authors used activity coefficients for $FeCl_2$ taken from [1938LAT] and for $FeSO_4$ values from [1941DEM/FED]. Potential values for the reference electrodes were taken from [1938LAT]: (A) 0.2676 V, (B) 0.6151 V, (C) 0.355 V. A potential, $E^{\circ}(Fe^{2+}/Fe(0))$ – 0.409 V *vs.* SHE, was obtained. However, – 0.44 V *vs.* SHE was obtained if impure $H_2(g)$ was used and – 0.473 V *vs.* SHE with completely deoxygenated $H_2(g)$. These correspond to values of $\Delta_f G^{\circ}_m(Fe^{2+}(aq))$ of – 78.92 kJ·mol^{-1}, – 84.90 kJ·mol^{-1}, and – 91.27 kJ·mol^{-1}. The results from this paper were not used further in the present review.

[1953WHI/DAV]

This paper deals with a study of the aqueous sulfato complexes of Fe(III), at I_c = 1 M and temperatures slightly above 28 °C. Two methods of investigation were used.

- variation of the Fe(III) distribution ratios between a cation-exchange resin and aqueous solutions of Fe^{3+} containing various concentrations of sulfate ions. (The cation-exchange resin preferentially binds the Fe^{3+} ions.)
- UV-visible spectrophotometry using the charge-transfer band of the Fe^{3+}sulfato complexes.

<u>Ion exchange</u>:

The variation of the Fe(III) distribution ratio Q_a in the presence of sulfate (L) was expressed by Eq. (A.28).

$$Q_0/Q_A = 1 + \beta_{1c}c_L + \beta_{2c}c_L^2 \qquad (L = SO_4^{2-}) \qquad (A.28)$$

where (Q_0) is the distribution ratio of free Fe^{3+} when there is no sulfate: $Q_A < Q_0$, and β_{1c} and β_{2c} are the formation constants of $FeSO_4^+$ and $Fe(SO_4)_2^-$.

The cation resin was DOWEX–50, 100-200 mesh in the H^+ form. The aqueous solutions were mixtures ($HClO_4$ + H_2SO_4) at I_c = 1 M containing 3×10^{-4} M inactive Fe^{3+} spiked with radioactive ^{59}Fe. The measurements of the iron concentrations were then carried out by radiometry.

Equation (A.28) was fitted to the experimental Q values, and the reported value of $\beta_{1c} = (95.1 \pm 3.6)\ M^{-1}$ was obtained by determining the limiting slope $d(Q_0/Q_A)/d(c_{SO_4^{2-}})$. The value of β_{2c} ((898 ± 159) M^{-2})[1] was found from the limiting slope of a plot of $\{Q_A/Q_0 - 1 - \beta_{1c}c_{SO_4^{2-}}\}$ *vs.* $c_{SO_4^{2-}}^2$. (These uncertainties are the reported *average* deviations, and are slightly greater than the average deviations recalculated from the reported results).

<u>Spectrophotometry:</u>

UV-visible spectrophotometry in the absorption region of the charge-transfer bands of the iron(III) sulfato complexes was used to measure the formation constants of the complexes at (27 ± 2) °C.

The samples were mixtures ($HClO_4$ + H_2SO_4) at I_c = 1 M, containing iron(III) and sulfate.

Equation (A.29) was used to correlate the variation of absorption with changes in sulfate concentration at constant iron(III) concentration:

$$c_{Fe(III)_{total}}/(D - D_0) = (1/(\varepsilon_1 - \varepsilon_0))\ (1 + 1/(\beta_{1c}c_{SO_4^{2-}}) \qquad (A.29)$$

---

[1] The value 893 M^{-1} in the caption to Figure 1 was assumed to be a typographical error.

where D and D_0 are the optical densities of equimolar Fe^{3+} solutions with and without sulfate, and ε_1 and ε_0 are the molar decadic absorption coefficients of $FeSO_4^+$ and Fe^{3+}.

The fit of Eq. (A.29) to the experimental points for two sets of measurements yielded:

$$\beta_{1c} = (101 \pm 2)\ M^{-1}, \text{ and } (121 \pm 2)\ M^{-1} \text{ at } I_c = 1\ M.$$

The Debye-Hückel-type formula used by the authors to attempt to extrapolate the β_{1c} value to zero ionic strength was:

$$-\log_{10} \gamma = 0.5\, z^2\{[I_c^{½}/(1 + I_c^{½})] - 0.2 I_c\} \qquad \text{(A.30)}$$

and this led to a value of 6.8×10^3 M^{-1} for β_1^{o}.

Another set of samples with greater sulfate concentrations (I_c = 2.76 M) was used to confirm the existence and the stability of $Fe(SO_4)_2^-$ by spectrophotometry. The value of K_{2c} found by ion exchange at lower ionic strength was roughly confirmed, and when combined with the β_{1c} value found by spectrophotometry yielded

$$\beta_{2c} = 1006\ M^{-2}$$

(and $\varepsilon_{01} = 220\ m^2\cdot mol^{-1}$; $\varepsilon_{02} = 290\ m^2\cdot mol^{-1}$ at 310 nm).

Finally considering all their results the authors estimated that: β_{1c} = $(107 \pm 20)\ M^{-1}$ and K_{2c} = 9.4 M^{-1} for the ionic strength $I_c \approx 1$ M.

The species $FeHSO_4^{2+}$ was not detected in this investigation, probably because its concentration was too low compared to $FeSO_4^+$.

SIT treatment:

The SIT treatment of the data of this paper is provided in detail in the main text because it addresses the main problems encountered in the application of the SIT formalism to sulfato-complex formation. The concentrations given in molarity have been converted to molalities using the ξ values given in Table II-5 for pure aqueous solutions of $HClO_4$ and H_2SO_4, and then using the proportionality rule.

A value of 0.075 $mol\cdot dm^{-3}$ for $K_{c1,1(HSO_4^-)}^{-1} = c_{SO_4^{2-}}\, c_{H^+} / c_{HSO_4^-}$ was used by the authors of the original paper.

First we recalculated the value of $K_{m1,1(HSO_4^-)}$ at 25 °C by applying the SIT equation:

$$\log_{10} K_{m1,1(HSO_4^-)}(1.046\ m) = \log_{10} K_{1,1(HSO_4^-)}^{o} - 4D - \Delta\varepsilon I_m \qquad \text{(A.31)}$$

According to CODATA, $\log_{10} K_{1,1(HSO_4^-)}^{o} = (1.98 \pm 0.05)$ at 25 °C.

$\Delta\varepsilon\, I_m$ for this study was $\{\varepsilon(H^+, HSO_4^-,)\, m_{H^+} - \varepsilon(H^+, SO_4^{2-})\, m_{H^+} - \varepsilon(H^+, SO_4^{2-})\, m_{SO_4^{2-}} - \varepsilon(H^+, HSO_4^-)\, m_{HSO_4^-} - \varepsilon(H^+, ClO_4^-)\, m_{ClO_4^-}\}$. The evaluation of the missing coefficients from the interaction coefficients tables are detailed in the main text.

Thus, at 25 °C the value of $\log_{10} K_{m1,1(\mathrm{HSO_4^-})}$ (1.046 m) is (1.19 ± 0.10). Then the temperature correction to 28 °C has been carried out using the value of $\Delta_r H^\circ_m$ = (22.4 ± 1.1) kJ·mol^{-1} given for the protonation reaction by Grenthe *et al.* ([1992GRE/FUG] Chapter VI, p. 379, Eq. (VI.23), and Eq. (A.32).

$$\Delta \log_{10} K^\circ_{1,1(\mathrm{HSO_4^-})} = -(\Delta_r H^\circ_m / R \ln 10)(1/T_2 - 1/T_1)$$

$$= -(22400 \times (1/301.15 - 1/298.15)/(8.314 \times 2.3026)) \qquad \text{(A.32)}$$

Thus, $\Delta \log_{10} K_{m1,1(\mathrm{HSO_4^-})}$ = (0.0391 ± 0.0019) which yields $\log_{10} K_{m1,1(\mathrm{HSO_4^-})}$ (1.046 m) at 28 °C = (1.23 ± 0.10) and $K^{-1}_{m1,1(\mathrm{HSO_4^-})}$ = (0.059 ± 0.014) mol·kg^{-1} at 28 °C.

Using this value and the list of experimental conditions given below Figure 1 of the original paper allowed recalculation of the Q_0/Q_A values as a function of the new $m_{\mathrm{SO_4^{2-}}}$ concentrations. A second-degree polynomial fitted to this function yielded:

β_{1m}(301.15°K) = (127 ± 23) mol·kg^{-1} and β_{2m} = (1443 ± 420) mol^2·kg^{-2}, and thus, K_{2m} = (11.4 ± 3.9) mol·kg^{-1}.

After correction to 298.15 K, using $\Delta_r H_1$ = (26.0 ± 6.3) kJ·mol^{-1} (see Appendix A [1952SYK] and $\Delta_r H_2$ = – 15.5 kJ·mol^{-1} (for the second stepwise complexation reaction, see Appendix A [1969ZVY/LYA]), the values β_{1m}(1.046 m, 298.15 K) = (114 ± 21) mol^{-1}·kg instead of (95.0 ± 8.6) M^{-1} (average of the reported values of β_{1c} at 28 °C with estimated 2σ standard deviation) and K_{2m}(1.046 m, 298.15 K) = (12.1 ± 4.1) mol^{-1}·kg instead of (9.4 ± 1.9) M^{-1} (the original value of K_{2c} at 28 °C) are obtained.

Because no table of numerical experimental values is available for the spectrophotometric data, the recalculation of the β_{1m} values has been done by multiplying the original β_{1c} spectrophotometric values at 27 °C by the correction factor obtained for the ion exchange (ix) data at 28 °C.

$$\beta_{1c} \text{ (recalculated for ix) } / \beta_{1m} \text{ (original for ix)} = (127 \pm 23)/(95.1 \pm 8.6)$$

$$= (1.34 \pm 0.27)$$

That yields: (135 ± 25) mol^{-1}·kg and (162 ± 30) mol^{-1}·kg based on the two separate sets of spectrophotometric results. The temperature correction from 300.15 to 298.15 K using the same value of $\Delta_r H_1$ as above yields:

β_{1m} spectrophotometry = (126 ± 25) mol^{-1}·kg and (151 ± 30) mol^{-1}·kg.

These values were used as part of the calculation of the optimized β°_n and $\Delta\varepsilon$ values with the SIT formulation.

[1954SYK]

This conference paper reported on a spectroscopic study of the complexation of Fe(III) with sulfate in low ionic strength (perchlorate) solutions (I = 0.15 M, 19 °C). The experimental details were to appear in a later paper that could not be found. For 0.15 M ionic strength, values for formation of $FeSO_4^+$ (from SO_4^{2-} and Fe^{3+}) and $FeHSO_4^{2+}$ (from HSO_4^- and Fe^{3+}) were reported as 228 M^{-1} and 60 M^{-1}, respectively. These values are not used further in the present review.

[1955CAT/STO2]

A preliminary description of the work was provided in an earlier note by Stout and Catalano [1954STO/CAT]. The authors carried out careful adiabatic calorimetry experiments at temperatures between 11 and 310 K, and reported values of ΔT and $\Delta H / \Delta T$. From these, smoothed values of the heat capacities were derived for the temperature range from 15 to 300 K. Extrapolation to 0 K was done using a plot of C_p / T^3 *vs.* temperature for temperatures between 11 and 20 K, and a value of (86.99 ± 0.17) $J\cdot K^{-1}\cdot mol^{-1}$ ((20.79 ± 0.04) $cal\cdot K^{-1}\cdot mol^{-1}$) was reported for S°_m (FeF_2, cr, 298.15 K). Later publications [1955STO/CAT], [1961STO] discussed the separation of the lattice and magnetic entropy contributions. A reintegration of C_p / T in the present review led to a value for S°_m that differed only by 0.05 $J\cdot K^{-1}\cdot mol^{-1}$ from the value reported originally. In the present review the authors' original value for S°_m is accepted, with an estimated uncertainty of 0.20 $J\cdot K^{-1}\cdot mol^{-1}$.

For the purpose of fitting a single function to the calorimetry results from this study ($T > 250$ K) and the later work of Macheteau and Barberi [1974MAC/BAR] at higher temperatures, the uncertainties in the individual values for the heat capacities were estimated as suggested by the authors, gradually increasing from 0.2% at 200 K to 0.5% at 300 K.

[1955GRE/MAC]

Gregory and MacLaren carried out transpiration measurements with $FeBr_2$(cr) in the presence of Br_2(g) at different partial pressures for temperatures from 473 to 673 K (200 to 400 °C). Based on the dependence of the results on the bromine pressures it was concluded that the data were best interpreted in terms of Fe_2Br_6(g) as the major gas-phase iron species. Total pressure measurements (diaphragm gauge) from 773 to 1073 K (500 to 750 °C) were used to determine the temperature dependence of the $FeBr_3$ monomer/dimer equilibrium. The authors' data analysis used estimated heat capacities of reaction. No values for gas-phase species in the iron-bromine system are selected in the present review. It is noted that $FeBr_3$(cr) decomposes to Br_2(l) + $FeBr_2$(cr) above 530 K, as the partial pressure of bromine necessary to maintain $FeBr_3$ exceeds the vapour pressure of bromine. Also, the measurements suggest that $FeBr_3$(g) dissolves appreciably in $FeBr_2$(l).

[1955HAR/GAR]

The authors used potential-difference measurements with a "Harned" cell at molal ionic strengths of 1, 3 and 5 ($AlCl_3$ + HCl). Note that the two concentrations listed where no HCl was added gave osmotic coefficients in excellent agreement with the more copious isopiestic data. The two sets of values are: m = 0.1667 mol·kg^{-1}, ϕ = 0.831, and m = 0.5000 mol·kg^{-1}, ϕ = 1.006.

These two results were included in the SIT for aqueous $AlCl_3$ at 298.15 K.

[1955LIS/RIV2]

This article reports the results of a spectrophotometric study of Fe(III) sulfato complexes and an investigation of the competition between sulfate and thiocyanate for association with iron(III). The Fe(III)-SCN interaction gives a charge-transfer absorption band with a higher molar absorption coefficient than the band from the Fe(III)-SO_4 interaction.

The speciation and the formation constants of the complexes have been deduced from absorption data. The pH, and total concentrations of sulfate, thiocyanate and Fe(III) were varied.

The temperature and the ionic strength were kept constant: 25 °C and I_c = 1.2 M, adjusted with $NaClO_4$.

$FeSO_4^+$ and $FeHSO_4^{2+}$:

For this study samples were prepared with an excess of Fe(III) (0.005 to 0.03 M) over sulfate at a constant concentration, 0.001 M. These chemical conditions limited the interference from $\mathrm{Fe(SO_4)_2^-}$.

Polynuclear species such as $\mathrm{Fe_2(SO_4)^{4+}}$ were excluded from the data analyses because the molar absorption coefficients were independent of iron(III) concentrations between 0.005 and 0.03 M.

Investigations at various acidities (0.05 to 0.5 M H^+) indicated the existence of the weak complex $\mathrm{FeHSO_4^{2+}}$.

The measurements of the optical density were carried out at 330 to 360 nm. The acidity constant value of $\mathrm{HSO_4^-}$ is important in the determination of $\mathrm{FeSO_4^+}$ stability constant. Its influence is shown in Table A-7 where the effect of using two fairly similar values of the $\mathrm{HSO_4^-}$ acidity constant ($K_{c1,1(\mathrm{HSO_4^-})}$) on the calculated formation constants of $\mathrm{FeSO_4^+}$ (K_{1c}) and $\mathrm{FeHSO_4^{2+}}$ ($K_{c\mathrm{FeHSO_4^{2+}}}$ for which the authors used the symbol k_m) is shown.

Table A-7: Results of the calculation of formation constants for Fe(III) sulfato complexes (I_c = 1 M) using the same experimental data and slightly different acidity constants for $\mathrm{HSO_4^-}$.

$K_{c1,1(\mathrm{HSO_4^-})} = c_{\mathrm{H^+}} c_{\mathrm{SO_4^{2-}}} / c_{\mathrm{HSO_4^-}}$	$K_{1c} = c_{\mathrm{FeSO_4^+}} / c_{\mathrm{Fe^{3+}}} c_{\mathrm{SO_4^{2-}}}$	$K_{c\mathrm{FeHSO_4^{2+}}} = c_{\mathrm{FeHSO_4^{2+}}} / c_{\mathrm{Fe^{3+}}} c_{\mathrm{HSO_4^-}}$
33.3	178	6.8
25	153	5.6

The reported average values were K_{1c} = (165 ± 10) $\mathrm{M^{-1}}$ and $K_{c\mathrm{FeHSO_4^{2+}}}$ = (6 ± 1) $\mathrm{M^{-1}}$.

The value of K_{1c} was greater than the other values quoted in the literature, and was dependent on the values of $K_{c1,1(\mathrm{HSO_4^-})}$. These values have been redetermined by conversion of concentrations to molalities and applying the SIT formulation (Eq. (A.33)).

$$\log_{10} K_{m1,1(\mathrm{HSO_4^-})} = \log_{10} K^{\circ}_{1,1(\mathrm{HSO_4^-})} - 4D - \varepsilon(\mathrm{H^+}, \mathrm{HSO_4^-})\ m_{\mathrm{H^+}} - \varepsilon(\mathrm{Na^+}, \mathrm{HSO_4^-})\ m_{\mathrm{Na^+}} + \varepsilon(\mathrm{H^+}, \mathrm{SO_4^{2-}})\ m_{\mathrm{H^+}} + \varepsilon(\mathrm{Na^+}, \mathrm{SO_4^{2-}})\ m_{\mathrm{Na^+}} + \varepsilon(\mathrm{H^+}, \mathrm{ClO_4^-})\ m_{\mathrm{H^+}} \quad (A.33)$$

According to Table IV.2, the value of $\log_{10} K^{\circ}_{1,1(\mathrm{HSO_4^-})}$ = (1.98 ± 0.05). The values from Appendix B for $\varepsilon(\mathrm{Na^+}, \mathrm{HSO_4^-})$, $\varepsilon(\mathrm{Na^+}, \mathrm{SO_4^{2-}})$ and $\varepsilon(\mathrm{Na^+}, \mathrm{ClO_4^-})$ are – (0.01 ± 0.02), – (0.12 ± 0.06) and (0.01 ± 0.01) $\mathrm{kg \cdot mol^{-1}}$, respectively. The value of $\varepsilon(\mathrm{H^+}, \mathrm{SO_4^{2-}})$ is not listed in Appendix B of previous TDB volumes, but is assumed here (as on p. 269 of the Am TDB volume [1995SIL/BID]) to be approximately equal to the value – (0.03 ± 0.04) $\mathrm{kg \cdot mol^{-1}}$ for $\varepsilon(\mathrm{Li^+}, \mathrm{SO_4^{2-}})$. Also, no value is listed for $\varepsilon(\mathrm{H^+}, \mathrm{HSO_4^-})$ in Appendix B of previous TDB volumes (*e.g.*, [2005GAM/BUG]), but a reasonable assumption might be that $\varepsilon(\mathrm{H^+}, \mathrm{HSO_4^-}) \approx \varepsilon(\mathrm{H^+}, \mathrm{ClO_4^-})$ but with an increased uncertainty; thus $\varepsilon(\mathrm{H^+}, \mathrm{HSO_4^-})$ = (0.14 ± 0.05) $\mathrm{kg \cdot mol^{-1}}$ [1].

That yields a value of (1.16 ± 0.09) for $\log_{10} K_{m1,1(\mathrm{HSO_4^-})}$ for the lower acidity (0.053 m) used by the authors and a value of (1.13 ± 0.08) for the higher acidity (0.53 m), corresponding to (14.5 ± 3.2) and (13.6 ± 2.5) for $K_{m1,1(\mathrm{HSO_4^-})}$. As the two values are not very different, their average, (14 ± 2) $\mathrm{kg \cdot mol^{-1}}$ has been used in our recalculation of the formation constants of the iron sulfato complexes. Conversion to the molar scale, I_c = 1.2 M, yields a value of ~15 $\mathrm{dm^3 \cdot mol^{-1}}$ for $K_{c1,1(\mathrm{HSO_4^-})}$. This is significantly different from the authors' values listed in Table A-7.

To interpret their data, the authors plotted $(A / c_{\mathrm{Fe(III)_{total}}})$ as a function of A at constant $c_{\mathrm{SO_4^{2-}}}$. A is the absorbance at a given wavelength. Values of A were measured at several wavelengths. They obtained straight lines. We have used the same method after converting amount substance concentrations to molalities and values of K_c to K_m. The resulting straight lines are expressed by Eq. (A.34).

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[1] In the U, Am Np-Pu and Ni volumes in the TDB series, the value used was – (0.01 ± 0.02) $\mathrm{kg \cdot mol^{-1}}$ (based on $\varepsilon(\mathrm{H^+}, \mathrm{HSO_4^-}) = \varepsilon(\mathrm{Na^+}, \mathrm{HSO_4^-})$). In the Ni volume the value (p. 294) was given as (0.01 ± 0.02) $\mathrm{kg \cdot mol^{-1}}$, but the omission of the minus sign was merely a typographical error. In the Se book (p. 147) the approximation was given that $\varepsilon(\mathrm{H^+}, \mathrm{HSeO_4^-}) = \varepsilon(\mathrm{H^+}, \mathrm{Cl^-})$ = 0.12 $\mathrm{kg \cdot mol^{-1}}$ (similar to the selection here for the sulfur-containing species), while in the Zr book (p. 189/190) there is an experimentally-derived value (using some extra assumptions) of $\varepsilon(\mathrm{H^+}, \mathrm{HSO_4^-})$ = – (0.17 ± 0.05) $\mathrm{kg \cdot mol^{-1}}$. The present reviewers believe that the more positive values are reasonable. It is noted that $\{\varepsilon(\mathrm{H^+}, \mathrm{ClO_4^-}) - \varepsilon(\mathrm{Na^+}, \mathrm{ClO_4^-})\}$ = 0.13 $\mathrm{kg \cdot mol^{-1}}$; $\{\varepsilon(\mathrm{H^+}, \mathrm{Cl^-}) - \varepsilon(\mathrm{Na^+}, \mathrm{Cl^-})$ = 0.09 $\mathrm{kg \cdot mol^{-1}}\}$ and $\{\varepsilon(\mathrm{H^+}, \mathrm{NO_3^-}) - \varepsilon(\mathrm{Na^+}, \mathrm{NO_3^-})$ = 0.11 $\mathrm{kg \cdot mol^{-1}}\}$, all >> 0.00 $\mathrm{kg \cdot mol^{-1}}$.

$$(\partial(A/m_{\mathrm{Fe(III)_{total}}})/\partial A)_{m_{\mathrm{SO_4^{2-}}}} = -[K_{1m}\,(\,(K_{m1,1(\mathrm{HSO_4^-})})\,)^{-1} + K_{m\mathrm{FeHSO_4^{2+}}}\,m_{(\mathrm{tot.\ acid})}\,]\,/\,[K_{m\mathrm{FeHSO_4^{2+}}} + m_{(\mathrm{tot.\ acid})}\,] \tag{A.34}$$

where $m_{\mathrm{Fe(III)_{total}}}$ is the total iron molality in each sample.

$(K_{m1,1(\mathrm{HSO_4^-})})^{-1} = m_{\mathrm{H^+}}\,m_{\mathrm{SO_4^{2-}}}\,/\,m_{\mathrm{HSO_4^-}}$ is the dissociation constant of $\mathrm{HSO_4^-}$

The authors used the average slope $(\partial(A/m_{\mathrm{Fe(III)_{total}}})/\partial A)_{c_{\mathrm{SO_4^{2-}}}}$.

The slopes have been redetermined here, and used to obtain a set of values of

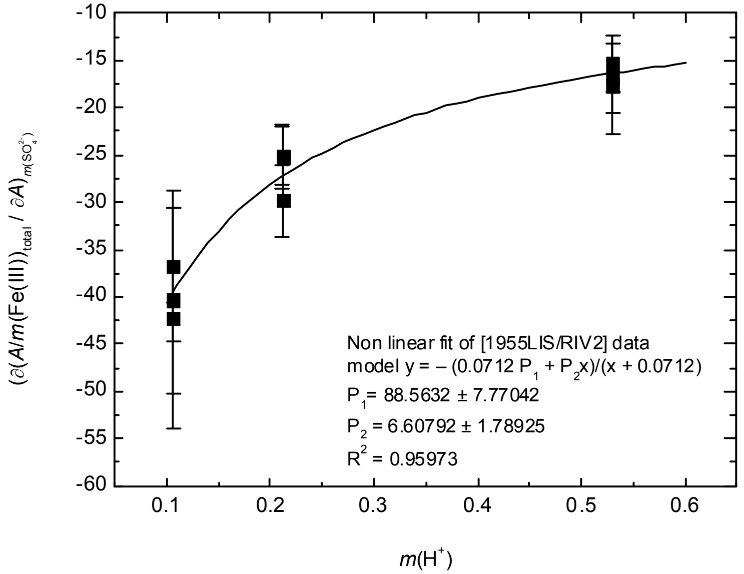
$$-\,\{K_{1m}\,(K_{m1,1(\mathrm{HSO_4^-})})^{-1} + K_{m\mathrm{FeHSO_4^{2+}}}\;m_{(\mathrm{tot.\ acid})}\}/\{K_{m\mathrm{FeHSO_4^{2+}}} + m_{(\mathrm{tot.\ acid})}\},$$

which have been plotted *vs.* the total acidity $m_{(\mathrm{tot.\ acid})}$. Then a non-linear fit was done to produce "best" values of K_{1m} and $K_{m\mathrm{FeHSO_4^{2+}}}$. If all the points for all the acidities are plotted one obtains $K_{1m} = (110 \pm 7)\ \mathrm{mol^{-1}\cdot kg}$, and $K_{m\mathrm{FeHSO_4^{2+}}} = (0.48 \pm 3.27)\ \mathrm{mol^{-1}\cdot kg}$. This indicates that the full set of data with their uncertainties cannot yield a defined value of $K_{m\mathrm{FeHSO_4^{2+}}}$.

At low acidity for the conditions used by the authors (excess of iron over the sulfate) there is some hydrolysis, and the concentration of the $\mathrm{FeHSO_4^{2+}}$ complex is low. Therefore, a second fit was carried out (Figure A-4) without using the data points at 0.053 m total acidity. The results are:

$$K_{1m} = (89 \pm 10)\ \mathrm{mol^{-1}\cdot kg};\ K_{m\mathrm{FeHSO_4^{2+}}} = (6.6 \pm 3.6)\ \mathrm{mol^{-1}\cdot kg}.$$

Figure A-4: Plot of $(\partial(A/m_{\mathrm{Fe(III)_{total}}})/\partial A)_{m_{\mathrm{SO_4^{2-}}}} = -\{K_{1m}\,(K_{m1,1(\mathrm{HSO_4^-})})^{-1} + K_{m\mathrm{FeHSO_4^{2+}}}\,m_{(\mathrm{tot.\ acid})}\}\,/\{K_{m\mathrm{FeHSO_4^{2+}}} + m_{(\mathrm{tot.\ acid})}\}$ as a function of the total acidity, $\mathrm{P_1} = K_{1m}$; $\mathrm{P_2} = K_{m\mathrm{FeHSO_4^{2+}}}$.



These are reasonable values, and have been included in the set of values used with the SIT procedure to determine the standard formation constants and values of $\varepsilon(\mathrm{FeSO_4^+}, \mathrm{ClO_4^-})$ and $\varepsilon(\mathrm{FeHSO_4^{2+}}, \mathrm{ClO_4^-})$.

$Fe(SO_4)_2^-$ and $Fe(SO_4)(HSO_4)(aq)$

Sets of absorbance measurements, from 330 to 360 nm, for samples with constant total sulfate (0.05 M) and iron (0.001 M) concentrations at various concentrations of H_2SO_4 (0.02 to 0.2 M) were used to investigate the formation of the higher sulfato complexes $\mathrm{Fe(SO_4)_2^-}$ and $\mathrm{Fe(SO_4)(HSO_4)(aq)}$. These must be introduced to interpret the data at high sulfate concentrations over a range of acid concentrations. The authors found formation-constant values of 16600 $\mathrm{M^{-2}}$ for β_2 ($\beta_2 = c_{\mathrm{Fe(SO_4)_2^-}}/(c_{\mathrm{Fe^{3+}}}c_{\mathrm{SO_4^{2-}}}{}^2)$) and (380 ± 50) $\mathrm{M^{-2}}$ for k_x ($k_x = c_{\mathrm{Fe(HSO_4)(SO_4)(aq)}}/(c_{\mathrm{Fe^{3+}}}c_{\mathrm{SO_4^{2-}}}c_{\mathrm{HSO_4^-}})$) as defined in [1955LIS/RIV2].

The value of β_2 is much higher than other values from the literature [1953WHI/DAV], [1959MAT], [1973NIK/PAL], and it was not used further in this review.

$Fe(SO_4)(SCN)(aq)$ and $Fe(SO_4)_2(SCN)^{2-}$

Experiments with constant total concentrations of iron (0.001 M), thiocyanate (0.001 M) and H_2SO_4 (0.02 M) but variable sulfate concentrations (0.025 to 0.05 M) were carried out. The measurements of optical density at 440 to 480 nm, where the Fe(III) thiocyanates absorb [1955LIS/RIV] and the sulfato complexes do not absorb, showed the existence of mixed complexes. The variation of the optical density did not correspond to the expected effect of simple substitution of $\mathrm{SCN^-}$ by $\mathrm{SO_4^{2-}}$.

The reported formation constant values for $\mathrm{Fe(SO_4)(SCN)(aq)}$ and $\mathrm{Fe(SO_4)_2(SCN)^{2-}}$ from the simple ions were (approximately) 1.15×10^4 $\mathrm{M^{-2}}$ and 4.9×10^5 $\mathrm{M^{-3}}$, respectively.

This work for determination of the formation constant of Fe(III) aqueous sulfato complexes is complete and well-analysed. Based on spectrophotometry at several wavelengths it gives reasonable speciation to interpret the data. The molar absorption coefficients of the pure species have been calculated. At 350 nm these are approximately 0 $\mathrm{m^2{\cdot}mol^{-1}}$ for $\mathrm{Fe^{3+}}$, 44 $\mathrm{m^2{\cdot}mol^{-1}}$ for $\mathrm{FeSO_4^+}$, 26.5 $\mathrm{m^2{\cdot}mol^{-1}}$ for $\mathrm{FeHSO_4^{2+}}$, 56 $\mathrm{m^2{\cdot}mol^{-1}}$ for $\mathrm{Fe(SO_4)_2^-}$ and $\mathrm{Fe(SO_4)(HSO_4)(aq)}$.

These values vary quite reasonably with the formula of the complex as expected for charge-transfer spectra.

However the formation constant values β_2 = 16600 $\mathrm{M^{-2}}$ for $\mathrm{Fe(SO_4)_2^-}$ and those of $\mathrm{Fe(SO_4)(SCN)(aq)}$, 11,500 $\mathrm{M^{-2}}$, and $\mathrm{Fe(SO_4)_2(SCN)^{2-}}$ 490,000 $\mathrm{M^{-3}}$ seem incredibly high in view of $\beta_1 \approx 160$ $\mathrm{M^{-1}}$ for the 1:1 sulfato complex; and they have not been used further in this review.

[1955LIS/RIV3]

This paper reports on a spectrophotometric study of formation of mixed complexes of Fe(III) and SCN^- with bromide and chloride at 25 °C. The chloride measurements were carried out between 440 and 480 nm using solutions 0.001 M in total iron, 0.00125 M in total thiocyanate, 0.2 M H^+(sln), and 0.0 to 1.2 M in total chloride. A constant total ionic strength at 1.2 M was maintained by addition of appropriate amounts of NaCl, $HClO_4$(sln) and $NaClO_4$(sln). Similar measurements were carried out between 400 and 470 nm for bromide-containing solutions. Measurements for bromide-containing solutions in the absence of thiocyanate were done between 380 and 460 nm.

The authors' data analysis was carried out assuming a literature-based value of 4.1 for the formation constant of the first chlorido complex [1937MOL], [1942RAB/STO], and using a value of K_1 of 130 M^{-1} for the formation constant of the first thiocyanato complex [1955LIS/RIV]. The experimentally-determined formation-constant (β) values from the simple ions (Fe^{3+}, SCN^-, Cl^-, Br^-) were reported to be 6.1 M^{-2} for $FeCl_2^+$, 0.61 M^{-1} for $FeBr^{2+}$, 0.2 M^{-2} for $FeBr_2^+$, 265 M^{-2} for $FeClSCN^+$, 120 M^{-3} for $FeCl_2SCN$(aq) and 21 M^{-2} for $FeBrSCN^+$. From this, the calculated value of the formation constant of the second chlorido complex, K_2, is 1.5 M^{-1}. In spite of a reasonable value of 4.1 M^{-1} for K_1, this value has not been used in the determination of K_1° because of the complexity of the medium and the indirect method of investigation, (especially when more than 40 K_1 values are available for the over all SIT fit for K_1°). The value of K_2 has been used for the fit with the SIT method in calculating the value of K_2°. In this case the scarcity of literature values weighs in favour of being less selective. No uncertainty estimate was given by the authors, and we assigned ± 0.8 M^{-1} to the K_2 value from this investigation, taking as a guide the scatter of the literature values.

[1955MAC/GRE]

This is a companion paper to [1955GRE/MAC], and reported the use of the same methods to determine the vapour pressure of $FeBr_2$ from 673 to 1113 K. However, in these experiments no bromine was added to the gas stream. An effusion method was also used between 623 and 718 K. The pressures from the effusion measurements were found to be lower than those from the transpiration measurements. Sime and Gregory later attributed part of this difference to formation of Fe_2Br_4(g), especially at temperatures above 660 K.

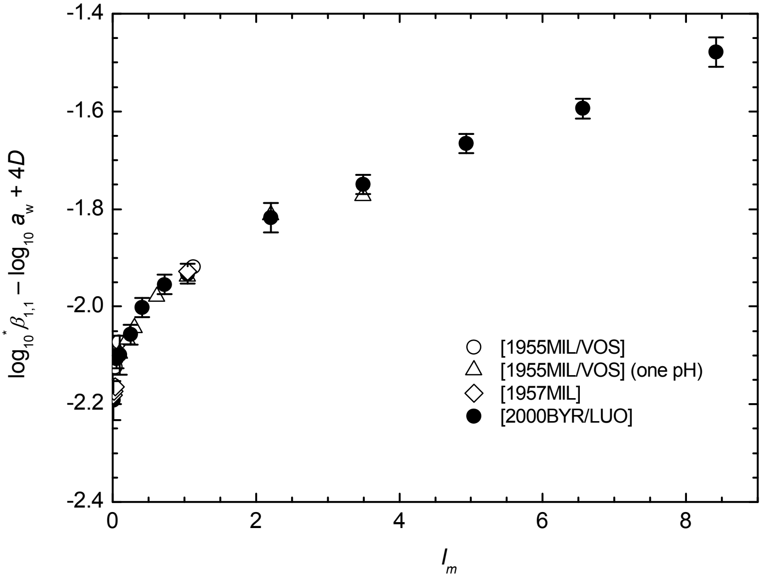
[1955MIL/VOS]

The authors used spectrophotometry to determine the hydrolysis of iron(III) as a function of iron(III) concentration (10^{-4} to 10^{-2} M) and ionic strength (0.0147 to 1.07 M $NaClO_4$) at (25.0 ± 0.1) °C. For an iron concentration of 10^{-4} M, the first hydrolysis constant, ${}^*K_{1,1}$, was derived alone, whereas at 10^{-3} to 10^{-2} M the dimerization reaction must also be considered: $2\,FeOH^{2+} \rightleftharpoons Fe_2(OH)_2^{4+}$. Results for the former equilibrium were measured at 340 nm with 10^{-4} M Fe(III) over an unknown range of $[H^+]$ and four ionic strengths and the resulting $\log_{10}{}^*K_{1,1}$ values are shown in Table A-8 converted to molal units (the individual experimental results are only shown on small figures). Additional values were reported at one acidity, 1.045 × 10^{-2} M $HClO_4$, and seven ionic strengths using the predetermined extinction coefficient of $FeOH^{2+}$. All of these data are shown in Figure A-5. The authors reported a value for $\log_{10} {}^*K^\circ_{1.1} = -2.172$.

Table A-8: Logarithm of the first hydrolysis constant for Fe^{3+} at 25 °C.

I_m	$\log_{10} {}^*K_{1.1}$ \
0.0147	2.372
0.0401	2.438
0.0904	2.496
1.081	2.768

Figure A-5: Plot of $\log_{10} {}^*\beta_{1,1} - \log_{10} a_w + 4D$ *vs.* I_m at 25.0 °C.



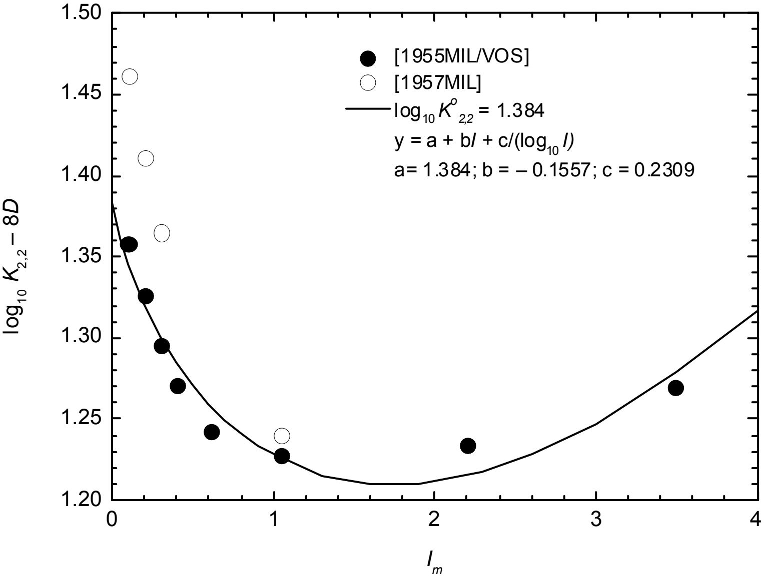
The authors gave the values of $\log_{10} {}^*K_{2,2}$ determined for [Fe] = 10^{-2} M, [$HClO_4$] = 0.0412 M (measured at 340 nm).

Table A-9: Logarithm of the dimerization constant of $FeOH^{2+}$ at 25 °C.

I_m	$\log_{10} K_{2,2}$
0.101	2.23
0.202	2.42
0.304	2.52
0.405	2.60
0.617	2.71
1.049	2.87
2.206	3.11
3.493	3.27

The $\log_{10} {}^{*}K_{1,1}$ values are consistent with previous and more recent studies and further indicate that the Fe^{3+}-ClO_4^- interaction coefficient is not constant over the range ionic strength studied (see [2000BYR/LUO]). The unweighted fit (Figure A-6) for the four lowest concentrations of ($\log_{10} \beta_{2,2} - 8D$) *vs.* I_m resulted in a $\log_{10} K^{\circ}_{2,2}$ value of 1.38 at 25 °C (*cf.*, 1.46 reported by the authors). The large projected uncertainties of these values preclude the use of weighting factors.

Figure A-6: Plot of $\log_{10} K_{2,2} - 8D$ *vs.* I_m at 25.0 °C.



[1955MUL/SEL]

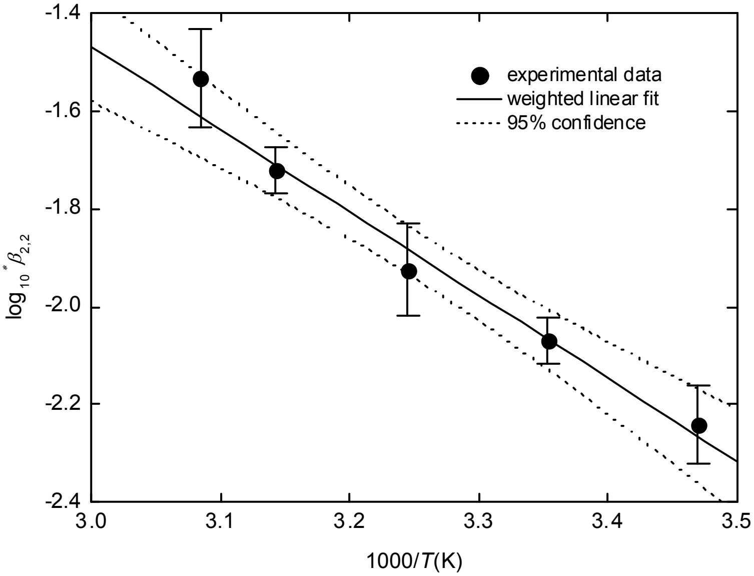
Iron(III) perchlorate was prepared from iron(III) nitrate by repeated evaporation in perchloric acid and recrystallization from water. A Gouy balance was used for the magnetic measurements of 0.04 M iron(III) solutions from 15 to 60 °C in 3 M $NaClO_4$ (pH = < 0 to 2.45, which were presumably calculated values and hence are $-\log_{10}$ [molarity H^+]). Spectrophotometric measurements were made at 15, 25 and 51 °C. They report a peak at 240 nm attributable to Fe^{3+} and $FeOH^{2+}$, and a second at 335 nm due to the dimer, $Fe_2(OH)_2^{4+}$. At the highest acidity where hydrolysis was assumed to be negligible, the effective magnetic moment of Fe^{3+} is reported to be 5.82 Bohr magnetons. They also reported that the dimer is diamagnetic. Using these two observations and the assumptions that $FeOH^{2+}$ has the same magnetic moment as Fe^{3+}, whereas the concentration of $Fe(OH)_2^+$ is negligible (based on the value of ${}^*\beta_{2,1}$ reported in [1953HED2]), they were able to calculate the concentrations of the three iron(III) species in solution. They list the following formation constants for the dimer based on smoothed plots of the molarities of Fe^{3+} and $Fe_2(OH)_2^{4+}$ *vs.* pH in the pH range 1.25 to 1.75.

$$2\,Fe^{3+} + 2\,H_2O(l) \rightleftharpoons Fe_2(OH)_2^{4+} + 2\,H^+ \qquad \text{(A.35)}$$

$\log_{10} {}^*\beta_{2,2}$ values at (t °C): $-(2.31 \pm 0.08)$ (15 °C), $-(2.14 \pm 0.05)$ (25 °C), $-(1.99 \pm 0.09)$ (35 °C), $-(1.79 \pm 0.05)$ (45 °C), and $-(1.60 \pm 0.10)$ (51 °C) on the molarity scale.

This appears to be a reliable and unique study aimed at conditions favouring the formation of the dimer and provides a useful independent measure of its formation constant. The $\log_{10} {}^*\beta_{2,2}$ values for Reaction (A.35) on the molality scale are plotted in Figure A-7 and have the following values: $-(2.24 \pm 0.08)$ (15 °C), $-(2.07 \pm 0.05)$ (25 °C), $-(1.92 \pm 0.09)$ (35 °C), $-(1.72 \pm 0.05)$ (45 °C), and $-(1.53 \pm 0.10)$ (51 °C). The linear weighted fit resulted in a $\Delta_r H_m$ of $-(69.4 \pm 7.7)$ kJ·mol^{-1} and $\Delta_r S_m$ of $-(7.7 \pm 2.4)$ J·K^{-1}·mol^{-1}.

Figure A-7: Plot of the logarithm of the molal hydrolysis constant according to Eq.(A.35) *vs*. the reciprocal temperature in kelvin (3 M $NaClO_4$).



[1956AND]

The octahedral sites in the spinel crystal structure are described as "one of the anomalous lattices in which it is possible to achieve essentially perfect short-range order while maintaining a finite entropy". For Fe_3O_4, this entropy is estimated to be ($0.404R$ + 10-20%) or about 3.9 $J \cdot K^{-1} \cdot mol^{-1}$. This possibility permeates the subsequent literature on the thermodynamic properties of magnetite for over 30 years, as discussed in Section VII.2.7.1.3, but appears not to be supported by the most recent thermodynamic data and structural models.

[1956GAY/WOO]

This paper describes measurements of the solubility of $Fe(OH)_2$ in basic solution at 25 °C, and of "ferric hydroxide" (discussed as FeOOH) in both acidic and basic solutions. The aim was to evaluate the importance of various hydrolysed aqueous iron species; stability constants are estimated for $HFeO_2^-$ (equivalent to $Fe(OH)_3^-$), FeO_2^{2-} (equivalent to $Fe(OH)_4^{2-}$), FeO^+ (equivalent to $Fe(OH)_3^+$), and neutral $Fe(OH)_3(aq)$.

The solid $Fe(OH)_2$ was precipitated by adding dilute aqueous $FeCl_2$ solution to saturated, carbonate-free NaOH in an air-free system, followed by repeated washing; it was determined to be free of detectable Fe(III) (based on colour: white by reflection and greenish tinged by transmitted light) or Cl^- (based on a test with silver nitrate). No further characterization, such as XRD, microscopy, or surface-area analysis, was performed.

Equilibrium constants K were obtained by calculating their apparent values at different base and acid concentrations shown in Tables A-10 and A-11, respectively, and assuming that a given hydrolysis reaction was preponderant over ranges of acidity or alkalinity where its apparent K value was more or less constant. The following values were obtained.

$$\mathrm{Fe(OH)_2(s) + OH^- \rightleftharpoons HFeO_2^- + H_2O(l)};\ K = a_{\mathrm{HFeO_2^-}} / a_{\mathrm{OH^-}} = 8.3 \times 10^{-6},$$

$$\mathrm{Fe(OH)_2(s) + 2\,OH^- \rightleftharpoons FeO_2^{2-} + 2H_2O(l)};\ K = a_{\mathrm{FeO_2^{2-}}} / a^2_{\mathrm{OH^-}} = 2.9 \times 10^{-6},$$

$$\mathrm{FeOOH(s) + H^+ \rightleftharpoons Fe(OH)_2^+};\ K = a_{\mathrm{Fe(OH)_2^+}} / a_{\mathrm{H^+}} = 1.2 \times 10^{-3},$$

$$\mathrm{FeOOH(s) + H_2O(l) \rightleftharpoons Fe(OH)_3(aq)};\ K = a_{\mathrm{Fe(OH)_3(aq)}} = 2.9 \times 10^{-7}.$$

The methods of pH measurement (and its conversion to acid or base concentration) and activity correction are not completely clear from the description in the paper. Moreover, given the difficulty in obtaining well-crystallized, pure iron(II) hydroxide and because the possible role of colloids in some of the lowest solubility measurements does not seem to have been addressed, in the absence of any additional confirmatory data, this value and the other values shown above are of general interest only.

Table A-10: Concentrations reported for the $Fe(OH)_2(s)$ solubility experiments with $\log_{10} K_{s,3}$ calculated assuming the equilibrium: $\mathrm{Fe(OH)_2(s) + OH^- \rightleftharpoons Fe(OH)_3^-}$ at 25 °C.

NaOH/M[a]	10^5Fe/M	NaOH/m[b]	10^5Fe/m[b]	$\log_{10} K_{s,3}$
0.131	0.108	0.131	0.108	– 5.08
0.316	0.275	0.316	0.275	– 5.06
0.445	0.356	0.445	0.356	– 5.09
0.645	0.550	0.645	0.550	– 5.07
0.774	0.630	0.774	0.630	– 5.09
2.30	3.17	2.30	3.17	– 4.86
3.09	3.92	3.11	3.94	– 4.90
3.50	4.26	3.52	4.28	– 4.92
3.52	4.71	3.55	4.74	– 4.87
5.57	9.60	5.70	9.82	– 4.76
5.75	10.5	5.89	10.7	– 4.74

[a] Given by [1956GAY/WOO] as NaOH concentration at equilibrium without any explanation of the sometimes significant differences between these values and those listed as "initial".

[b] Converted to molal units using the densities of [1985SOH/NOV].

Table A-11: Solubility measurements of iron(III) hydroxide in $HClO_4$ and NaOH solutions at 25 °C.

[NaOH]/M	[$HClO_4$]/M	[Fe]/M
	4.6×10^{-7}	3.6×10^{-7}
	6.6×10^{-6}	5.2×10^{-7}
	2.5×10^{-4}	7.2×10^{-7}
	8.9×10^{-4}	1.2×10^{-6}
	0.0038	3.6×10^{-6}
	0.016	1.8×10^{-5}
	0.045	6.0×10^{-5}
	0.406	1.5×10^{-4}
	0.714	3.2×10^{-4}
	1.044	3.7×10^{-4}
2.2×10^{-8}		3.6×10^{-7}
1.6×10^{-7}		3.1×10^{-7}
1.2×10^{-5}		2.5×10^{-7}
4.9×10^{-5}		2.9×10^{-7}
1.3×10^{-3}		2.6×10^{-7}

[1956GRO]

Relative vapour pressure measurements at 20 and 25 °C were reported using a mercury manometer of a wide range of electrolytes including those of $FeCl_2$ and $FeCl_3$ solutions.

Table A-12: The relative pressures of iron(II) chloride solutions and their corresponding osmotic coefficients at 20 and 25 °C.

Molality $FeCl_2$	($\Delta p/p_0$) 20 °C	($\Delta p/p_0$) 25 °C	ϕ 20 °C	ϕ 25 °C
1.264	0.0745	0.0726	1.132 (7)	1.102 (7)
2.017	0.1386	0.1372	1.367 (5)	1.352 (5)
2.550	0.1900	0.1874	1.527 (4)	1.504 (4)
3.267	0.2600	0.2553	1.703 (3)	1.667 (3)
4.164	0.3422	0.3377	1.859 (3)	1.829 (3)
4.810	0.3977	0.3920	1.948 (3)	1.912 (3)
4.994*	0.4134		1.974 (3)	
5.087*		0.4158		1.953 (3)

* Reported as being a supersaturated solution.

Table A-13: The relative pressures of iron(III) chloride solutions and their corresponding osmotic coefficients at 20 and 25 °C.

Molality $FeCl_3$	$(\Delta p/p_0)$ 20 °C	$(\Delta p/p_0)$ 25 °C	ϕ 20 °C	ϕ 25 °C
0.644	0.0410		0.901 (10)	
1.060	0.0755	0.0741	1.026 (6)	1.007 (6)
2.332	0.2072	0.2032	1.380 (3)	1.350 (3)
2.534	0.2305		1.433 (3)	
3.140	0.2974		1.558 (3)	
3.948	0.3850	0.3783	1.707 (3)	1.667 (3)
5.262	0.5184	0.5089	1.925 (2)	1.873 (2)
7.050	0.6613	0.6498	2.129 (3)	2.063 (3)
8.626	0.7391	0.7254	2.160 (3)	2.078 (3)
10.715	0.7995	0.7877	2.080 (3)	2.006 (3)
12.950	0.8582	0.8501	2.092 (3)	2.032 (3)
15.798	0.9203	0.9154	2.221 (5)	2.168 (5)

The uncertainty in the osmotic coefficient was calculated assuming a 0.1 Torr experimental uncertainty.

The calculated osmotic coefficients of $FeCl_2$(sln) and $FeCl_3$(sln) are shown in Figure A-8 and Figure A-9, respectively, together with the smoothed values tabulated in the thesis.

Figure A-8: The osmotic coefficients of iron(II) chloride solutions at 20 and 25 °C.

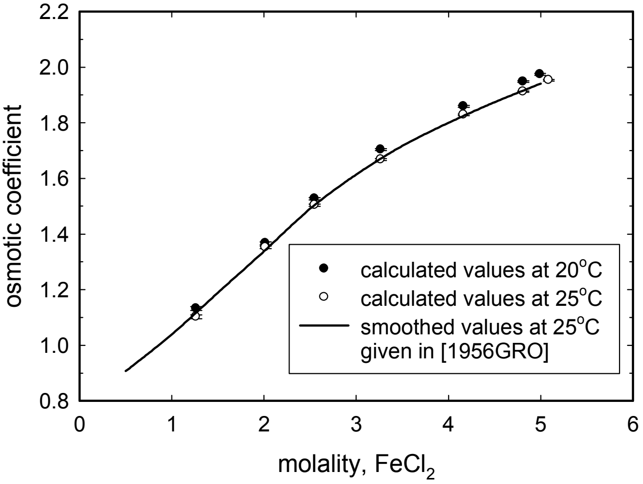
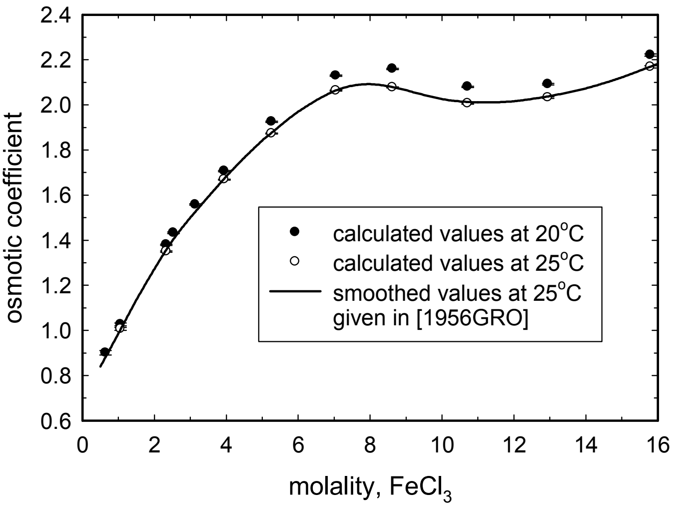


Figure A-9: The osmotic coefficients of iron(III) chloride solutions at 20 and 25 °C.



Note that the results shown in Figure A-8 are in satisfactory agreement with those accepted from other studies by this review, although only the four lowest concentrations were utilized to obtain the interaction coefficient for $FeCl_2$(sln) at 25 °C in keeping with the departure from linearity observed for all results above an ionic strength of 10 $mol\cdot kg^{-1}$.

Only the lowest molality of $FeCl_3$(sln) at 25 °C falls into the acceptable concentration range of the data of [2004MOO/HAG], but this value is in excellent agreement with their numerous data and is therefore accepted by this review.

[1956HUF/DAV]

The oxidation of Fe(II) by O_2 (1 atm) was studied photometrically in solutions of varying sulfate concentrations. Analysis of the overall rate expression in terms of uncomplexed Fe(II) and of the $FeSO_4$(aq) complex led to a reported value of (1.1 ± 0.2) M^{-1} for $\beta_1(FeSO_4$, aq, 30.5 °C, $I_c = 1.0$ to 1.3; M ($NaClO_4$)). The reported value depends on a rate constant $k_u = 1.4 \times 10^{-6}$ $dm^3\cdot mol^{-1}\cdot atm^{-1}\cdot sec^{-1}$ for

$$2\,Fe^{2+} + O_2(g) + 2\,H^{+} \rightarrow 2\,Fe^{3+} + H_2O_2(sln)$$

as given by George [1954GEO].The actual solution composition that corresponds to this formation constant is difficult to "reconstruct". In their Figure 3 caption the authors indicate "*μ = 1.0-1.3 (sodium perchlorate)*", but this may be misleading as the medium changed within the series of solutions investigated. The experimental solutions included up to 0.58 M of H_2SO_4/Na_2SO_4 mixtures to provide the necessary sulfate ligand. Hence, the actual ionic strength may have been as great as I_m = 1.21 mol·kg^{-1} without any added $NaClO_4$ or may have been I_m = 1.04 mol·kg^{-1} ($NaClO_4$ = 0.788 M) when considering the experimental point with the lowest possible sulfate concentration of 0.068 M (H_2SO_4). In this case the factor for conversion of solution molarities to molalities is 1.043 dm^3/kg$_{H_2O}$ and m_{NaClO_4} is 0.822 mol·kg^{-1}. The recalculated value of β_1($FeSO_4$, aq) is (1.04 ± 0.19) kg·mol^{-1} or $\log_{10}\beta_1$($FeSO_4$, aq) = (0.02 ± 0.08). It is worth noting that the authors used a formation constant of 13.33 dm^3·mol^{-1} for the protonation constant of the sulfate ion to estimate the speciation of the sulfate species at I_c = 1.0 to 1.3. When recalculating this constant from I_m = 1.001 to I_m = 0 using the presently accepted SIT parameters, a value of 95.5 kg·mol^{-1} ($\log_{10}K$ = 1.98, at 30.5 °C) is obtained, corresponding very well with the presently accepted formation constant at 25 °C. This is a typical case of experiments in which a nearly complete medium change from $NaClO_4$ to H_2SO_4/Na_2SO_4 takes place. However, the present reviewer believes that the lowest sulfate experimental point mentioned above is close enough to having been obtained in a pure $NaClO_4$ system that it can be used.

[1956KOB/FRE]

Kobe and Fredrickson reported solubility data for $FeSO_4\cdot xH_2O$ in H_2SO_4-H_2O mixtures (from 100% H_2SO_4 to 100% H_2O) for temperatures between 0 and 100 °C. The reported solubilities are in reasonable agreement with those from other studies [1907FRA], [1941BEL/SHP], [1948BEL/KOL], [1952BUL/CAN], and augment the discussion of Kobe and Couch [1954KOB/COU]. The authors found evidence for the existence of the tetrahydrate at equilibrium in water and dilute sulfuric acid solutions at temperatures between 56 °C and 62 °C. The measurements were complicated by the strong tendency toward supersaturation with respect to the monohydrate. Furthermore, it was found to be necessary to make the solutions at least 0.067 m H_2SO_4 to preclude hydrolysis (at least at the higher temperatures). Equilibration times of 1 to 6 days were used (less than the 15 days that were used in the study by Bullough *et al.* [1952BUL/CAN]). Only smoothed data were reported, and the existence of the tetrahydrate phase was based exclusively on chemical analysis. Dehydration of the monohydrate was found only for solvent sulfuric acid mole fractions greater than 0.8.

[1956LIN]

This is a particularly well-described and detailed study of the $FeCl_3$-H_2O and $FeCl_3$-HCl-H_2O systems at low temperatures. In equilibrium with the saturated aqueous solution in the absence of added HCl, $FeCl_3\cdot10H_2O$(cr) was found to melt incongruently at (0.0 ± 0.2) °C, and form $FeCl_3\cdot6H_2O$(cr). A stable eutectic with H_2O(cr) and $FeCl_3\cdot10H_2O$(cr) was found to occur at – 35 °C.

[1956SCH/HON]

This paper reports on a transpiration study of FeI_2(cr, l) from 790 to 959 K using nitrogen as a carrier gas in the presence and absence of added iodine. The results have been reanalyzed by others (*e.g.*, [1966ZAU/GRE], [1968BAR/BAR], [1996SCA/PIA]) to incorporate the results of later studies of iron-iodine gas-phase species. The results of this study are not used directly in the present review.

[1956SCH/WIT]

Schäfer *et al.* measured the enthalpy of solution of FeOCl(cr) in concentrated (17 m) aqueous solutions of hydrogen chloride at 298.15 K. The final solutions were approximately 0.15 m in iron(III) (initial H_2O:FeOCl molar ratios from 114.48 to 118.35). The enthalpy of solution of $FeCl_3$(cr) was also measured as a function of HCl molality (17.2 m, 15.0 m and 13.5 m), but at somewhat lower final iron(III) molalities (~ 0.055 to 0.110 m). The heat of solution of the water in the ~ 17 m HCl solution was measured, and the reported value is approximately 0.2 $kJ\cdot mol^{-1}$ more negative than calculated from the assessment of Parker [1965PAR]. No allowance seems to have been made with respect to the different heats of dilution of the iron(III). The authors report – 9.20 $kJ\cdot mol^{-1}$ for the reaction

$$FeCl_3(cr) + \tfrac{1}{2}O_2(g) \rightleftharpoons FeOCl(cr) + Cl_2(g). \qquad (A.36)$$

This appears to be careful experimental work. The enthalpy of reaction of the FeOCl(cr) at 298.15 K was reported to be – 48.48 $kJ\cdot mol^{-1}$ for an initial H_2O:HCl ratio of 3.221 (and a final H_2O:HCl ratio of 3.286). The enthalpy of solution of the $FeCl_3$(cr) at 298.15 K was reported to be – 34.39 $kJ\cdot mol^{-1}$ for a H_2O:HCl ratio of 3.286. The latter was determined from triplicate measurements in solutions with three different H_2O:HCl ratios. The value calculated for a H_2O:HCl ratio of 3.372 at 298.15 K is – 35.28 $kJ\cdot mol^{-1}$. This agrees reasonably well with – 37.17 $kJ\cdot mol^{-1}$ determined by Kangro and Flügge [1935KAN/FLU] at 293.15 K (see also the entry for [1959KOE/COU]); however, correction of the values to a common temperature would require better heat-capacity data than are available at present.

When the results are recalculated using current auxiliary data (and values for HCl based on the compilation of Parker [1965PAR]), the value of $\Delta_r H^\circ_m$ (A.36) is – 8.25 $kJ\cdot mol^{-1}$. The combined uncertainty in the enthalpies of dissolution of the iron solids is only 0.25 $kJ\cdot mol^{-1}$. However, the lack of a correction for the heats of dilution of the iron(III) chloride, the uncertainties in the acid concentration (of the order of 0.1 in m), and in the L_1 and L_2 values for HCl suggest a considerably greater overall uncertainty. In the present review, this uncertainty is estimated as ± 2.00 $kJ\cdot mol^{-1}$.

[1956SHC/ORA]

Vapour pressures above samples of FeI_2(l) were reported for five temperatures from 1032 to 1128 K, and the average heat of dissociation was calculated based simply on the assumption of a linear relation between $\log_{10} p_{I_2}$ and $1/T$. However, at the temperatures and pressures of the experiments, a major iodine-containing species is likely I(g), not just I_2(g). Some reanalysis of the limited data (for temperatures above the melting point of FeI_2) was reported by Bartovská *et al.* [1968BAR/BAR], but the work is not used directly in the present review.

[1957BIE/SCH]

The solubility product of "precipitated iron(III) hydroxide", presumably a 2-line ferrihydrite, was monitored electrochemically for periods up to 500 hours after precipitation in 3 M (Na,H)ClO_4 media. A cell was used (glass electrode *vs.* AgCl/Ag reference) with the test solution containing $Fe(ClO_4)_3$ (at five concentrations from 1 to 100×10^{-3} M) and equimolar $Fe(ClO_4)_2$ mixed with sufficient $NaHCO_3$ solution to cause precipitation and sufficient $NaClO_4$ to give $[ClO_4^-] = 3$ M at 25 °C. Liquid-junction potentials were calculated. No XRD pattern of the solid phase recovered from the experiments could be attributed to an iron phase, although the authors assumed it to be FeOOH. This is the "active $Fe(OH)_3$" value used in the later, comparative solubility study of [1963SCH/MIC]. The corresponding value for the concentration product, $[Fe^{3+}]\cdot[OH^-]^3/M^4$, is $10^{-(38.7 \pm 0.2)}$. The authors were unable to reverse this reaction so that true equilibrium was not claimed. Clearly no thermodynamic information on the solubility of a distinct iron(III) phase can be gleaned from this paper.

[1957KIU/WAG]

This paper is primarily important for "proof of principle" of the application of solid-state electrochemical (potential-difference) measurements, using a stabilized ZrO_2 electrolyte, to obtain precise measurements on the high-temperature thermodynamic properties of solid oxides. The systems investigated include: Fe-wüstite *vs.* Co-CoO; Fe-wüstite *vs.* Ni-NiO; Fe-wüstite *vs.* Cu-Cu_2O; Fe–wüstite *vs.* wüstite-Fe_3O_4; wüstite-Fe_3O_4 *vs.* Cu-Cu_2O. Note that Fe-wüstite is one of the preferred reference couples for such measurements, and many subsequent electrochemical potential-difference studies involve this couple.

[1957MIL]

This study is an extension of [1955MIL/VOS] that incorporates the temperature dependencies of ${}^*K_{1,1}$ and ${}^*K_{2,2}$ for Fe(III) from 18 to 32 °C in $NaClO_4$ media using the same spectrophotometric method. The dimerization constants were calculated after correction involving removal of the contribution from the $FeOH^{2+}$ species. No raw experimental data were provided and only the following tabulated results were provided in molar units.

An evaluation of the uncertainties was needed, especially for the $\log_{10} {}^*K_{2,2}$ values in Table A-15. See figures in [1955MIL/VOS] for comparison of results.

Table A-14: Logarithm of the first hydrolysis constant for Fe^{3+} at 25 °C ([Fe] = 9.97×10^{-5} M, [$HClO_4$] = 0.01113 M, measured at 340 nm).

I/m	$-\log_{10} {}^*K_{1,1}$ 18 °C	$-\log_{10} {}^*K_{1,1}$ 25 °C	$-\log_{10} {}^*K_{1,1}$ 32 °C
0.0117	2.55	2.37	2.19
0.0217	2.60	2.42	2.25
0.0318	2.63	2.45	2.28
1.049	2.94	2.77	2.59

Table A-15: Logarithm of the dimerization constant of $FeOH^{2+}$ at 25 °C ([Fe] = 9.97×10^{-3} M, [$HClO_4$] = 0.0412 M, measured at 340 nm).

I/m	$\log_{10} {}^*K_{2,2}$ 18 °C	$\log_{10} {}^*K_{2,2}$ 25 °C	$\log_{10} {}^*K_{2,2}$ 32 °C
0.104	2.43	2.35	2.23
0.206	2.63	2.51	2.39
0.308	2.71	2.60	2.49
1.052	3.01	2.89	2.73

[1957NEA]

The author reported adiabatic calorimetry measurements of the heat capacities of $FeBr_2$(cr) between 330 and 720 K. The calorimeter was checked using samples of Al_2O_3(cr) over the same temperature range (average deviation 0.5%, maximum deviation 2%), and was found to give results in agreement with the literature. Measurements were done using samples of $FeBr_2$(cr) having hexagonal close-packed and random-packed structures. Above 630 K, for both solids, an apparent second-order λ-type transition was found. The magnitude of the transition heat was inconsistent, but small (0.2 to 0.6 $kJ \cdot mol^{-1}$). The heat-capacity results above 695 K are too few to properly establish the slope of $C_{p,\mathrm{m}}(T)$ above the transition, and are badly scattered for different series of measurements (± 3 $J \cdot K^{-1} \cdot mol^{-1}$).

[1957SMI]

This paper describes a method of calculating the Gibbs energy of the stoichiometric Reaction (A.37),

$$4\,Fe_3O_4(cr) + O_2(g) \rightleftharpoons 6\,Fe_2O_3(cr, \alpha) \qquad (A.37)$$

by correcting the measured equilibrium at the phase boundary for non-stoichiometry in the magnetite phase. The calculation is based on experimental data from Darken and Gurry [1945DAR/GUR] for the T-composition relationship and phase boundary of magnetite in pure O_2, in air, in a mixture of 96.09 vol.-% CO_2 + 3.91 vol.-% O_2, and in pure CO_2 (at its own decomposition partial pressures of O_2 and CO), complemented by the author's own measurements for a gaseous mixture of 99.89 vol.-% CO_2 + 0.11 vol.-% O_2. The author thereby derives composition-p_{O_2} relationships for magnetite at five temperatures between 1081 °C (the temperature of the magnetite-hematite phase boundary in CO_2) and 1458 °C (the corresponding temperature in pure O_2).

The Gibbs energy of Reaction (A.38) is then calculated using Eq. (A.39) (rearranged by this reviewer from that given in the paper).

$$\mathrm{FeO_{x'}}\ [\text{magnetite}] + 0.5\,(\mathrm{x''}-\mathrm{x'})\mathrm{O_2(g)} \rightleftharpoons \mathrm{FeO_{x''}}\ [\text{hematite}] \qquad \text{(A.38)}$$

$$\Delta_{\mathrm{r}} G^{\mathrm{o}}_{\mathrm{m}}(T) = 0.5RT\left((x''-x')\ln P_b + \int_{x'}^{x'(br)} \ln\left(\frac{P'}{P_b}\right) dx \right) \qquad \text{(A.39)}$$

where x" = 1.500 (effectively constant for hematite), x' is the O : Fe ratio for any given magnetite composition (the stoichiometric value being 1.333), and x'(br) is the O : Fe ratio for magnetite at the magnetite–hematite phase boundary at a given temperature. The term P_b denotes the [measured] partial pressure of O_2 at the phase boundary, and P' is the equilibrium partial pressure for magnetite with the composition $\mathrm{FeO_{x'}}$. A manual procedure (visual smoothing of pressure-ratio *vs.* composition curves, and use of a planimeter) was employed to perform the integration.

The author obtained the following, tabulated $\Delta_{\mathrm{r}} G^{\mathrm{o}}_{\mathrm{m}}(T)$ values for the stoichiometric Reaction (A.37), with an estimated uncertainty of ± 2.5 $\mathrm{kJ \cdot mol^{-1}}$ at 1100 to 1300 °C and ± 1.7 $\mathrm{kJ \cdot mol^{-1}}$ at 1400 °C. The magnitude of the correction (the integral term in Eq. (A.39)) ranges from zero below 800 °C (no significant deviation from magnetite stoichiometry) to – 1.82 $\mathrm{kJ \cdot mol^{-1}}$ at 1081 °C and – 9.15 $\mathrm{kJ \cdot mol^{-1}}$ at 1458 °C.

Table A-16: Gibbs energy of Reaction (A.37) at 1081 to 1458 °C.

t/°C	$\Delta_{\mathrm{r}} G^{\mathrm{o}}_{\mathrm{m}}(T)$ /$\mathrm{kJ \cdot mol^{-1}}$
1081	– 116.87
1179	– 84.03
1308	– 46.91
1393	– 27.95
1458	– 9.15

This appears to be a rigorous treatment of equilibria in the magnetite-hematite system, from which the author has derived useful values for the Gibbs energy of oxidation of stoichiometric magnetite to stoichiometric hematite. Normally, neither such high-temperature data nor the treatment of magnetite solid solutions would lie within the scope of the OECD/NEA review. However, since high-temperature magnetite-hematite equilibrium measurements appear to be the most reliable route to the standard enthalpy of formation of hematite (see, in particular, [1988NEI] and [1990HEM]), this paper is included here for comparison purposes.

[1958FON]

See the discussion under [1958FON2].

[1958FON2]

Fontana wrote several reports in the period in 1946 and 1947, and almost identical information based on these reports appeared in several publications through 1958. Parker and Khodakovskii [1995PAR/KHO] noted a value for the heat of oxidation of Fe^{2+} to Fe^{3+} using peroxide from a report by Fontana (report MDDC-1452). That reference [1947FON] gives no values, and is not relevant to the discussions for "47FON" in the reaction catalogue of [1995PAR/KHO].

The values reported in [1958FON2] appear to be the source for the values of Parker and Khodakovskii [1995PAR/KHO] reaction catalogue entries 11 and 12, *i.e.*, $-(150.16 \pm 0.50)$ $kJ\cdot mol^{-1}$ for "$Fe^{2+}(ao) + ½H_2O_2(ao) + H^+(ao) \rightleftharpoons Fe^{3+}(ao) + H_2O(l)$" and $-(40.08 \pm 0.50)$ $kJ\cdot mol^{-1}$ for "$Fe^{3+}(ao) + ½H_2(g) \rightleftharpoons Fe^{2+}(ao) + H^+(ao)$", respectively. The authors used "(ao)" as defined by Wagman *et al.* [1982WAG/EVA]. The reported uncertainties are assumed here to be 1σ uncertainties.

The reference list for [1995PAR/KHO] also includes "47FON2". That citation is for report MDDC-1603 [1947FON2], and except for typographical errors, the contents of that report are identical to those in the later Chapter 36 of "Chemistry of Uranium" - Collected Papers, TID-5290, edited by Katz and Rabinowitch USAEC (1958)), here referred to as [1958FON]. There appear to be no new experimental values in [1958FON] except a heat of dilution for $Fe(ClO_4)_3$ and a heat of solution for $FeCl_2(cr)$ in 0.5 M $HClO_4$. Fontana [1958FON] did report a value, $-(39.87 \pm 0.29)$ $kJ\cdot mol^{-1}$ ($-(9.53 \pm 0.07)$ $kcal\cdot mol^{-1}$), for the hydrogen reduction of Fe^{3+} to Fe^{2+}, citing earlier reports. However, the reviewer has been unable to obtain a copy of either of the original reports (CC-3693 and CC-3482).

$$Fe^{2+} + ½H_2O_2(sln) + H^+ \rightleftharpoons Fe^{3+} + H_2O(l) \qquad (A.40)$$

In the present review, approximate ionic strength corrections were calculated using an ion interaction model [1996PLY/GRE]. A value of 2.1×10^{-3} $kg\cdot K^{-1}\cdot mol^{-1}$ was used for $\Delta\varepsilon_L$(A.40) (where ε_L is defined as $(\partial\varepsilon / \partial T)_p$ [1997GRE/PLY2]). This was calculated from $\varepsilon_L(H^+, ClO_4^-) = 0.9 \times 10^{-3}$ $kg\cdot K^{-1}\cdot mol^{-1}$ [1997GRE/PLY2], $\varepsilon_L(Fe^{2+}, ClO_4^-) = 2.60 \times 10^{-3}$ $kg\cdot K^{-1}\cdot mol^{-1}$ (estimated by adding the values of $\varepsilon_L(Mg^{2+}, ClO_4^-)$ and $2\varepsilon_L(H^+, ClO_4^-)$, and subtracting $2\varepsilon_L(H^+, Cl^-)$ [1996PLY/GRE]), and $\varepsilon_L(Fe^{3+}, ClO_4^-) = 5.6 \times 10^{-3}$ $kg\cdot K^{-1}\cdot mol^{-1}$ based on $\Delta\varepsilon_L$ for the oxidation of iron with $H_2O_2(sln)$ (see Appendix A entry for [1976VAS/RAS], Reaction (A.111)). The uncertainty in the ionic strength correction is estimated as ±2.5 $kJ\cdot mol^{-1}$. This leads to a value of $-(151.4 \pm 2.5)$ $kJ\cdot mol^{-1}$ for $\Delta_r H^\circ_m$(A.40).

[1958GUG/STO]

This paper discusses improved two-parameter equations for fitting existing osmotic activity coefficient data for 2:1 and 1:2 electrolytes, including data for $FeCl_2$.

No new experimental results are given in this paper and the data treatment is not consistent with NEA guidelines.

[1958SHC/VAS2]

The heat of solution of $FeCl_3$(cr) in aqueous hydrochloric acid (2% HCl, 0.5 mass-% $FeCl_3$ final (~ 0.03 m)) was reported to be – (127.90 ± 1.13) $kJ \cdot mol^{-1}$. This value is consistent with other measurements, but in the absence of appropriate values for the enthalpy of dilution in the mixed electrolyte solution, the heat of solution is not used in the calculation of $\Delta_f H^o_m$ (Fe^{3+}).

[1959BAB/MAR]

This was a spectroscopic study of the complexation of Fe^{3+} with SO_4^{2-} by competition with thiocyanate. Measurements carried out in aqueous 0.1 M HNO_3 at 20 °C led to a reported dissociation constant of (2.2 ± 0.3) × 10^{-3} M for $FeSO_4^+$. The solutions had total Fe(III) concentrations of 2.5×10^{-4} M and total thiocyanate concentrations of 2.5 × 10^{-3} M. The sulfate concentrations were between 2.5×10^{-3} M and 2.5×10^{-2} M. Measurements were also done in 20, 40 and 80% acetone-water mixtures and in 0.025 M nitric acid solutions. The ionic strength of the solutions was not held constant, no allowance was made for hydrolysis, and only four sulfate-containing solutions were used. The values from this paper are not used further in the present review.

[1959BER/DAS]

This appears to be the first paper to describe collectively the structures and transformations between Fe oxides and oxyhydroxides in a "rational crystallochemical manner". Particular attention is paid to $Fe(OH)_2$, β- and δ-FeOOH, green rust, and the thermal decomposition of $FeCO_3$.

[1959COL/NAU]

The study described in this paper was an investigation of the stability constant of $FeCl^{2+}$, (inner-sphere complex) and was carried out using spectrophotometry with special precautions to avoid the interference of the higher chlorido-Fe^{3+} associated species (Fe^{3+}/Cl^- = 100). The effect of the ionic strength, the medium at constant ionic strength and changes in temperature were investigated.

As observed by previous authors, an increase in the ionic strength led to an increase in the formation constant of $FeCl^{2+}$. The reported K_1 value increased from (4.2 ± 0.1) to (6100 ± 100) $mol^{-1} \cdot dm^3$ when the $HClO_4$ concentration was increased from 2.5 to 9 M.

The substitution of Na^+ ions by H^+ ions, keeping the same ionic strength, increases the value of the stability constant. The effect of the cations of the medium has been correlated to the variation of the water activity. A decrease in water activity imparts greater stability to the complex. The water vapour pressure over these solutions, at 25 °C, was measured and varied between 20.81 and < 4 mm Hg (27.74 and < 5.3 kPa).

The authors claimed that the wavelength of the maximum absorption of $FeCl^{2+}$ varies from 336 to 352 nm as the acidity of the solution increases from 2.5 to 9 M. This change of the absorption spectra with the medium could only be apparent, due to the presence of some outer-sphere complex $FeCl^{2+}_{(out)}$ which does not possess the same charge-transfer bands in its UV-visible spectrum. The existence and the relative stability of the outer-sphere complex were not known in 1959. The ratio $FeCl^{2+}_{(out)}/FeCl^{2+}_{(in)}$ is important only for ionic strengths in the range 0.5 to 3 M.

The variation of K_1 with temperature between 25 and 45 °C in 3 and 8.5 M $HClO_4$ was used to calculate the values of $\Delta_r H$ and $\Delta_r S$ of the complex formation reaction by applying the van't Hoff equation and the second law of thermodynamics.

It was found that, respectively, $\Delta_r H = 15.9$ and -9.62 kJ·mol^{-1} and $\Delta_r S = 66.9$ and 34.3 J·K^{-1}·mol^{-1}.

In addition to the important variations of $\Delta_r G$ with the ionic strength and the medium, a strong dependence of $\Delta_r H$ and $\Delta_r S$ upon the medium composition was observed.

In the present review the molar concentrations and formation constants were converted to molal values by the values from Table II-5. A polynomial fit to the values has been carried out and the coefficients were used to calculate the conversion factors to any concentration of $NaClO_4$ or $HClO_4$. For mixed $NaClO_4$, $HClO_4$ solutions a weighted average has been used.

Though all of the solutions had high ionic strengths, the SIT formulation was used to analyze part of the data in this paper. The least-squares values found were: (1.29 ± 0.09) for $\log_{10} K_1^{\circ}$ and $-(0.14 \pm 0.00)$ kg·mol^{-1} for the interaction coefficient difference $\Delta\varepsilon$ (for the aqueous solutions containing only $HClO_4$ as the supporting electrolyte and with ionic strengths lower than 6.4 m). The value of $\log_{10} K_1^{\circ}$ is lower than values reported by most of the other authors and lower than the final values recommended after the SIT analysis. This could be due to reduced formation of $FeCl^{2+}_{(out)}$, as the experimental concentrations of Fe^{3+} were much greater than those of Cl^- in this study; therefore the free Cl^- concentrations were depleted more than in the other investigations. Before the results of this study were used as part of the SIT analysis to determine of the values of K_1° and $\varepsilon(FeCl^{2+}, ClO_4^-)$, the uncertainties given by the authors were increased to take into account possible systematic errors (the values are listed in Table VIII-4 of the main text).

[1959CON/COP]

A stopped flow spectrophotometric device was used to study the kinetics of the formation of $FeCl^{2+}{}_{(in)}$. Values of the rate constants were compared with results obtained by NMR. The kinetic rate law is: $\mathrm{d}c_{FeCl^{2+}}/\mathrm{d}t = k_1(c_{Fe^{3+}}c_{Cl^-}) + k_2(c_{Fe^{3+}}c_{Cl^-})/c_{H^+}$; at 25 °C, I = 1 M (k_1 = (9.4 ± 1.0) $\mathrm{mol^{-1}\cdot s^{-1}}$ and k_2 = (18 ± 2) $\mathrm{s^{-1}}$). The activation enthalpy and entropy determined from k_1 as a function of the temperature were $\Delta H_1^* = (44.3 \pm 8.\ 36)$ $\mathrm{kJ\cdot mol^{-1}}$, $\Delta H_2^* = (72.38 \pm 8.36)\ \mathrm{kJ\cdot mol^{-1}}$, $\Delta S_1^* = -(87 \pm 25)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, $\Delta S_2^* =$ $(8 \pm 25)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, respectively.

This early kinetics investigation employed a technique limited to relatively slow reactions, and was not able to detect the fast formation of the outer-sphere 1:1 iron(III)-chlorido complex.

The authors also carried out spectrophotometric measurements (370 nm) of the formation constant of $FeCl^{2+}$ at temperatures from 22 to 45 °C. The solution contained 0.01222 M $Fe(ClO_4)_3$, 0.0111 M NaCl and 1.298 M $HClO_4$ (I = 1.38 M). A linear relationship between $\log_{10} K_1$ and $1/T$ was found, and a value of (25.1 ± 0.4) $\mathrm{kJ\cdot mol^{-1}}$ was reported for the average enthalpy of reaction over this temperature range. The numerical values of the formation constants were reported, but no attempt was made to retrieve the experimental values precisely from the authors' graph. However, the values seemed to be similar to those from other studies (~ (4.74 ± 0.20) $\mathrm{mol^{-1}\cdot dm^3}$, at 25 °C).

After conversion of the formation constant and the ionic strength molar values to the molal scale, I_m = 1.48 $\mathrm{mol\cdot kg^{-1}}$ and K_{1m} = (4.4 ± 0.2) $\mathrm{mol^{-1}\cdot kg}$. This has been used as one of the data points in the determination of the values of K_1° and $\varepsilon(FeCl^{2+}, ClO_4^-)$ with the SIT formalism.

[1959GRE/NEA]

This paper reports the results for $FeBr_2$(cr) from O'Neal's thesis [1957NEA] (see the corresponding Appendix A entry), but with less detail. The equation for $C^{\circ}_{p,\mathrm{m}}$ ($FeBr_2$, cr, T)/$\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ generates a slightly different value (80.23 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$) for $C^{\circ}_{p,\mathrm{m}}$ ($FeBr_2$, cr, 298.15 K) than the 80.08 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ reported from extrapolation in the thesis. However, the equation itself does not appear in the thesis. Average and maximum uncertainties were reported as 0.65% and 2.0%, respectively.

[1959GRO/WES3]

The heat capacity of a 170.914 g sample of α-Fe_2O_3 (hematite) was measured, using a gold-plated copper calorimeter with a capacity of 92.8 $\mathrm{cm^3}$, backfilled with about 5 kPa of He to assure thermal contact. The adiabatic calorimeter and procedure are described elsewhere by E.F. Westrum, Jr. and A.F. Beale, Jr. ["to be published"; possibly "Heat capacities and chemical thermodynamics of cerium(III) fluoride and of cerium(IV) oxide from 5 to 300 K" University of Michigan Technical Report TID-6515]. The hematite was prepared by heating pure iron to constant weight in air at 1000 °C and characterized by XRD, chemical analysis, and magnetic measurements. Manganese

(~ 0.01%) was the only measurable impurity, with < 0.05% Fe(II), < 0.01% Al, Co, Mg, Ni and Si, and < 0.001% Ca, Cu, and Sn. The particle size was estimated to be ~5 µm. The accuracy of temperature measurements was estimated to be ±0.1 K at 5 to 10 K, ± 0.03 K at 10 to 90 K, and ±0.04 K at 90 to 350 K, with a precision of about 0.001 K in corrected temperature increments. Sixty-one C_p measurements are tabulated for temperatures from 5.58 to 345.42 K.

The paper includes a useful review of the magnetic properties of hematite. The heat-capacity curve has no obvious anomalies, even at the known magnetic anomaly (Morin transition) near 250 K. There is reasonable agreement with the earlier data of Parkes and Kelley [1926PAR/KEL] for a natural, "specular" hematite, but results are about 3% lower at 90 K, and hence the calculated standard entropy is slightly lower than the value obtained by those authors. The results yielded: $C^{\circ}_{p,\mathrm{m}}$ (Fe_2O_3, α, 298.15 K) = 24.80 cal·K^{-1}·mol^{-1} = 103.76 J·K^{-1}·mol^{-1}, and S°_{m} (Fe_2O_3, α, 298.15 K) = 20.889 cal·K^{-1}·mol^{-1} = 87.40 J·K^{-1}·mol^{-1}, based on a molar mass of 159.70 g. Smoothed values of thermodynamic properties at 5 to 350 K are tabulated, in addition to the heat-capacity data,

Along with a later, high-temperature study from the same research group [1975GRO/SAM], this work constitutes the definitive source of heat-capacity data for hematite. Data from [1926PAR/KEL] and [1951COU/KIN] are also included in the current (OECD/NEA) assessment (see Section VII.2.2.2).

[1959KOE/COU]

Koehler and Coughlin measured the heats of dissolution of Fe(cr) and $FeCl_2$(cr) in 4.360 m HCl(sln) at 30 °C (final iron molality 0.018 m). The average experimental heats were:

$$\mathrm{Fe(cr)} + 2\,\mathrm{H^+(sln)} \rightleftharpoons \mathrm{Fe^{2+}(sln)} + \mathrm{H_2(g)} \qquad -(87.132 \pm 0.177)\ \mathrm{kJ\cdot mol^{-1}} \qquad \text{(A.41)}$$

$$\mathrm{FeCl_2(cr)} \rightleftharpoons \mathrm{Fe^{2+}(sln)} + 2\,\mathrm{Cl^-(sln)} \qquad -(62.739 \pm 0.054)\ \mathrm{kJ\cdot mol^{-1}}$$

$$\mathrm{H_2O(l)} \rightleftharpoons \mathrm{H_2O(sln)} \qquad -(0.33406 \pm 0.002766)\ \mathrm{kJ\cdot mol^{-1}}$$

where the uncertainties are 95% confidence limits. The enthalpy for the reaction:

$$\mathrm{Fe(cr)} + 2\,\mathrm{H^+(sln)} + 2\,\mathrm{Cl^-(sln)} \rightleftharpoons \mathrm{FeCl_2(cr)} + \mathrm{H_2(g)} \qquad \text{(A.42)}$$

at 30 °C is – (15.887 ± 0.220) kJ·mol^{-1}. Based on the heat capacities (Chapters III, IV and [1965PAR]) $\Delta_{\mathrm{r}}C_p$ is (0.235 ± 0.040) J·K^{-1}·mol^{-1} the correction to 25 °C is – (1.176 ± 0.08) kJ·mol^{-1}, and $\Delta_{\mathrm{r}}H^{\circ}_{\mathrm{m}}$ ((A.42), 298.15 K) = – (17.062 ± 0.243) kJ·mol^{-1}. Then, using a value of – (162.390 ± 0.209) kJ·mol^{-1} for $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ (HCl, 4.36 m in H_2O) at 25 °C [1965PAR], $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($FeCl_2$, cr, 298.15 K) is – (341.84 ± 0.48) kJ·mol^{-1}. The value assumes that all hydrogen produced was released as H_2(g), and did not go into aqueous solution. If some dissolution of H_2(g) occurred, the calculated value for $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($FeCl_2$, cr, 298.15 K) would be less negative.

The solution from the dissolution of Fe(cr) was then oxidized at 30 °C with an aqueous hydrogen peroxide solution to form Fe(III) in the acid solution, and $\Delta_f H_m^o$ (FeCl$_3$, cr, 298.15 K) was calculated by comparison with the experimentally determined heat of solution of FeCl$_3$(cr) in the acid medium.

$$\mathrm{Fe^{2+}(sln) + \tfrac{1}{2}(H_2O_2\cdot 12.580H_2O(l)) + H^+(sln) \rightleftharpoons Fe^{3+}(sln) + 7.290\,H_2O(sln)} \quad \text{(A.43)}$$

$$\Delta_r H_m^o\,((\text{A.43}), 298.15\ \text{K}) = -\,(131.18 \pm 0.19)\ \text{kJ}\cdot\text{mol}^{-1}$$

$$\mathrm{FeCl_3(cr) \rightleftharpoons Fe^{3+}(sln) + 3\,Cl^-(sln)} \quad \text{(A.44)}$$

$$\Delta_r H_m^o\,((\text{A.44}), 298.15\ \text{K}) = -\,(102.327 \pm 0.072)\ \text{kJ}\cdot\text{mol}^{-1}$$

where the uncertainties are 95% confidence limits. The enthalpy for the reaction

$$\mathrm{Fe(cr) + 3\,H^+(sln) + 3\,Cl^-(sln) + \tfrac{1}{2}(H_2O_2\cdot 12.580H_2O(l)) \rightleftharpoons FeCl_3(cr) + H_2(g) + 7.290\,H_2O(sln)} \quad \text{(A.45)}$$

at 30 °C is – (100.793 ± 0.336) kJ·mol^{-1}. Based on the heat capacities (Chapters III, IV, [1955GIG/MOR] and [1965PAR]) $\Delta_r C_p$ is (362 ± 50) J·K^{-1}·mol^{-1}, the correction to 25 °C is – (1.813 ± 0.250) kJ·mol^{-1}, and $\Delta_r H_m^o$ ((A.45), 298.15 K) = – (102.61 ± 0.38) kJ·mol^{-1}. Then, using a value of – (162.390 ± 0.10) kJ·mol^{-1} for $\Delta_f H_m^o$ (HCl, 4.36 m in H$_2$O) at 25 °C [1965PAR] and – (191.12 ± 0.25) kJ·mol^{-1} for $\Delta_f H_m^o$ (H$_2$O$_2$, 4.41 m in H$_2$O) [1982WAG/EVA] at 25 °C, $\Delta_f H_m^o$ (FeCl$_3$, cr, 298.15 K) is – (399.51 ± 0.56) kJ·mol^{-1}.

It was noted above that if some dissolution of H$_2$(g) occurred during the reaction of Fe(cr) with the hydrochloric acid, the calculated value for $\Delta_f H_m^o$ (FeCl$_2$, cr, 298.15 K) would be less negative. In that case, the calculated value for $\Delta_f H_m^o$ (FeCl$_3$, cr, 298.15 K) would be too negative by a similar amount. However, the differences in $\Delta_f H_m^o$ (FeCl$_2$, cr, 298.15 K) – $\Delta_f H_m^o$ (FeCl$_3$, cr, 298.15 K) from this study [1959KOE/COU] and the work of Evdokimova and Efimov [1989EVD/EFI2] are different by 3 kJ·mol^{-1}, well outside the uncertainty bounds.[1]

Stuve *et al.* [1980STU/FER] measured the enthalpy of solution at 298.15 K of FeCl$_3$(cr) in an HCl solution of similar molality, finding – (103.33 ± 0.02) kJ·mol^{-1}. For the two results to be compatible, the value of $\Delta_r C_p$ (A.44) at 303.65 K would need to be 144 J·K^{-1}·mol^{-1}. Rough calculations based on literature data [1988HOV], [1965PAR], [1996LEM/CAM2] suggest that $\Delta_r C_p$ (A.44) at 303.65 K is ~ – 400 J·K^{-1}·mol^{-1}. Hence, $\Delta_r H_m^o$ ((A.45), 303.15 K) = – 105.3 kJ·mol^{-1}, and $\Delta_f H_m^o$ (FeCl$_3$, cr, 298.15 K) is – 395.5 kJ·mol^{-1}. The corrections of the apparent molar heat capacities to the high ionic strength of the reaction medium are much too crude to permit this value to be used. Nevertheless, the result suggests that one possible reason for the discrepancy between

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[1] It may or may not be significant that the sign and magnitude of FeCl$_3$ heat of solution values from [1935KAN/FLU] for 20 °C and [1956SCH/WIT] for 25 °C (in 17 m acid) are similar to those in 4.6 m acid at 30 °C [1959KOE/COU] and 25 °C [1980STU/FER]

the results of Koehler and Coughlin and those from other studies [1984LAV/TIM2], [1989EVD/EFI2] might have been the purity of their sample of $FeCl_3(cr)$.

[1959MAT]

This article deals with identification of iron(III) complexes formed with nitrate and sulfate ions, and determination of the formation constants of these complexes. It was a potentiometric investigation using the cell:

$$\begin{array}{r|ll}
\text{Pt} & \text{Fe(II)}, HClO_4, & \text{complexing} \;\vdots\; \text{saturated calomel} \\
\text{Glass} & \text{Fe(III)}, NaClO_4 & \text{anion} \;\vdots\; \text{electrode}
\end{array}$$

The work was carried out at (25.00 ± 0.05) °C using aqueous solutions with ionic strengths of 0.25, 0.75, and 1.53 M.

The acidity constants ($K^{-1}_{c1,1(HSO_4^-)}$ in the nomenclature of the present review) were estimated using literature values (0.0104 $mol\cdot L^{-1}$ at $I_c = 0$ [1955ROB/STO], and 0.084 $mol\cdot L^{-1}$ at $I_c = 2.0$ [1951ZEB/ALT]) and measurements from solutions with an ionic strength of 0.275 M (0.034 $mol\cdot L^{-1}$ at $I_c = 0.275$). These values were used to estimate the acidity constants at the ionic strengths of the experimental potentiometric measurements.

The values of K_1 and K_2, the stability constants of the 1:1 and 2:1 complexes were extrapolated to zero ionic strength using modified Debye-Hückel equations:

$$\log_{10} K_1^{\circ} = [\log_{10} K_1 + 6\sqrt{I_c}/(1+1.7\sqrt{I_c})] - bI_c = 4.04$$

$$\log_{10} K_2^{\circ} = [\log_{10} K_2 + 2\sqrt{I_c}/(1+1.9\sqrt{I_c})] - bI_c = 1.34$$

where the values 1.7 and 1.9 in the denominators of the $\sqrt{I_c}$ terms correspond to reasonable distances of closest approach a, of 5.1 Å and 5.7 Å, respectively, for the two systems. (For the SIT, using 1.5 in the denominator in the Debye-Hückel equation for all species does not change the result significantly (*cf.* Appendix B).) The bracketed quantities were plotted against I_c to obtain the values of $\log_{10} K_1^{\circ}$ and $\log_{10} K_2^{\circ}$, and slopes of 0.233 and – 0.077 $dm^3\cdot mol^{-1}$ as values for b.

The author claimed that $Fe(SO_4)_3^{3-}$ was formed at an ionic strength of 3 M, and reported the value of K_3 as 0.85 M^{-3}. Formation of the weak $FeHSO_4^{2+}$ complex was confirmed, but a precise stability constant could not be determined from the data. The potentiometry results were interpreted using the assumption that no sulfato complex of Fe(II) was formed.

The SIT treatment of Mattoo's data has been carried out by:

a) using the experimental conditions and the results contained in Table 1 of the paper. The application of the SIT formalism is only approximate because of the complexity of the solutions containing ClO_4^-, HSO_4^-, SO_4^{2-} anions for which many interaction coefficients with the cations are unknown. The concentration of SO_4^{2-} given in the Table 1 of the original paper has been taken as the concentration of total sulfate. It must be stressed that the pH values given in the original paper are only approximate because only one buffer, potassium hydrogen phthalate, was used for the glass electrode calibration. The dissociation constants of HSO_4^- as a function of the ionic strength were determined by graphical interpolation from a plot of $K^{-1}_{c1,1(HSO_4^-)}$ as a function of $\sqrt{I_c}$ with the starting values: $K^{-1}_{c1,1(HSO_4^-)}$ = 0.0104 at I_c = 0, $K^{-1}_{c1,1(HSO_4^-)}$ = 0.034 at I_c = 0.275 and $K^{-1}_{c1,1(HSO_4^-)}$ = 0.084 at I_c = 2.0.

The ClO_4^- concentration was evaluated from the ionic strength and the concentration of the other components as shown by Eq. (A.46).

$$I_c = ½(c_{H^+} + c_{Na^+} + c_{NH_4^+} + 4\,c_{Fe^{2+}} + 9\,c_{Fe^{3+}} + c_{FeSO_4^+} + c_{ClO_4^-} + c_{HSO_4^-} + c_{NO_3^-} + 4\,c_{SO_4^{2-}} + c_{Fe(SO_4)_2^-}) \quad (A.46)$$

As $c_{ClO_4^-}$ came from two sources, $HClO_4$ to adjust the pH and $NaClO_4$ to adjust the ionic strength, Na^+ came from $NaClO_4$ and Na_2SO_4 so one has:

$$c_{Na^+} = c_{ClO_4^-} - c_{HSO_4^-} - c_{H^+} + 2\,c_{SO_4^{2-}\,\mathrm{total}}\,. \quad (A.47)$$

That transforms Eq. (A.47) into:

$$2\,c_{ClO_4^-} = 2I_c - (c_{NH_4^+} + 4\,c_{Fe^{2+}} + 9\,c_{Fe^{3+}} + c_{NO_3^-} + 4\,c_{SO_4^{2-}} - c_{FeSO_4^+} - c_{Fe(SO_4)_2^-}) \quad (A.48)$$

The $c_{NH_4^+}$ came from the added Fe^{2+} salt ($c_{NH_4^+} = c_{Fe^{2+}}$) and the $c_{NO_3^-}$ from the Fe^{3+} salt ($c_{NO_3^-} = 3\,c_{Fe^{3+}}$). The concentrations of the free ions and iron were small compared with $c_{ClO_4^-}$ and $c_{SO_4^{2-}}$ and finally one has:

$$c_{ClO_4^-} \approx (I_c - c_{SO_4^{2-}\,\mathrm{total}} - 2\,c_{SO_4^{2-}}) \quad (A.49)$$

Equation (A.49) has been used to select the points for which one had:

$$c_{ClO_4^-} > 5\,c_{SO_4^{2-}}\,.$$

b) converting the molar concentrations to molal ones by using values in Table II-5.

c) The data of Table 1 of the original paper have been used as follows to recalculate the formation constants of the iron(III) sulfato complexes:

- Determination of the ratio Fe^{3+}/Fe^{2+} from the potential measurements. The initial point taken in the original paper was very slightly greater than 0 m sulfate (because of the sulfate from the added iron(II) ammonium sulfate), so to take that into account we added 0.003 V to the potential differences.

- Determination of the Fe^{2+} concentrations from the sulfate concentrations and the formation constant of $FeSO_4(aq)$ calculated by applying Eq. (A.51)

$$Fe^{2+} + SO_4^{2-} \rightleftharpoons FeSO_4(aq) \quad (A.50)$$

$$\log_{10} K\,(A.50) = \log_{10} K^{o}\,(A.50) - 8D - \Delta\varepsilon I_m \quad (A.51)$$

$$\log_{10} K\,(A.50) = 2.44 - 8D - (0.25\,I_m)$$

- Use of the $m_{\mathrm{Fe(III)\,total}} / m_{\mathrm{Fe^{3+}}}$ ratio to determine the Fe^{3+} sulfato complexes formation constants.

This ratio has been used in different models:

1:1 and 2:1 sulfato complexes :

$$m_{\mathrm{Fe(III)\,total}} / m_{\mathrm{Fe^{3+}}} - 1 = \beta_{11}\ m_{\mathrm{SO_4^{2-}}} + \beta_{21}\ m_{\mathrm{SO_4^{2-}}}{}^{2} \qquad \text{(A.52)}$$

1:1, 2:1 and 3:1 sulfato complexes :

$$m_{\mathrm{Fe(III)\,total}} / m_{\mathrm{Fe^{3+}}} - 1 = \beta_{11}\ m_{\mathrm{SO_4^{2-}}} + \beta_{21}\ m_{\mathrm{SO_4^{2-}}}{}^{2} + \beta_{31}\ m_{\mathrm{SO_4^{2-}}}{}^{3} \qquad \text{(A.53)}$$

The formation constants determined from the third- or second-degree polynomial fitting of Eqs (A.52) and (A.53) to the data were used to calculate the total iron(III) concentrations. These corresponded to the reported initial concentrations ± 2%, except for the points in the more concentrated sulfate solutions.

As mentioned in the main text, the existence of the 3:1 sulfato complex is dubious; but the potentiometric data of Mattoo indicates clearly that new complex species beyond $\mathrm{Fe(SO_4)_2^-}$ were present in the solutions with higher sulfate concentrations. As these solutions also had higher pH values, the possibility of mixed hydroxidosulfato species and/or hydrolytic species is highly probable (see discussion for the existence of mixed hydroxidosulfato complexes in the main text). Investigations of mixed hydroxidosulfato species in solution are scarce, however two such papers were analysed in this review [1969ZVY/LYA], [1988KHO/ROB].

Potentiometry using the Fe^{3+}/Fe^{2+} couple is insufficient to determine the formula of the species of systems containing several complexes. In the case of sulfato complexes the problem becomes still more complicated because of the possibility of protonation of the ligand which also can form complexes.

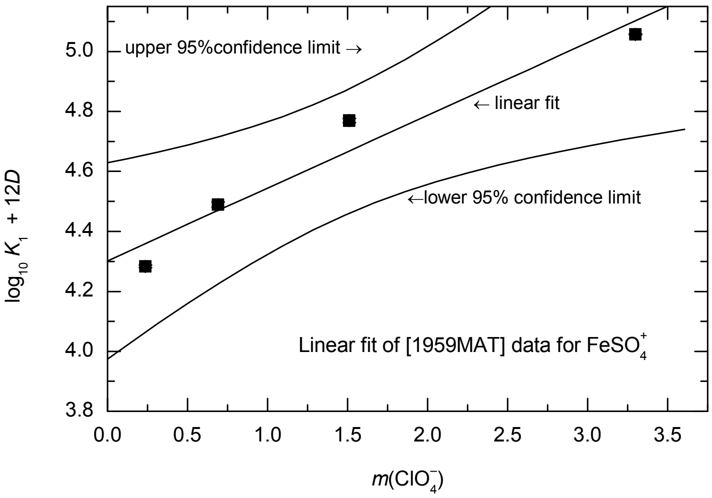
To simplify the interpretation of the data with the SIT formalism we considered that it is adequate to assume that the solutions were mixtures of $NaClO_4$ plus Na_2SO_4. We excluded the data points for which $m_{\mathrm{ClO_4^-}} / m_{\mathrm{SO_4^{2-}}} < 5$. The SIT diagrams for the work of Mattoo are given in Figure A-10.

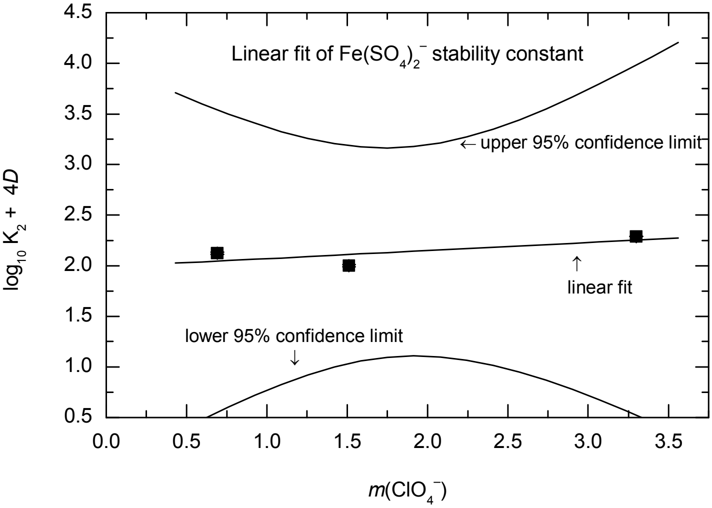
Because of the limited number of data points the statistical uncertainties are rather high, but the $\log_{10} K_n^{\circ}$ values are in reasonable agreement with other literature results; so the $K_{1m\mathrm{FeSO_4^+}}$ and $K_{2m\mathrm{Fe(SO_4)_2^-}}$ values found here are used in the determination of the constants in the present TDB review.

Figure A-10: SIT treatment of data of Mattoo [1959MAT] for the stability constant of the 1:1 (upper graph) and 2:1 (lower graph) Fe^{3+} sulfato complexes.

$$\log_{10} K_1^\circ = (4.31 \pm 0.16),\ \Delta\varepsilon = -(0.24 \pm 0.08)\ \text{kg·mol}^{-1},\ R^2 = 0.94$$

$$\log_{10} K_2^\circ = (1.99 \pm 0.32),\ \Delta\varepsilon = -(0.08 \pm 0.08)\ \text{kg·mol}^{-1},\ R^2 = 0.53$$





The number of data points is too small to treat the complexes formed in the highest concentrated sulfate solutions by the SIT formalism. The introduction of Fe^{2+} associates in the SIT calculations enhances the increase of values of $Fe(III)_t/Fe^{3+}$ and clearly shows the need for the third-degree term in Eq. (A.53), even for the low ionic strength data. One can only get estimates of K_3, (3.0 ± 0.5) $mol^{-1}\cdot kg$ at 1.65 m ionic strength and (11 ± 2) $mol^{-1}\cdot kg$ at 0.78 m, if it is assumed that the relevant species is $Fe(SO_4)_3^{3-}$. As discussed before, this work by Mattoo indicates the existence of species beyond $Fe(SO_4)_2^-$, which cause a decrease of Fe^{3+} activity; but this work and other literature data are too limited to assign any formula to such species. They could be polymeric hydroxidosulfato mixed complexes as claimed in the papers of Zvyagintsev and Lyakhmanov [1969ZVY/LYA] and Khoe and Robins [1988KHO/ROB]. Mattoo used solutions at lower pH than those authors. Also the potentiometric measurements based on redox properties needed less concentrated iron solutions, and probably the solutions were in a domain in which monomeric species were predominent. Further experimental work focused on that problem would be necessary to improve the understanding of the complete iron(III)-hydroxidosulfato system.

[1959PER]

Perrin measured the oxidation-reduction potentials and the pH of 1 M $NaClO_4$ solutions at 20 °C in the absence and presence of chloroacetic, formic, acetic, propionic and isobutyric acids. The acid dissociation constants for these aliphatic acids were also measured at the same conditions. However, of interest to this review are the hydrolysis constants obtained in the absence of these acids. The author refers to a previous publication [1958PER] for all experimental details. No experimental data are provided and the following iron(III) molar hydrolysis constants are simply listed in the text without any explanation other than to cite the methods employed in [1958PER] and [1953HED2] as: ${}^*K_{1,1} = 1.8 \times 10^{-3}$, ${}^*K_{2,1} = 8.9 \times 10^{-7}$, ${}^*K_{2,2} = 1.4 \times 10^{-3}$.

The logarithm of the corresponding molal hydrolysis constants are, -2.72, -5.73 and -2.83, respectively, at 20 °C in 1.05 "molal" ionic strength. Due to the lack of experimental details these values were not considered further in this review.

[1960BEU/HER]

Distribution ratios between solution and a cation exchange resin were investigated in acidic $FeSO_4$ solutions ($H_2SO_4/HClO_4 < 2.2$ M). The temperature for the experiments was not given, but the supposition can be made that it was "room" temperature (between 18 and 30 °C?). Elution was performed at varying H^+ concentrations, and gave a slope of -2 for a plot of log(distribution coefficient) *vs.* $\log_{10} c_{H^+}$ in H_2SO_4, and a slightly different slope for experiments at higher $HClO_4$ concentrations. The distribution ratio and the charge per "Fe(II)" species in solution were interpreted with a model that included the complexes $FeHSO_4^+$ and $FeSO_4$(aq). The resulting formation constants were $\beta_1(FeSO_4, aq) = 1.7\ dm^3\cdot mol^{-1}$ and $K_1(FeHSO_4^+) = 0.61\ dm^3\cdot mol^{-1}$ (0.12 $dm^3\cdot mol^{-1}$ is also reported as the value for the formation constant of the iron(II) perchlorato complex, ($c_{\text{FeClO}_4^+}/c_{\text{Fe}^{2+}}c_{\text{ClO}_4^-}$)). However, it is unclear at which ionic strength these constants would be valid (0.1 M $FeSO_4$(sln) was used to feed the column, up to 3 M H^+ was used to elute). For 2.2 M H_2SO_4 at ~20 °C the correction to molal units requires a factor of 1.0909 $dm^3 \cdot kg^{-1}$ [1985SOH/NOV] and $\beta_1 = 1.56$ $kg \cdot mol^{-1}$. I_m is not above 2.2 because H_2SO_4 dissociates to H^+ and HSO_4^- under these conditions. Also it is not clear on which basis the average "charge per atom" is calculated. Ionic strength correction is not discussed, and recalculation to $I = 0$ is not possible. Furthermore, it is unclear, why hydrolysis species are discussed in more or less concentrated acid solutions where obviously no hydrolysis species would be formed. The formation constants given in this paper should not be used (even though the actual numerical values seem to lie within reasonable ranges).

[1960BEW]

The heat of oxidation of aqueous Fe(II) to Fe(III) was measured by five successive additions of aliquots of H_2O_2(sln) (0.5 to 1.1 mL, 0.005 M) into an aqueous sulfuric acid solution (100 mL, 0.0925 M (two experiment sets) or 0.4 M H_2SO_4) containing iron(II) ammonium sulfate (initially ~0.001 M). Corrections were made for dilution of the acid by the aqueous peroxide solution.

The authors reported average heats of reaction for

$$2\,Fe^{2+}(sln) + H_2O_2(sln) + 2\,H^+(sln) \rightleftharpoons 2\,Fe^{3+}(sln) + 2\,H_2O(sln)$$

of −295.0 and −302.9 $kJ \cdot mol^{-1}$ (−70.5 and −72.4 $kcal \cdot mol^{-1}$) from the experiments in 0.0925 M H_2SO_4, and −297.1 $kJ \cdot mol^{-1}$ (−71.0 $kcal \cdot mol^{-1}$) from the experiments in 0.4 M H_2SO_4. They also noted that the heats appeared to be greater for each successive peroxide addition to a solution. The heats of reaction from the initial peroxide addition for each experiment set were also reported: −290.8 and −290.0 $kJ \cdot mol^{-1}$ (−69.5 and − 69.3 $kcal \cdot mol^{-1}$) for the experiments in 0.0925 M acid, and −296.2 $kJ \cdot mol^{-1}$ (− 70.8 $kcal \cdot mol^{-1}$) for the experiment in 0.4 M sulfuric acid. Similar difficulties were reported by Sousa-Alonso *et al.* [1968SOU/CHA], and were attributed to a side reaction involving the peroxide (but also see [1968WEL/SAL]). It is probable that the heat from the initial addition is closer to being the correct heat of reaction between iron(II) and peroxide.

Any reanalysis of the data from the solutions in H_2SO_4 is complicated by partial deprotonation of the hydrogensulfate ion. In the 0.4 M solution, the major anion was HSO_4^-, so aside from association/interaction with iron species, the heat of reaction can be considered to have been determined in the presence of a 1:1 electrolyte. But a major reaction was likely to have been:

$$Fe^{2+}(sln) + SO_4^{2-}(sln) + \tfrac{1}{2}H_2O_2(sln) + H^+(sln) \rightleftharpoons FeSO_4^+(sln) + H_2O(sln).$$

A complete analysis of the species in solution, accurate values for the heats of complexation (*cf.* Sections IX.1.2.1.2 and IX.1.2.1.3), as well as several unknown enthalpies of dilution would be required to use the data to determine the enthalpy of oxidation of Fe^{2+} to Fe^{3+} at $I = 0$. The results from this study are not used further in the present review except for comparison purposes.

[1960HUR]

Electrochemical kinetics investigations were done for iron dissolution and iron deposition in the presence of the H^+/H_2 couple. The kinetics of electron-exchange at the iron electrode by the couple H^+/H_2 were investigated separately. Various electrolytes were used. The test cell had two iron electrodes and two Haber-Luggin capillaries were used to connect the Fe electrodes to two external saturated potassium chloride calomel electrodes (0.245 V). Junction potentials were estimated to be of the order of 1-2 mV [1952MIL], but were not taken into account in the calculations. The electrolytes were 0.001 to 1 m HCl for the study of the behaviour of the H^+/H_2 couple and 0.05 to 0.5 m $FeCl_2$(sln) with 0.001 m HCl(sln) for the study of the behaviour of the Fe^{2+}/Fe(0) couple. Constant ionic strengths (see Table VI-3 of the main text) were maintained by addition of KCl.

The Fe electrodes (0.03% C, 0.01% Si, 0.19%, 0.027 P, 0.03% S) were circular iron sheets 4.5 cm in diameter, 0.5 mm thickness. They were vacuum annealed at 700 °C, polished, etched, cleaned, dried and weighed before use. Fe electrode potentials as a function of the current density were measured for the dissolution and deposition of iron and also for the H^+ discharge.

The extrapolation of the dissolution and deposition Tafel line to zero current gave the formal potential for the medium investigated. The exchange current i_0 was expressed as an equation of the hydrogen-ion activity.

MacInnes and Guggenheim assumptions [1959ROB/STO] were used for the calculation of activity coefficients in the mixed electrolytes. It has been found that

$$E^{\circ}\,(\mathrm{Fe^{2+}/Fe(0)}) = -\,0.467\ \mathrm{V}\ \textit{vs.}\ \mathrm{SHE\ at\ 20\ °C\ and}$$

$$\Delta_{\mathrm{f}} G^{\circ}_{\mathrm{m}}\,(\mathrm{Fe^{2+}}) = -90.11\ \mathrm{kJ \cdot mol^{-1}\ at\ 20\ °C.}$$

The reanalysis of the results of these experiments using the SIT is described in some detail in Section VI.1.1.2.4 of the main text. Only $\log_{10} i$ = f(E) curves were available in the original paper, and only the linear parts of the best Tafel diagrams (obtained with solutions identified as V, VI and VII in Table 1 of the Hurlen paper) were selected to recalculate the $E^{\circ\prime}$ values. They correspond to the solutions with the higher Fe^{2+} concentrations, 0.1 to 0.5 m, and 0.001 m acidity. Solution VIII which was 0.05 m in $FeCl_2$ did not yield as clear a Tafel diagram as the three selected solutions for the reduction of Fe^{2+}, This is probably because only part of the cathodic current was from the reduction of the iron. Equation VI-7 in the main text shows the influence of iron(II) concentration on the exchange current.

The accepted $E^{\text{o}'}$ values from the recalculation were the abscissa values of the crossing points of the Tafel straight lines for the anodic dissolution of Fe metal and the cathodic discharge of Fe^{2+}. Corrections for the weak Fe^{2+} interaction with chloride were introduced. In contrast to what was noted for Fe^{3+}, there are no major differences between the activity coefficients of Fe^{2+} calculated with SIT and those in the original publication.

No tables of numerical values for $i = \mathrm{f}(E)$ were given in the original paper. The values of the current densities as a function of the potentials of the iron electrodes have been recovered by us from the drawings in the original paper. For example, Figure VI-1 in Section VI.1.1.2.2 was constructed using the values for solution VI of Table 1 in the original paper. These values are listed in Table A-17. The value of $E^{\text{o}'}$ for Hurlen's solution VI then was calculated using the linear parts of the Tafel diagrams for the dissolution of Fe (to Fe^{2+}) and deposition of Fe^{2+} (as Fe(s)).

Table A-17: Values of current densities as a function of potentials measured from the Tafel diagrams of Figures 7 and 8 (anodic part) and 9 (cathodic part) of [1960HUR] for solution VI at 20 °C.*

Anodic dissolution			Cathodic deposition		
E_a/V *vs*. SHE	i_a/A·cm^{-2}	$\log_{10} i_a$	E_c/V *vs*. SHE	i_c/A·cm^{-2}	$\log_{10} i_c$
– 0.393	1.35×10^{-5}	– 4.870	– 0.635	3.00×10^{-5}	– 4.523
– 0.380	4.00×10^{-5}	– 4.398	– 0.652	1.20×10^{-4}	– 3.824
– 0.368	1.00×10^{-4}	– 4.000	– 0.667	3.00×10^{-4}	– 3.523
– 0.360	2.00×10^{-4}	– 3.699	– 0.672	5.00×10^{-4}	– 3.301
– 0.354	3.00×10^{-4}	– 3.523	– 0.681	1.00×10^{-3}	– 3.000
– 0.347	6.00×10^{-4}	– 3.222	– 0.692	2.00×10^{-3}	– 2.699
– 0.339	1.00×10^{-3}	– 3.000	– 0.696	3.00×10^{-3}	– 2.523

* 0.2 m $FeCl_2$, 0.001 m HCl, 0.6 m KCl.

From the values of $\log_{10} i_a$ and $\log_{10} i_c$ plotted as functions of E_a and E_c using linear regression, the following results are obtained:

- for the anodic dissolution: $\log_{10} i_a = (8.88 \pm 0.65) + (34.95 \pm 0.89)E$ ($R^2 = 0.999$);
- for the cathodic deposition: $\log_{10} i_c = -(25.00 \pm 0.86) - (32.28 \pm 1.28)E$ ($R^2 = 0.997$).

The parameters from these linear plots are given with the 95% confidence limits obtained as twice the uncertainties yielded by the statistical treatment of the numbers in Table A-17. The coordinates of the intersection point of the straight lines, i_0 and $E^{\text{o}'}$, were obtained by applying: $E_c = E_a$ or $\log_{10} i_c = \log_{10} i_a$.

Thus, $E^{\text{o}'} = -(0.504 \pm 0.018)$ V and $i^{\text{o}'} = (1.84\times10^{-9} \pm 3.52\times10^{-9})$ A·cm^{-2}.

[1960KUM]

This spectroscopic study (270 to 360 nm) was carried out using 5×10^{-4} M solutions of iron(III) in perchloric acid solutions containing different amounts of sulfuric acid. In their calculations the values used by the authors for $K^{-1}_{\mathrm{c}1,1(\mathrm{HSO}_4^-)}$, the deprotonation constant of HSO_4^- (the notation in the original paper was $K_{\mathrm{HSO}_4^-}$), were 0.0371, 0.0515, 0.0733, 0.0917 and 0.0995 M for I_c = 0.10, 0.20, 0.40, 0.69 and 1.0 M, respectively, at 20 °C, and 0.0813 M for I_c = 1.0 M at 30 °C. The reported molar formation constants of FeSO_4^+, K_1, were (417 ± 8), (243 ± 4), (131 ± 2), (94.5 ± 2.0) and (67.7 ± 1.0) M^{-1} for, respectively, I_c = 0.1, 0.2, 0.4, 0.60 and 1.0 M at 20 °C, and (85.6 ± 1.0) M^{-1} for I_c = 1.0 at 30 °C.

The authors fitted the equation

$$\log_{10} K_1 = 3.854 - 0.6 I_c^{½}/(1+1.7 I_c^{½}) + 0.222\, I_c$$

to their 20 °C data. Also, from the formation constants found for I_c = 1.0 M at 20 and 30 °C, they estimated a value of 17.6 $\mathrm{kJ\cdot mol^{-1}}$ (4.2 $\mathrm{kcal\cdot mol^{-1}}$) for ΔH_1.

These results are in line with the literature data and after conversion to the molal scale and calculation of the values at 25 °C they have been used as part of the overall determination of the $K^{\circ}_{1\mathrm{FeSO}_4^+}$ and $\Delta\varepsilon$ values with the SIT formalism.

The conversion to the molal scale has been carried out using the factors ξ of the Table II-5. For the temperature correction of the values of $K_{c1,1(\mathrm{HSO}_4^-)}$ and $K_{1\mathrm{cFeSO}_4^+}$ from the original papers to 25 °C the van't Hoff equation was used with 22400 $\mathrm{J\cdot mol^{-1}}$ and 26000 $\mathrm{J\cdot mol^{-1}}$, respectively, for the enthalpies of reaction. Thus, to get the value of $K^{\circ}_{1\mathrm{FeSO}_4^+}$, at 25 °C the original value at 20 °C needed two corrections in addition to the molar to molal scale conversion. The values of the $K'_{1\mathrm{FeSO}_4^+}$ constants for which the $K_{c1,1(\mathrm{HSO}_4^-)}$ values are those used by the authors of the original paper, were calculated first by conversion of the 25 °C, $K_{1\mathrm{cFeSO}_4^+}$, to the molal scale. Then the corrections needed to take into account the differences between the TDB-consistent $K_{1,1(\mathrm{HSO}_4^-)}$ values and those used originally were applied.

The TDB-consistent values of $K_{m1,1(\mathrm{HSO}_4^-)}$ were determined by applying the formula given in Eq. (A.54).

$$\log_{10} K_{m1,1(\mathrm{HSO}_4^-)} = (1.98 \pm 0.05) - 4D - 0.03 I_m \qquad \text{(A.54)}$$

where 0.03 $\mathrm{kg\cdot mol^{-1}}$ is the value estimated for $\Delta\varepsilon = \varepsilon(\mathrm{H}^+,\mathrm{HSO}_4^-) - \varepsilon(\mathrm{H}^+,\mathrm{SO}_4^{2-}) - \varepsilon(\mathrm{H}^+,\mathrm{ClO}_4^-)$ and it is based on the assumptions: $\varepsilon(\mathrm{H}^+,\mathrm{HSO}_4^-) \approx \varepsilon(\mathrm{H}^+,\mathrm{ClO}_4^-)$; $\varepsilon(\mathrm{H}^+,\mathrm{SO}_4^{2-}) \approx \varepsilon(\mathrm{Li}^+,\mathrm{SO}_4^{2-}) = -0.03$ $\mathrm{kg\cdot mol^{-1}}$.

The correction to take into account the difference in $K_{m1,1(\mathrm{HSO}_4^-)}$ is expressed by Eq. (A.55).

$$K_{1\mathrm{FeSO}_4^+}(\mathrm{TDB})/K_{1\mathrm{FeSO}_4^+}(\mathrm{orig.}) = [1 + K_{m1,1(\mathrm{HSO}_4^-)} m_{\mathrm{H}^+}(\mathrm{TDB})]/[1 + K_{m1,1(\mathrm{HSO}_4^-)} m_{\mathrm{H}^+}(\mathrm{orig.})] \qquad \text{(A.55)}$$

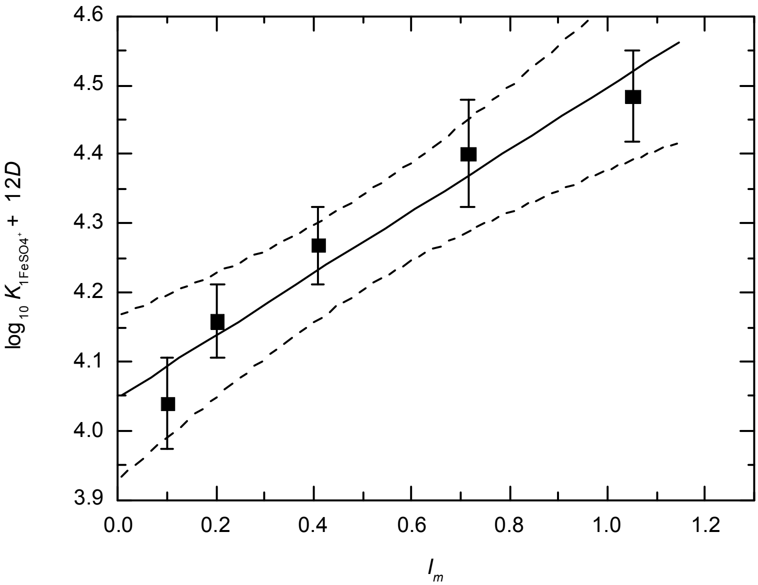
For 25 °C it is found that the values of $K_{1m\mathrm{FeSO}_4^+}$ at the different values of I_m are: for 0.1007 m, (533 ± 80) $\mathrm{mol^{-1}\cdot kg}$; for 0.2026 m, (330 ± 40) $\mathrm{mol^{-1}\cdot kg}$; for 0.4026 m, (188 ± 24) $\mathrm{mol^{-1}\cdot kg}$; for 0.7026 m, (133 ± 20) $\mathrm{mol^{-1}\cdot kg}$; for 1.046 m, (104 ± 16) $\mathrm{mol^{-1}\cdot kg}$.

At 30 °C the value of $K_{1m\mathrm{FeSO}_4^+}$ (I_m = ~ 1.05 $\mathrm{mol\cdot kg^{-1}}$) is (122 ± 20) $\mathrm{mol^{-1}\cdot kg}$.

The results were plotted according to the SIT formalism (Figure A-11).

To recalculate the value of Δ_rH_1 for 1.046 m, the value of $K_{1\mathrm{FeSO}_4^+}$ at 30 °C was recalculated. For that we tried to correct the original value, (85.6 ± 1.0) at 30 °C, by introducing the TDB value for $K_{c1,1(\mathrm{HSO}_4^-)}$, 18.0 $\mathrm{mol^{-1}\cdot kg}$, in place of the original value, 11.7 $\mathrm{mol^{-1}\cdot kg}$. That led to an erroneous value of Δ_rH_1. The values of $K_{c1,1(\mathrm{HSO}_4^-)}$ as a function of temperature given in Kumai's paper are probably incorrect. The $\Delta_rH(\mathrm{HSO}_4^-)$ calculated from their values gives Δ_rH_1 = 14.9 $\mathrm{kJ\cdot mol^{-1}}$, when the recommended value in the TDB reviews is 22.4 kJ $\mathrm{mol^{-1}}$.

Figure A-11: SIT plot of the recalculated data of [1960KUM]: $\log_{10} K^{\mathrm{o}}_{1\mathrm{FeSO}_4^+}$ = (4.05 ± 0.10), $\Delta\varepsilon$ = – (0.45 ± 0.15) $\mathrm{kg\cdot mol^{-1}}$, R^2 = 0.95.



If the SIT K_{1m} values at 20 and 30 °C are taken into account, one can estimate by applying Eq. (A.56) that $\Delta_r H_1$ is (25 ± 18) kJ·mol^{-1}.

$$\mathrm{d}(\ln K_{1m}) / \mathrm{d}(1/T) = -\, \Delta_r H_1 / R \qquad \text{(A.56)}$$

This high uncertainty results from the experiments having been done only at two temperatures that are fairly close together, 20 and 30 °C, and to the rather high uncertainties assigned to the $FeSO_4^+$ formation constants, ± 20 mol^{-1}·kg in each case.

[1960MAR]

In this study, the stability constants of higher chlorido-iron(III) associated species $FeCl_2^+$, $FeCl_3$(aq) and $FeCl_4^-$ were evaluated. $FeCl_4^-$ is the limiting complex in aqueous solution as shown previously [1952FRI], [1953GAM/JOR]. The distribution ratios $D_{\mathrm{Fe(III)}}$ between an anion-exchange resin (DOWEX 1) and aqueous lithium chloride solutions of iron(III) served to determine the species present and allowed their stability constants to be calculated.

From the variation of $D_{\mathrm{Fe(III)}}$ as a function of Cl$^-$ activity in LiCl solutions the following values were found: $K_2^\circ > 0.199$, $K_3^\circ = 0.0398$ and $K_4^\circ = 0.012$ which correspond respectively to $\Delta_r G_3^\circ = +7.99$ and $\Delta_r G_4^\circ = +10.96$ kJ·mol^{-1}. With this method, only the formation constants of the anionic or neutral complexes could be determined precisely.

[1960NOV/MAK]

Novikov *et al.* measured the equilibrium amount of HCl(g) in a stream of H_2(g) and HCl(g) equilibrated over $FeCl_2$(cr) and Fe(cr) at four temperatures from 673 to 823 K. At each temperature the equilibrium measurements were done using both gas mixtures initially deficient in HCl(g) and mixtures with HCl(g) in excess of the equilibrium gas fraction. Values for the enthalpy of reaction at 298.15 K were obtained from a third-law calculation using the selected values for the entropies and heat-capacity functions for Fe(α) and $FeCl_2$(cr) (Sections V.2 and VIII.3.2.1.1) and for H_2(g) and HCl(g) [1989COX/WAG]. The third-law $\Delta_r H_m^\circ$ values, corrected to 298.15 K, drift to markedly to more positive values when the equilibrium data from the higher temperature measurements are used. An average value of $\Delta_r H_m^\circ$ ((A.57), 298.15 K) = (157.6 ± 3.9) kJ·mol^{-1} was obtained.

$$FeCl_2(\mathrm{cr,l}) + H_2(\mathrm{g}) \rightleftharpoons Fe(\mathrm{cr}) + 2\,HCl(\mathrm{g}). \qquad \text{(A.57)}$$

[1960OET]

The author reported adiabatic calorimetry measurements of the heat capacities of $FeCl_2$(cr) and FeI_2(cr) between 340 and 770 K. The calorimeter was checked using samples of Al_2O_3(cr) over the same temperature range, and was found to give results in agreement with data from the U.S. National Bureau of Standards (average deviation 0.57%, maximum deviation 2%). For $FeCl_2$(cr) three sets of measurements were done using a sample of cubic close-packed $FeCl_2$ (average deviation was 0.91% from a smoothed curve, maximum deviation 2%), and measurements were also done using a sample of random-packed solid. Although the latter was found to convert irreversibly to the close-packed form on heating to ~ 770 K, the heat-capacity results were for the two forms were indistinguishable. The experimental heat-capacity values were not tabulated in the thesis, but were plotted as a function of temperature on a graph showing the equation of Moore [1943MOO][1]. The scatter about the line of the equation is essentially random, with all points falling within a 3% band. For the purposes of fitting a single function to all the calorimetry results, the individual values for the heat capacities (digitized from the author's graph) were estimated in the present review to have uncertainties of 1.5%. This may be somewhat high, but incorporates uncertainties in the temperatures, not just uncertainties in the values of the heat capacities.

For $FeI_2(cr)$, a reversible second-order transition was found between 340 and 410 K. The enthalpy of the transition was determined graphically to be between 0.5 and 0.9 $kJ \cdot mol^{-1}$ for three different samples. The samples of $FeI_2(cr)$ were all found to be slightly substoichiometric with respect to iodine.

[1960SHE/CHA]

The dehydration of $FeCl_2 \cdot 4H_2O$ (probably in air) was examined by differential thermal analysis (DTA), thermogravimetric analysis (TGA) and X-ray powder diffraction. The transition temperatures from the DTA and TGA are consistent, but do not agree well with those from a static transition study [1949SCH]. The transition temperatures above 100 °C agree moderately well with those reported by Bogatskii *et al.* [1971BOG/GOR].

[1960WAR/ING]

Warner and Ingraham reported decomposition pressures (903 to 997 K) over samples of iron(III) sulfate. Few details were provided on the synthesis of the solid. The pressures were attributed to the mixture of $SO_3(g)$, $SO_2(g)$ and $O_2(g)$ in equilibrium with $Fe_2(SO_4)_3(cr)$ and $Fe_2O_3(cr)$. The results are consistent with those from other similar studies (*cf.* the discussion in the Appendix A entry for [1964KEL]).

[1961BLA]

Equilibrium pressures over $Fe_2(SO_4)_3$-Fe_2O_3 between 845 and 976 K were determined using a static method (values were reported graphically and in the author's Table 5.4, but not in the author's Table 1.2 (as was stated incorrectly on page 22 of the thesis)). In a plot of $\Delta_r G$ *vs.* T the results at the lowest temperatures showed some deviation from linearity. Measurements were done both with increasing and decreasing temperatures. The methods used in earlier studies were reviewed, and the values obtained by Blanks were compatible with those from other careful static studies. The values were used by Kellogg [1964KEL] in his review.

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[1] In the thesis [1960OET], there is a typographical error in the equation of Moore [1943MOO], which appears to have been carried through into the author's Figure II. The effect on the comparison is negligible.

[1961BLU/WHI]

This is apparently the first solid-state electrochemical determination of the oxygen potential for the magnetite-hematite buffer since the pioneering effort by Treadwell [1916TRE]. It follows the landmark study of numerous other oxide systems, using the newly developed ZrO_2-based electrolytes that revolutionized such research, by Kiukkola and Wagner [1957KIU/WAG]. Data are also reported for the MnO-Mn_3O_4 buffer. Both buffers were measured against an Fe–wüstite reference electrode with a CaO-stabilized ZrO_2 solid electrolyte, using a stacked-pellet configuration and high-purity materials. The estimated accuracy of temperature and precision of potential-difference measurements were ± 1°C and ±0.1 mV, respectively. Calibration runs on an Ni-NiO/iron-wüstite cell gave agreement within ±3 mV of data from [1957KIU/WAG].

About 41 measurements from four runs, using three different magnetite-hematite pellets, yielded the following relationship for magnetite-hematite *vs.* Fe-wüstite at 1089 to 1321 K.

$$E/\text{mV} = \{32.7 + 0.4310\ (T/\text{K})\} \pm 7$$

This relationship is discussed further in Section VII.2.2.1. The authors used a combination of gas-solid equilibrium data for Fe-wüstite from several sources to determine absolute oxygen chemical potentials.

[1961LEN/BUS]

The solubilities of "Fe(III) hydroxide" and α-FeOOH were measured in 3 M $NaClO_4$ media at 20 °C by using ^{59}Fe tracer methods. The mixtures were left unstirred for 7 to 10 days and were then separated by ultracentrifugation. The remaining activity in the liquid phase was measured as well as the pH, although the latter measurement was not described. The value of pK_w = 14.40 was estimated for these conditions. While measurements were made over the pH range from 3 to 14, special attention was paid to aging effects on the solubility in alkaline solutions. For the iron(III) hydroxide, the equilibrium constant K for the following reaction varied with aging of the precipitate. Values for K appear to be in mixed units: concentration for $Fe(OH)_4^-$ and activity for OH^-.

$$\text{“}Fe(OH)_3\text{”(am)} + OH^- \rightleftharpoons Fe(OH)_4^-$$

$K = c_{Fe(OH)_4^-} / a_{OH^-} = 10^{-(4.50\pm0.15)}$ after 2 hours, $10^{-(4.80\pm0.15)}$ after 24 hours, $10^{-(5.00\pm0.15)}$ after 96 hours.

Equilibrium solubility with α-FeOOH was probably not achieved, but it was estimated to be 100 to 1000 times less soluble than the "$Fe(OH)_3$".

[1961LEN/BUS2]

These authors made one of the first attempts to determine the solubility of amorphous $Fe(OH)_3$ by dissolution and precipitation experiments (I = 3 M, $NaClO_4$ at *ca.* 20 °C) and used the isotope ^{59}Fe as a trace additive to provide a sensitive measure of the iron concentration in solution. They claimed that simple filtration with a sintered glass filter was sufficient to separate the solid and solution phases at pH > 12 whereas ultracentrifugation was necessary at lower pH (equilibration times: pH ≤ 3.5, *ca.* five days; pH = 3.5 to 5, 20 to 30 days without assurance of reaching a metastable equilibrium; pH > 5, *ca.* 4 days). The method employed for calibration of the glass/calomel electrode cell was not mentioned. A plot of $-\log_{10} c_{\mathrm{Fe}}$ *vs.* pH (their Figure 1) showed a broad minimum solubility from pH 5 to 11 with an average of the 20 points being $10^{-(7.2\pm0.6)}$ M, which is lower by *ca.* 0.7 $\log_{10}$-units than the average of five points attributed to Gayer and Wootner [1956GAY/WOO], $10^{-6.5}$ M, and probably represents the solubility in terms of $Fe(OH)_3(aq)$ for 2-line ferrihydrite. Taking the single data point from their Figure 1 at the most acidic pH = 2.78 where $\log_{10} c_{\mathrm{Fe}} = -4.03$, a molal $\log_{10} K_{\mathrm{s}}$ value of -38.88 is derived at 20 °C, assuming only Fe^{3+} was present in solution.

Another experimental series was run with amorphous $Fe(OH)_3$ at high base concentrations (pH = 12.45 to 14.25) where a constant solubility was almost attained after four days (sampling at two hours, and one and four days, and finally in selected cases after one month with minimal change). The solid phase could be effectively removed by filtration. Note that the higher pH samples violated the supporting electrolyte approach because approximately one third of the electrolyte was made up of NaOH. The molar solubilities over the initial three sampling periods were given in a table and are shown here in Figure A-12 after conversion to molal units. Regression of these three data sets produced slopes of 0.999, 0.982 and 0.988, respectively; very close to the theoretical unit slope for the equilibrium, $\mathrm{Fe(OH)_3(s) + OH^- \rightleftharpoons Fe(OH)_4^-}$, which appears to be quite remarkable in view of the high concentration of NaOH used (note that the OH^- concentration could be obtained from the stoichiometry of the prepared starting solutions, thereby considerably increasing the reliability of the pH reported) and the typical experimental difficulties in carrying out such measurements. Fixing the slopes to the theoretical value, the corresponding $\log_{10} {}^*K_{\mathrm{s},4}$ values are: $-(18.74 \pm 0.14)$, $-(19.04 \pm 0.18)$ and $-(19.22 \pm 0.14)$, respectively, with standard deviations shown as 2σ. The recovered solid phases were analyzed by the XRD and SEM instruments of that time, and the four-day material was recognized as being goethite, α-FeOOH. From these results, the Gibbs energies of reaction for:

$$\mathrm{Fe(OH)_3(am) + H_2O(l) \rightleftharpoons Fe(OH)_4^- + H^+} \qquad (1)$$

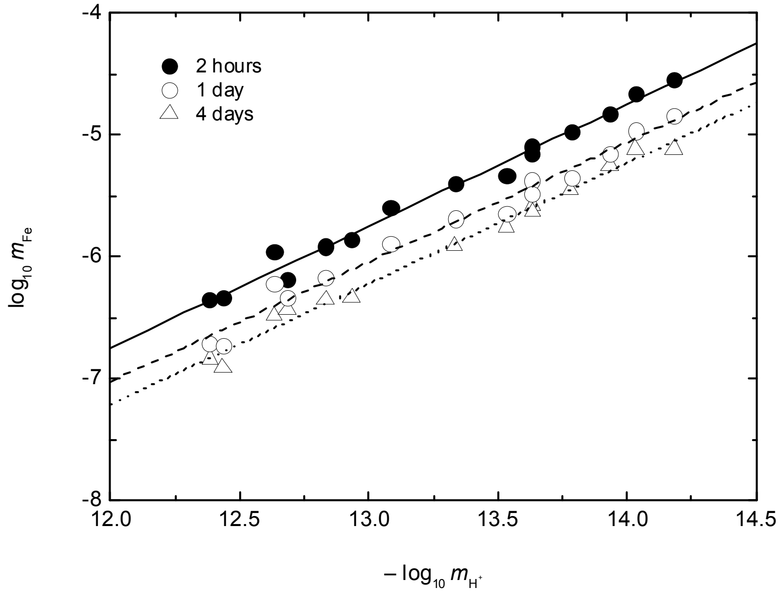
$$\mathrm{\alpha\text{-}FeOOH + 2\,H_2O(l) \rightleftharpoons Fe(OH)_4^- + H^+} \qquad (2)$$

were calculated to be 105.18 and 107.87 kJ·mol^{-1} at 293.15 K, respectively, which leads to a difference in $\Delta_{\mathrm{f}} G_{\mathrm{m}}$ of 2.7 kJ·mol^{-1} for these two solid phases.

Interestingly, when the authors tried to measure the solubility of α-FeOOH, which they had prepared and characterized, much lower (1.5 $\log_{10}$-units) and far more scattered (*ca*. 0.5 $\log_{10}$-units) values were obtained that continued to increase slowly after 40 days equilibration.

This appears to be a well conceived experimental study of the solubility of amorphous $Fe(OH)_3$ which also yielded a rare, if not precise, measure of the corresponding solubility of α-FeOOH at near ambient conditions (293.15 K and I_m = 3.5). If the $Fe(OH)_3$(am) solid used in pH range from 5 to 12 was identical to that in the two-hour experiments at high pH, a value of $\log_{10}{}^*K_{4,1} = (7.2 - 19.2) = -(12.0 \pm 0.6)$ would result. The $\log_{10}K_s$ value of −38.88 for the amorphous phase, and the $\log_{10}{}^*K_{s,4}$ values of −(18.74 ± 0.14) for $Fe(OH)_3$(am) and −(19.22 ± 0.14) for α-FeOOH, are worthy of consideration. Finally, this study underlines the futility of trying to measure the solubility of crystalline iron(III) phases at ambient conditions by conventional methods due to their extremely slow dissolution kinetics, whereas the more rapid *in situ* crystallization of an amorphous phase may allow equilibrium solubilities to be attained from over-saturation conditions.

Figure A-12: Plot of $-\log_{10} m_{Fe}$ *vs*. pH at 20 °C and I_m = 3.5 ($NaClO_4$) over the pH range 5 to 11.



[1961OET/GRE]

This paper reports the results for $FeCl_2$(cr) from Oetting's thesis [1960OET] (see the corresponding Appendix A entry), but with less detail.

[1961OET/GRE2]

This paper reports the results for FeI_2(cr) from Oetting's thesis [1960OET] (see the corresponding Appendix A entry), but with less detail.

[1961SAL]

The main aim was to obtain and interpret T–composition–activity relationships for Fe_3O_4 and Fe_2O_3, based on direct measurement of equilibrium p_{O_2}, either manometrically (for values between about 0.005 and 1 bar) or with a McLeod gauge (10^{-8} to 0.005 bar). Tables present 20 measurements for different magnetite compositions (up to an Fe_2O_3 mole fraction of 0.4) at 1375 to 1700 K, and 34 measurements for hematite (up to an Fe_3O_4 mole fraction of 0.023) at 1375 to 1700 K. The saturation mole fraction of Fe_3O_4 in hematite is shown to vary from ~0.003 at 1273 K to ~0.02 at 1773 K.

There is less emphasis on the magnetite-hematite equilibrium; however, combining his data with those from [1946DAR/GUR] and [1955NOR], the author drew an Fe_3O_{4+x}–Fe_2O_{3-y} phase boundary with the approximate locus (estimated from the figure by the reviewer):

$$\log_{10}(p_{O_2}/\text{bar}) = 14.5 - \frac{25000}{(T/\text{K})}.$$

This is not used in the current review, because of the relatively high temperatures and large deviations from stoichiometry for both Fe_3O_4 and Fe_2O_3, as compared with more recent, solid-state cell-potential measurements on the magnetite-hematite buffer. The data are thus unlikely to improve the accuracy of values for $\Delta_f H^\circ_m$ (Fe_2O_3, α, 298.15 K), which is the principal use for magnetite–hematite equilibrium data in the current review.

[1961STO]

In this paper the author discusses the nature of magnetic transitions in transition metal salts. Figure 6 in the paper shows at least some of the actual data points (19 to 29 K) from Westrum's unpublished study on the specific heats of $FeCl_2$(cr) (as also referenced in [1958WIL/GRE], [1960OET] and [1998CHA]). The data points were digitized from Figure 6. The maximum in the heat-capacity anomaly was found to lie at 23.6 K, in good agreement with values from other studies [1935TRA/SCH], [1972LAN/CAR], [1982WON/MOL]. The experimental heat-capacity values are similar to the values determined by Lanusse *et al.* [1972LAN/CAR] and, except at the lowest temperatures, those of Trapeznikowa and Schubnikow [1935TRA/SCH], but there is less scatter than is found in the values from that early study. For the purposes of fitting functions to the calorimetry results, the uncertainties in the individual values for the heat capacities were estimated in the present review as ± 0.2 $J\cdot K^{-1}\cdot mol^{-1}$.

[1961SUT/ROW]

This paper is a report of a UV-visible spectral kinetic study of electron exchange between Fe(II) and the Fe(III) chlorido 1:1 complex in H_2O and D_2O. The reaction was the exchange in solution between radioactive ^{55}Fe(III) and inactive Fe(II). After the reaction had been allowed to progress for a time, the Fe(II) was quenched with 2-2' bipyridine and the Fe(III) precipitated with ammonia. The kinetics of the exchange reaction, $^{55}FeCl^{2+}$ + inactive $Fe^{2+} \rightleftharpoons$ inactive-$FeCl^{2+}$ + $^{55}Fe^{2+}$, is 2.5 times more rapid in H_2O than in D_2O.

The formation constants of the 1:1 complex were also determined spectrophotometrically:

$$K_{1c} = 4.4 \text{ in } H_2O,\ 8.7 \text{ in } D_2O \text{ at } 25\ °C \text{ and } I = 0.5\ M.$$

Experiments were done at temperatures between 16.5 and 35.5 °C. From the $\log_{10}K_1$ values $\Delta_r H_1$ (H_2O) = 20.92 kJ·mol^{-1} at 25 °C and I = 0.5 M. After conversion to the molal scale these values were included in the data which has been used in the determination of K_1° and $\varepsilon(FeCl^{2+}, ClO_4^-)$.

The authors compared their K_1 value to those from the earlier literature. For that they used the equation of Rabinowitch and Stockmayer (see the Appendix A entry for [1942RAB/STO]) for the ionic strength corrections to I_c = 0.5 M. Only fair agreement is found between their values for K_1 and ΔH and the values recommended in the present review. The results from this paper were later reanalysed by Rowley *et al.* [1970ROW/SUT], and further comments on the analysis were made by Schwartz and Dodson [1976SCH/DOD].

[1961WHI/KEL]

In this study, the stability constants of the chlorido complexes of Fe(III) were evaluated by extraction of Fe^{3+} ions into HDNNS (dinonylnaphthalene sulfonic acid) or HCl·TOA (trioctylamine hydrochloride) from aqueous chloride solutions. The mother liquor of Fe(III) was spiked with radioactive ^{55}Fe. The Fe(III) distribution ratios, $D_{Fe(III)}$, were determined by radiometric analysis of the two phases. The cationic complex stability constants were deduced from the variation of $D_{Fe(III)}$ between an aqueous solution 1 M in ($HClO_4$,HCl) and an organic phase, 0.147 F HDNNS in benzene. It was found that K_1 = 4.57 for I = 1 M and K_1 =6.02 for I = 0.2 M. The value of K_2 was not given because of the lack of sensitivity of the method.

The stability constants of the anionic complexes were determined from the variation of $D_{Fe(III)}$ between HCl aqueous solution and 0.1 M TOA in benzene. From the distribution coefficients at constant HCl concentrations and variable TOA concentrations it was claimed that the Fe(III) complex in the organic phase is $FeCl_5(HTOA)_2$.

The results of this paper are roughly in accord with others in the literature and with the recommended value of this review. In spite of the lack of numerical values for the solution compositions, which were $HClO_4$, HCl mixtures, the data have been reanalyzed using the SIT method in the overall calculation of the K_1° and $\varepsilon(\mathrm{FeCl}^{2+}, \mathrm{ClO}_4^-)$ values. This is possible because it has been found that the values of $\varepsilon(\mathrm{Fe}^{3+}, \mathrm{ClO}_4^-)$ and $\varepsilon(\mathrm{Fe}^{3+}, \mathrm{Cl}^-)$ are not too different, and $\varepsilon(\mathrm{H}^+, \mathrm{ClO}_4^-)$ and $\varepsilon(\mathrm{H}^+, \mathrm{Cl}^-)$ also have similar values (0.14 and 0.12 kg·mol^{-1}). Therefore, HCl can be assumed to replace $HClO_4$ without changing the ionic strength effects greatly.

[1962AHA/FRE]

This short paper reports TGA measurements between about 90 and 1000 K on a Fisher commercial hematite (α-Fe_2O_3) powder of unstated purity. The apparatus is described elsewhere [1961AHA/FRE], [1960REI]. Three transition points were observed, at about 243, 948, and 998 K. Additional features at about 593 and 773 K, attributed in this paper to Chevalier [1951CHE], were not confirmed. The 243 K feature was identified as the Morin transition, at which the sublattice magnetization rotates by 90° (parallel to the [111] axis below the transition, within the (111) plane above the transition). The authors argue that the third transition must be the Curie [Néel] point, previously thought to be at about 948 K. The second transition, at 948 K, is interpreted using the theory of Dzialoshinskii (three references are given), to be a point at which the basal plane anisotropy changes sign.

No figures are shown of TGA traces, and there is no indication of the relative size of the thermal effects for the three transitions. Note that Grønvold and Westrum [1959GRO/WES3] detected no heat-capacity anomaly at the Morin transition. Grønvold and Samuelsen [1975GRO/SAM] found a large magnetic contribution to the heat capacity at all temperatures from 300 to 1050 K, with a sharp peak in the measured $C^\circ_{p,\mathrm{m}}$ at 955 K, identified as the Néel temperature. The results of [1975GRO/SAM] appear to supersede those of [1962AHA/FRE].

[1962BRO/MIN]

Spectrophotometric measurements (at 302 nm) were carried out for $Fe(NH_4)(SO_4)_2$ solutions (1.02×10^{-4} to 1.02×10^{-3} M) in aqueous H_2SO_4 (0.1 N) at 21.5 °C (the reported temperature variation was ± 2 °C). The formation constant for FeSO_4^+ at that temperature was reported as (114 ± 9) M^{-1} at an ionic strength of 0.15 M (?). The effect of hydrolysis was neglected and the reported ionic strength was approximate. The information provided is insufficient for a proper recalculation of the data, and the rather low value of K_1 is not used further in the present review.

[1962DAV/SMI]

A spectroscopic study was carried out using 0.5 M perchloric acid solutions containing 1×10^{-2} to 3×10^{-2} M iron(III) and 1×10^{-3} M sulfuric acid. The reported "molar" concentrations at all temperatures were probably the room-temperature molar concentrations. These experiments were supplemental to a kinetics study. In their calculations the values used by the authors for $K^{-1}_{\mathrm{c1,1(HSO_4^-)}}$, the deprotonation constant of HSO_4^- (the notation in the original paper was K_a), were (0.0740 ± 0.0010), (0.0540 ± 0.0010), (0.0433 ± 0.0005) and (0.0336 ± 0.0090) M for 1.4, 15.0, 25.0 and 35.0 °C, respectively. The reported molar formation constants of $FeSO_4^+$, K_1, were (95 ± 6), (149 ± 10), (205 ± 18) and (280 ± 22) M^{-1} for 1.4, 15.0, 25.0 and 35.0 °C, I_c = 0.5. From the formation constants found for I_c = 0.5 M, and assuming that the value of ΔC_{p1} was zero, the authors calculated a value of 23.0 $kJ\cdot mol^{-1}$ (5.5 $kcal\cdot mol^{-1}$) for ΔH_1.

The value of $K_{1FeSO_4^+}$ at 25 °C is in line with most of the other literature values and it is used in the overall optimization for the determination of $K^o_{1FeSO_4^+}$ and $\Delta\varepsilon$ for the $\Delta\varepsilon$ of the reaction. The TDB-SIT value of $K_{m1,1(HSO_4^-)}$ has been used and the correction was carried out as described for the paper of Kumai [1960KUM]. The conversion to the molal scale used the ξ coefficient of Table II-5, and the calculated value of $K_{1FeSO_4^+}$ (0.51 m) for 25 °C is (180 ± 20) $mol^{-1}\cdot kg$.

The calculation of the $K_{1FeSO_4^+}$ (0.51 m) values at 1.4, 15 and 35 °C yielded: (70 ± 7) $mol^{-1}\cdot kg$, (119 ± 12) $mol^{-1}\cdot kg$ and (258 ± 30) $mol^{-1}\cdot kg$. These values were used by applying the formula:

$$d(\ln K_m)/d(1/T) = -\Delta_r H_m/R \qquad (A.58)$$

to obtain (27.5 ± 2.0) $kJ\cdot mol^{-1}$ for $\Delta_r H_m$ (0.51 $mol\cdot kg^{-1}$ $HClO_4$).

[1962FEI/MIC]

The authors established that the presence of Fe^{2+} accelerates the formation of goethite. They claim the Fe^{2+} ions adsorb on the surface of α-FeOOH particulates and are then oxidized *in situ* indicating that the adsorbed Fe^{3+} ions on the surface are more readily arranged into the structure than would be hydrolyzed iron(III) species. Thus, amorphous phases are generally formed by rapid precipitation from Fe(III) solutions rather than by oxidation reactions.

The authors were able to prepare the following crystalline phases as indicated by their X-ray diffractograms: α-FeOOH and α-Fe_2O_3. These were prepared from 3 $mol\cdot dm^{-3}$ $NaClO_4$ solutions containing high concentrations of $NaHCO_3$ and NaOH for periods up to 2.5 years.

This article contains no thermodynamic data.

[1962KAN/GRO]

Smoothed values of the vapour pressure of $FeCl_2$ and $FeCl_3$ solutions, among others, are tabulated based on the thesis work of Groenveld [1956GRO] in which the original experimental data are given.

The experimental results provided in [1956GRO] were utilized in this review in preference to the smoothed values reported in [1962KAN/GRO].

[1962LEB/LEV]

Equilibrium constants of the reduction reaction

$$\alpha\text{-}Fe_2SiO_4 + 2\,CO(g) \rightleftharpoons 2\,Fe(cr) + SiO_2(cr) + 2\,CO_2(g)$$

were reported for nine temperatures between 1123 and 1423 K. These equilibrium constants, when combined with consistent auxiliary data for quartz ([1989COX/WAG], [1998CAR/SAL]) and carbon dioxide and carbon monoxide [1989GUR/VEY], and with the values selected in this review for the heat capacity and entropy of α-Fe_2SiO_4 (Section X.2.1.1.1) and Fe(cr) (Section V.2) led to values of $\Delta_f H_m^\circ$ (Fe_2SiO_4, α, 298.15 K) that ranged between − 1476.6 and − 1479.7 kJ·mol^{-1}. The average value is − (1478.4 ± 0.4) kJ·mol^{-1} (95% confidence limits) based on 17 measurements. The calculated values become more negative for the higher temperatures, indicating that there likely were minor systematic experimental problems. The form of the product SiO_2 was not explicitly stated. In the present review, the uncertainty in the average value is estimated as ± 3.0 kJ·mol^{-1} (2σ).

[1962POH]

To assess the solubilities of iron sulfides such as troilite, pyrrhotite and marcasite at elevated temperatures, the available data for H_2S and iron sulfide solubility were collected. The values for $K = (c_{Fe^{2+}}\, c_{H_2S(aq)} / c^2_{H^+})$ were selected as 1300 at 14 °C, 1380 at 25 °C and 60 at 90 °C. No original experimental data were given.

[1962TRE/KHO]

Static, manometric measurements of equilibrium p_{O_2} over Fe_3O_{4+x} + Fe_2O_{3-y} at ~ 1370 to 1730 K yielded the following relationship (when the pressure units are adjusted from atmospheres to bar, and a sign error is corrected):

$$\log_{10}(\,p_{O_2}\,/\text{bar}) = 13.53 - 23330/(T/\text{K}).$$

This is not used in the current review, for similar reasons to those given in the synopsis of [1961SAL].

The paper includes a useful compilation of data from seven earlier studies covering the period 1908 - 1957.

[1962VIC]

In this letter, the author briefly presents a simple “membrane” model to describe the excess heat capacity in finely divided specimens of MgO, NaCl, and BeO (as previously investigated by various other authors cited in this letter). The peak values for this excess heat capacity range from ~ 0.06 mJ·m^{-2} for NaCl to ~ 0.17 mJ·m^{-2} for MgO (estimated by this reviewer from data reproduced in this letter). The model appears to improve on an earlier theory of Montroll [1950MON].

While in the author's own words the model is crude, the measurements cited (from several sources) may be helpful in estimating particle-size effects on the heat capacities of iron oxyhydroxides and other finely divided solids, no attempt has been made to seek more recent publications on this subject. Overall, surface entropy in oxide solids has received much less attention than surface enthalpy, which appears to be the dominant factor in the thermochemical differences between fine oxide powders and their well-crystallized forms (see, in particular, [2005MAZ/NAV] and references therein).

Diakonov *et al.* [1994DIA/KHO] have estimated surface entropies (298 K) of $0.6 \cdot \text{J} \cdot \text{K}^{-1} \cdot \text{m}^{-2}$ for BeO and $0.5\ \text{J} \cdot \text{K}^{-1} \cdot \text{m}^{-2}$ for MgO (based on data cited in this paper), and $0.2\ \text{J} \cdot \text{K}^{-1} \cdot \text{m}^{-2}$ for Ni(OH)_2 (based on data from other sources).

[1962WEN/STR]

This investigation of the kinetics of complex formation by the pressure-jump method was the first that showed the occurrence of two different monochlorido iron(III) species. The progress of the reaction was followed by spectrophotometry. It was demonstrated that the formation of the inner-sphere monochlorido complex is preceded by a rapid (≈ 15 μs) process of ion association which yields $\text{Fe(H}_2\text{O)}_6\text{Cl}^{2+}$. No evidence for higher-order outer-sphere complexes was found.

The formation of the inner-sphere $\text{FeCl(H}_2\text{O)}_5^{2+}$ is the rate-determining step (≈ 100 ms). The presence of OH^- ions increases the rate of complex formation. It was found that at an ionic strength of 2.6 $\text{M(NaClO}_4)$, a temperature of 25 °C and a hydrogen ion concentration of 0.027 M, the molar formation constant values are $K_{1(\text{out})} = (2 \pm 1)\ \text{M}^{-1}$ and $K_{1(\text{in})} = (1.0 \pm 0.5)\ \text{M}^{-1}$. The latter value obtained by this indirect experimental method is rather low, and is not used further in the present review.

[1962WOO/GAL]

Woods *et al.* used various methods of investigation, including calorimetric measurements, to get the thermodynamic constants for the formation of FeCl^{2+} in perchloric acid. The results from the three methods used are first discussed separately.

Spectrophotometry:

According to the authors, the best consistency for K_1 values in 1 M HClO_4 could be obtained by using the absorption at 335 nm or at 220 nm because these wavelengths correspond to two maxima of absorption of inner sphere FeCl^{2+}, and then the interference of any FeCl_2^+ is limited. The reported values were $K_{1c} = (2.94 \pm 0.09)\ \text{M}^{-1}$ and $K_{1c} = (3.16 \pm 0.22)\ \text{M}^{-1}$. The variation of K_1 with temperature, 25 to 45 °C, yielded values for $\Delta_r H_1^\circ$ and $\Delta_r S_1^\circ$ of $17.15\ \text{kJ} \cdot \text{mol}^{-1}$ and $69.45\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.[1]

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[1] The reported set of $\log_{10} K$, $\Delta_r H$ and $\Delta_r S$ values does not close particularly well.

Potentiometry:

Measurements were made of the potential difference of electrochemical cells composed of two identical half cells having Pt electrodes and containing mixtures of Fe(II) and Fe(III) perchlorates in perchloric acid. Solid KCl was added to one of the half cells, and that permitted measurements for several concentrations of Cl^- changing the iron concentrations or the ionic strength only slightly. Measurements were made for a range of ionic strengths (0.1 M to 3.7 M). The results obtained were $K_{1c} = 2.89$ M^{-1} at $I = 1$ M and $K_1^\circ = 33$ at $I = 0$ (using a Debye-Hückel type extrapolation).

The variation of K_1 with temperature between, 14.3 and 44.3 °C, yielded values for $\Delta_r H_1^\circ$ and $\Delta_r S_1^\circ$ of 18.41 kJ·mol^{-1} and 69.45 J·K^{-1}·mol^{-1}.

The influence of Fe(II) chlorido complexes was not mentioned. It is certain that this influence was small but not taking it into account could have masked other effects such the influence of the 2:1 iron(III) complex and some medium effects —two phenomena that were considered negligible by the authors.

Calorimetry:

Samples of three stock Fe(III) perchlorate solutions were prepared. Aliquots were added to 1.0 and 3.7 M $HClO_4$ solutions, and to HCl(sln)/$HClO_4$(sln) mixtures with total ionic strengths of 1.0 M. After corrections for the heats of mixing and the heats of dilution, and extrapolation to zero chloride in 1.0 and 3.7 M $HClO_4$, a value of $\Delta_r H_1^\circ$ 17.57 kJ·mol^{-1} was found for dissolution in 1.0 M $HClO_4$. When combined with the value of K_1 chosen by the authors (2.9 kcal·mol^{-1}) the value of $\Delta_r S_1^\circ$ is 67.78 J·K^{-1}·mol^{-1} in 1 M $HClO_4$. In the present review, the experimentally derived enthalpy of complexation is assigned an uncertainty of ± 3.0 kJ·mol^{-1}. This was chosen to take into account the spread in the results from the three sets of experiments, the extrapolations to zero chloride and the lack of correction for the presence of $FeCl_2^+$ in any of the solutions.

Summary

The stability constants reported for the formation of the complex $FeCl^{2+}$ are lower than those found by most other authors at the same ionic strengths. The results of these investigations at 25 °C were extrapolated to zero ionic strength (extended Debye-Hückel limiting law) by the authors to obtain a standard value ($K_1^\circ = 30$). A value of zero was used for $\Delta_r C_{p1}^\circ$, so that $\Delta_r H_1^\circ$ was assumed to be independent of temperature. There is fair internal agreement between the values of the thermodynamic constants obtained using the various methods of investigation. However, agreement with results reported in other papers is poorer. For this investigation, the concentration of Cl^- varied from 0.20 to 0.95 M, and the Fe(III) concentrations were around 0.00015 M. For these conditions some $FeCl_2^+$ would have been present ($K_2^\circ \approx 5$) and would have interfered. However, even if this is taken into account in the interpretation of the data, the value of K_1 is not as reliable as in the investigations in which low Cl^-/Fe^{3+} concentration ratios were maintained, and only the 1:1 species could be present.

The value of $\Delta_r H_1$ at 25 °C and 1 M $HClO_4$ (1.05 m) is in rough agreement with that of Vasil'ev and Lobanov [1967VAS/LOB2].

Another striking problem is seen in the two values for the formation constant K_1. It would be expected that a higher value would be found from potentiometry because the formation of both inner- and outer-sphere complexes might influence the potential-difference values. In the spectrophotometry study only the inner-sphere complex is likely to contribute to the charge-transfer band, which is used to determine the formation constant. It is a tedious process to evaluate the errors introduced by neglect of the outer-sphere complexes, nor are there good estimates of the effect of ionic strength on the formation of outer-sphere complexes. Most of the experimental results from the early papers, including this one, are not sufficiently accurate for such a correction to be significant. The change in the values would probably be less than the uncertainties inherent in the extrapolation of the K_1 values to zero ionic strength. The similar values of K_1 found by potentiometry and spectrophotometry show that the two methods are sensitive to the formation of the same type of complex, that is to say the inner-sphere complex.

In the present review the molar concentrations and formation constants from the potentiometric measurements were converted to molal values (Table II-5), and an SIT extrapolation ($m \leq 4.46$ m) was used to obtain a value of (1.44 ± 0.02) for $\log_{10} K_1^{\circ}$. Application of the SIT is detailed in Section VIII.2.3 of the main text.

[1963ADA/KEL]

Adami and Kelley determined the heats of solution of $FeSO_4 \cdot 6.952H_2O$ and $FeSO_4 \cdot 1.008H_2O$, into a 4.36 m solution of HCl in water at 303.15 K. Based on the heats of solution of iron, water and aqueous sulfuric acid in the same solvent, literature heat-capacity data and literature values for the enthalpies of formation of the aqueous sulfuric acid and water, values were calculated for the enthalpies formation of the stoichiometric monohydrate and heptahydrates.

The reported heats of solution of $FeSO_4 \cdot 6.952H_2O$ and $FeSO_4 \cdot 1.008H_2O$ are (47.816 ± 0.102) $kJ \cdot mol^{-1}$ and $-(6.220 \pm 0.060)$ $kJ \cdot mol^{-1}$, respectively, (with recalculated 95% confidence limits). The value of the heat of solution of Fe(cr) into an acid solution of the same composition was reported as $-(87.132 \pm 0.177)$ $kJ \cdot mol^{-1}$ from the work of Koehler and Coughlin [1959KOE/COU] (see the corresponding Appendix A entry for further details). The heats of solution of $H_2SO_4 \cdot 7.068$ and $H_2O(l)$ in the 4.36 m HCl were $-(2.838 \pm 0.137)$ $kJ \cdot mol^{-1}$, and (0.337 ± 0.042) $kJ \cdot mol^{-1}$, respectively.

Thus, $\Delta_r H_m^{\circ}$ (A.59) = $-(81.618 \pm 0.344)$ $kJ \cdot mol^{-1}$ and $\Delta_r H_m^{\circ}$ (A.60) = $-(137.747 \pm 0.246)$ $kJ \cdot mol^{-1}$ at 303.15 K for

$$Fe(cr) + H_2SO_4 \cdot 7.068H_2O(l) \rightleftharpoons FeSO_4 \cdot 1.008H_2O + 6.060\,H_2O(l) + H_2(g) \quad (A.59)$$

and

$$\mathrm{Fe(cr)} + \mathrm{H_2SO_4{\cdot}7.068H_2O(l)} \rightleftharpoons \mathrm{FeSO_4{\cdot}6.952H_2O} + 0.116\,\mathrm{H_2O(l)} + \mathrm{H_2(g)}. \quad \text{(A.60)}$$

The differences in the values of $\Delta_r C_p$ for 298.15 K and of $\Delta_r C_p$ for the average reaction temperature, 300.65 K, are small enough that they can be ignored relative to the uncertainties in the values of the heat capacities. Using the values at 298.15 K, $C^{\circ}_{p,\mathrm{m}}$ ($FeSO_4{\cdot}1.008H_2O$, cr, 298.15 K) = (141.1 ± 10) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, $C^{\circ}_{p,\mathrm{m}}$ ($FeSO_4{\cdot}6.952H_2O$, cr, 298.15 K) = (392.5 ± 2.0) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$,[1] $C^{\circ}_{p,\mathrm{m}}$ (Fe, cr, 298.15 K) = (25.084 ± 0.500) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ (see Section V.2), $C^{\circ}_{p,\mathrm{m}}$ (H_2, g, 298.15 K) = (28.836 ± 0.002) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ (Table IV-1), $C^{\circ}_{p,\mathrm{m}}$ (H_2O, l, 298.15 K) = (75.351 ± 0.080) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ (Table IV-1) and $C^{\circ}_{p,\mathrm{m}}$ ($H_2SO_4{\cdot}7.068H_2O$, l, 298.15 K) = (614 ± 10) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ [1956HOR/BRA], [1982WAG/EVA][2], we obtain $\Delta_r C_p$ ((A.59), 298.15 K) = – (13 ± 10) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, $\Delta_r C_p$ ((A.60), 298.15 K) = – (209 ± 10) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, $\Delta(\Delta_r H^{\circ}_{\mathrm{m}}$ (A.59)) = (0.06 ± 0.05) $\mathrm{kJ{\cdot}mol^{-1}}$, $\Delta(\Delta_r H^{\circ}_{\mathrm{m}}$ (A.60)) = (1.05 ± 0.05) $\mathrm{kJ{\cdot}mol^{-1}}$. Hence, $\Delta_r H^{\circ}_{\mathrm{m}}$ (A.59) = – (81.66 ± 0.35) $\mathrm{kJ{\cdot}mol^{-1}}$ and $\Delta_r H^{\circ}_{\mathrm{m}}$ (A.60) = – (131.70 ± 0.26) $\mathrm{kJ{\cdot}mol^{-1}}$. The value of $\Delta_f H^{\circ}_{\mathrm{m}}$ (H_2O, l, 298.15 K) is – 285.83 $\mathrm{kJ{\cdot}mol^{-1}}$ and $\Delta_f H^{\circ}_{\mathrm{m}}$ ($H_2SO_4{\cdot}7.068H_2O$, l, 298.15 K) is – (2896.85 ± 0.64) $\mathrm{kJ{\cdot}mol^{-1}}$ based on the US NBS tables [1982WAG/EVA], and adjusted to allow for the differences in the values for $\Delta_f H^{\circ}_{\mathrm{m}}$ (SO_4^{2-}, 298.15 K) from Table IV-1. Hence $\Delta_f H^{\circ}_{\mathrm{m}}$ ($FeSO_4{\cdot}1.008H_2O$, cr, 298.15 K) is – (1246.38 ± 0.77) $\mathrm{kJ{\cdot}mol^{-1}}$ and $\Delta_f H^{\circ}_{\mathrm{m}}$ ($FeSO_4{\cdot}6.952H_2O$, 298.15 K) is – (3000.40 ± 0.69) $\mathrm{kJ{\cdot}mol^{-1}}$. If these values are assumed to apply to mixtures of the two hydrates, values for the stoichiometric hydrates, $\Delta_f H^{\circ}_{\mathrm{m}}$ ($FeSO_4{\cdot}H_2O$, cr, 298.15 K) = – (1244.02 ± 0.80) $\mathrm{kJ{\cdot}mol^{-1}}$ and $\Delta_f H^{\circ}_{\mathrm{m}}$ ($FeSO_4{\cdot}7H_2O$, cr, 298.15 K) = – (3014.56 ± 0.70) $\mathrm{kJ{\cdot}mol^{-1}}$ are calculated. This does assume that the mixtures do not involve the tetrahydrate. However, based on the available information on the enthalpies of solution of the hydrates [1968LAR], any additional uncertainties from this source are expected to be minor, and can be accounted for by increasing the uncertainty in the enthalpy of formation of each stoichiometric hydrate to ± 1.00 $\mathrm{kJ{\cdot}mol^{-1}}$.

[1963BAC/LIE]

This was primarily a study of the electron-exchange reactions between Fe(II) and Fe(III) in the presence of sulfate (0 to 20 °C), but some values for Fe(III)-sulfato complexation constants also were obtained and reported. The equilibrium constant measurements were determined spectroscopically (290 to 350 nm) over an unspecified range of temperatures that either included (or bracketed) 25 °C. Although the paper indicates that the medium was "1 m" $HClO_4$, the reported 25 °C stepwise constants and

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[1] The heat-capacity values were based on the selected values for the heptahydrate and anhydrous salts, respectively, and the assumption of a contribution of 40 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ per mole of water of hydration. Estimates based strictly on extrapolation between the values between the same two solids are not significantly different.

[2] The re-evaluation by Zeleznik [1991ZEL] of data for the H_2SO_4-H_2O system leads to an insignificantly different value of ~ 617 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ for $C^{\circ}_{p,\mathrm{m}}$.

enthalpies of complexation are molar values (K_1 = 171 M^{-1}, ΔH_1 = – 21.8 $\mathrm{kJ{\cdot}mol^{-1}}$ (– 5.15 $\mathrm{kcal{\cdot}mol^{-1}}$), K_2 = 8.8 M^{-1}, ΔH_2 = 60.2 $\mathrm{kJ{\cdot}mol^{-1}}$, (14.4 $\mathrm{kcal{\cdot}mol^{-1}}$). Comparison of the reported enthalpy of complexation values with those from other studies [1960KUM], [1962DAV/SMI] and with values noted by the authors for the enthalpy of dissociation of $\mathrm{HSO_4^-}$ indicate that there is an error in sign in the reported values of ΔH_1 and ΔH_2. Contrary to the text, these seem to be values for enthalpies of dissociation, rather than enthalpies of association. Insufficient data and experimental information have been provided to allow a proper re-evaluation of the results of this study.

[1963BER/KOV]

The authors performed thermal-analysis measurements of the decomposition of $\mathrm{Fe(OH)_2(s)}$ as a function of applied $\mathrm{N_2}$ pressure. They observed a p-dependent endotherm at 308 to 386 K and a p-independent crystallization endotherm at ~613 K (onset temperatures). Specimens heated to 673 K were identified by electron diffraction as pure $\mathrm{Fe_3O_4}$. Similar measurements were performed on $\mathrm{Mn(OH)_2}$.

The authors' interpretation of the onset T of the endothermic feature as a function of applied p as an equilibrium decomposition,

$$3\,\mathrm{Fe(OH)_2(cr)} \rightleftharpoons \mathrm{Fe_3O_4(cr)} + \mathrm{H_2(g)} + 2\,\mathrm{H_2O(g)},$$

is dubious, though this is a reasonable overall stoichiometry for the decomposition-recrystallization sequence. The reverse reaction is not observed (ever?). The possibility of a transitory, metastable wüstite intermediate is not addressed. The large recrystallization exotherm implies major particle-size (surface and/or defect energy) contributions to the thermochemistry. Indeed, the authors note that their value of $\Delta_r H$ = 233.5 $\mathrm{kJ{\cdot}mol^{-1}}$ (presumably based on $3\mathrm{Fe(OH)_2}$) is affected by the "large heat content of the very finely divided [magnetite] formed in the reaction"; the thermal effect associated with magnetite crystal growth was estimated to be about – 130 $\mathrm{kJ{\cdot}mol^{-1}}$.

[1963BOL/ARV]

The first hydrolysis constants for $\mathrm{Fe^{2+}}$ were reported at 20, 25, 35 and 40 °C from potentiometric titrations with a glass electrode over a range of $\mathrm{NaClO_4}$-controlled ionic strengths, but are more than two orders of magnitude higher than the wide ranging values reported by other workers. The simplest explanation for this discrepancy would be the presence of major iron(III) impurities.

No useful thermodynamic data can be obtained from this work.

[1963DAU/DAU]

See the entry for [1964DAU/DAU] in this Appendix.

[1963DAU/DAU2]

See the entry for [1964DAU/DAU] in this Appendix.

[1963HEI/CLE]

This paper reported the results of a spectrophotometry study on the effect of the nature of the supporting electrolyte (perchlorate salts, 1 to 5 M) upon the value of the formation constant for the 1:1 chlorido complex of Fe^{3+}. The spectral effect observed when Na^+ is replaced by H^+ at constant ionic strengths is due to the increase in the formation constant of the inner-sphere complex $FeCl^{2+}$. Li^+ has a weaker effect than H^+. The reported experimental uncertainties assigned by the authors were deemed to be satisfactory, and were used in the present review.

The molar concentrations and formation constants have been converted to molal values by using values from Table II-5 (with the same method described for the mixed-electrolyte solutions in the Appendix A entry for [1942RAB/STO]). SIT extrapolations (*cf.* Section VIII.2.3, main text) have been used to obtain values of (1.51 ± 0.04) ($HClO_4$ solutions) and (1.46 ± 0.05) (mixed $HClO_4$/$NaClO_4$ solutions) for $\log_{10} K_1^\circ$ (statistical uncertainties). In the present review the uncertainties in the logarithmic values from these extrapolations are estimated as ± 0.10.

[1963ING]

This report was not available to the present reviewer, but the data were used by Kellogg (see the entry for [1964KEL] in this review).

[1963KAL]

The author reported measurements of the heat capacity of a natural sample of siderite (97% $FeCO_3$, but the composition of the other components was not reported) from 1.6 to 20 K using a "vacuum calorimeter" and from 12 to ~ 63 K using an adiabatic vacuum calorimeter. As the temperature increases, the heat-capacity values go through a rather broad maximum near 30.6 K. There is no indication of a maximum in the plot of C_p *vs.* T at lower temperatures near 0 K.

These measurements appear to have been done with considerable care. Unfortunately, the original data were not reported, though they are plotted in a small figure. The integrated value of C_p / T from 0 to 70 K is reported as 16.8 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ in a later paper from the same group [1964KOS/KAL]. Approximate heat-capacity values were estimated from the author's Figure 1. Functions of C_p / T were fitted to these values, and integration of these functions generated a somewhat smaller value for the entropy, 15.0 $J{\cdot}K^{-1}{\cdot}mol^{-1}$. The maximum was found at a temperature almost 10 K lower than the Néel temperature, and is much broader than was reported by Robie *et al.* [1984ROB/HAS].

Also see the discussion of [1964KOS/KAL].

[1963SCH/MIC]

Solubility measurements are reported for "amorphous inactive $Fe(OH)_3$" and α-FeOOH, characterized by XRD. This is another experimental study of the solubility of amorphous iron(III) hydroxide that was either precipitated *in situ* from a 3 M ionic strength ($NaClO_4$) solution at (25.0 ± 0.5) °C whereby the solution was sampled after one year had elapsed, or a "dissolution" method was employed with a two-year equilibration period and no $Fe(ClO_4)_2$ added to the starting solution. These experiments yielded values for the concentration quotients, ${}^*K_{s,0}/M^{-2} = c_{Fe^{3+}}/c^3_{H^+}$ of $10^{(3.55 \pm 0.1)}$ for "inactive" $Fe(OH)_3$ and $10^{(1.4 \pm 0.8)}$ for α-FeOOH. Comparison with a value of $10^{(3.96 \pm 0.1)}$ from [1957BIE/SCH] for "active $Fe(OH)_3$", *i.e.,* material aged for 200 hours, yielded the following Gibbs energies of reaction:

$$\Delta_r G^o_m\ (Fe(OH)_3,\ am,\ \text{“active”} \rightarrow Fe(OH)_3,\ am,\ \text{“inactive”},\ 298\ K) = -(2.34 \pm 0.81)\ kJ{\cdot}mol^{-1}$$

$$\Delta_r G^o_m\ (Fe(OH)_3,\ am,\ \text{“inactive”} \rightarrow \alpha\text{-}FeOOH + H_2O(l),\ 298\ K) = -(12.27 \pm 4.60)\ kJ{\cdot}mol^{-1}.$$

The solubility data for 13 solutions are tabulated for the former method, broken down into two sets of initially different hydrogen ion concentrations. An average of these values, most of which were measured in duplicate, in fact yields $\log_{10} {}^*K_{s,0}$ = (3.51 ± 0.16).

The exact nature of the "$Fe(OH)_3$" specimens is unknown, since this work predates the characterization of ferrihydrites. Although both solids were described as amorphous, the "active" material was probably either a 2-line or intermediate ferrihydrite, while the "inactive" material (given the long period of aging) was most likely a 6-line ferrihydrite.

The results for only five solutions were tabulated where the second "dissolution" approach was utilized, and in these cases the solids were characterized as being: "inactive" $Fe(OH)_3$, "inactive" $Fe(OH)_3$ + α-FeOOH + α-Fe_2O_3, and α-FeOOH + α-Fe_2O_3, and yet the average $\log_{10} {}^*K_{s,0}$ is (3.26 ± 0.14), which is within the combined uncertainties from the two approaches.

A third series of five experiments was tabulated in which the freshly prepared $Fe(OH)_3$(am) mixture was treated with additional $Fe(ClO_4)_2$ in aqueous solution, which according to Glemser and Rieck [1958GLE/RIE] has the effect of catalyzing the conversion of the amorphous precipitate to largely α-FeOOH; a process that is claimed to occur within one hour at pH ~ 7. Acidification of this mixture was believed to dissolve the remaining "active" $Fe(OH)_3$(am) so that after *ca.* 13 days (further sampling after *ca.* 34 days showed almost no change in $\log_{10} {}^*K_{s,0}$) $\log_{10} {}^*K_{s,0}$ values of 2.19, 1.34, 0.62 and −0.18 were reported (the fifth experiment resulted in the complete dissolution of the solid). As mentioned above, the authors provided an average for all four results as (1.4 ± 0.8) (this reviewer finds (1.7 ± 0.7)), which they attributed to the solubility of fine needle-like crystals of α-FeOOH. Finally, combining these very scattered and limited results for α-FeOOH with those for the "inactive" $Fe(OH)_3$(am) gives a difference in $\Delta_f G$ between these two solids of (10.3 ± 0.9) $kJ{\cdot}mol^{-1}$.

The solubility product reported here for "inactive" $Fe(OH)_3$ aged for one year ($\log_{10} K_{s,0} = -(39.0 \pm 0.1)$ at 25 °C, $I_m = 3.5$, $NaClO_4$) is virtually identical to that reported in the same year by one of the same authors, Feitknecht [1961LEN/BUS] for $Fe(OH)_3$ aged for only two hours: $\log_{10} K_{s,0} = -38.9$ at 20 °C ($I_m = 3.5$, $NaClO_4$), albeit from only one experimental point in the latter study. Also the projected difference in the Gibbs energy of the fresh *vs*. aged $Fe(OH)_3$ and that of α-FeOOH is very different from these two studies. Clearly identification of the exact morphology of the solid phases must be uncertain in these early studies, particularly in reference to the degree of crystallinity and size of the particulates formed, such that no reliable thermodynamic data can be gleaned from this and the companion study.

[1963SUS/PRO]

The vapour pressures over solutions of $FeCl_3$-HCl-H_2O are reported at 25 °C with some measurements being made for the $FeCl_3$-H_2O and HCl-H_2O binaries. The concentrations of the component ions were determined analytically by wet-chemistry techniques. The reported mole fractions and pressures (units were not defined but are in fact, mm Hg) for the $FeCl_3$-H_2O system are converted to molalities and osmotic coefficients in the following table.

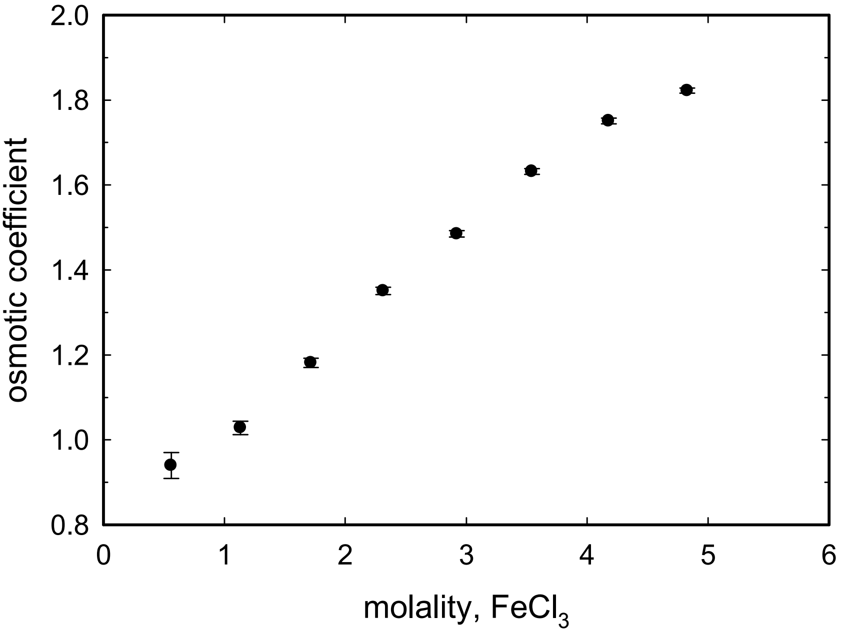
The uncertainties in the osmotic coefficient were calculated assuming an experimental error in reading the vapour pressure amounting to ± 0.02 mm Hg.

In view of the unknown contributions of HCl to the vapour pressure of the solvent, the values above 1.717 $mol \cdot kg^{-1}$ were not used in determining the interaction parameters. However, all of these results are plotted in Figure A-13 and with the exception of the lowest value appear to be in very good agreement with osmotic coefficients derived from isopiestic measurements [2004MOO/HAG]. All but the first equilibration, which they may have rejected without comment, were recalculated in [2004MOO/HAG], although they obtained slightly lower coefficients.

Table A-18: Osmotic coefficients of $FeCl_3$ at 25 °C.

Molality $FeCl_3$	Osmotic coefficient	1σ
0.5607	0.9396	0.0306
1.133	1.0284	0.0158
1.717	1.1816	0.0111
2.313	1.3507	0.0089
2.921	1.4849	0.0077
3.543	1.6320	0.0071
4.178	1.7510	0.0067
4.827	1.8224	0.0064

Figure A-13: Osmotic coefficient of iron(III) chloride solutions as a function of concentration at 25 °C.



[1963WIL]

This paper deals primarily with the influence of the iron(III) complex formation upon the kinetics of electron-exchange reactions. As a complement to the kinetics investigations, Willix reported results of spectroscopic and potentiometric experiments leading to values for the association constant between Fe^{3+} and SO_4^{2-}. The spectrophotometric measurements were carried out between 330 and 360 nm and at 1, 11 and 22 °C. The solutions were 4.35×10^{-3} M in total sulfate, 0.0078, 0.0156, 0.0234 and 0.0313 M in iron(III), 0.111, 0.223 and 0.334 M in total acid ($HClO_4$). The ionic strength in all solutions was 0.5 M ($NaClO_4$ was used as the other supporting electrolyte). From the linear variation of the optical density with respect to total iron(III) molarity, and then from the average slopes with respect to total acid concentration, values for K_{1c} were calculated to be 86, 129 and 199 M^{-1} for 1, 11 and 22 °C, respectively.

Potentiometric measurements were done using the cell

$$\begin{array}{c|l::l::l|c} & \mathrm{HClO_4(sln,c_1),\ NaClO_4(sln,c_2)} & \text{agar} & \mathrm{HClO_4(sln,c_1),\ NaClO_4(sln,c_2)} & \\ \mathrm{Au} & \mathrm{Fe(ClO_4)_3(sln,c_3),} & 2\ \mathrm{M} & \mathrm{Fe(ClO_4)_3(sln,c_3),} & \mathrm{Au} \\ & \mathrm{Fe(ClO_4)_2(sln,c_4)} & \mathrm{NaClO_4} & \mathrm{Fe(ClO_4)_2(sln,c_4)} & \\ & & & \mathrm{Na_2SO_4(sln,\ variable)} & \end{array}$$

($c_{\mathrm{H^+}_{\mathrm{total}}}$ = 0.100 to 0.499 M; for other solutes, for one specific titration the concentrations used were: $c_{\mathrm{Fe(III)}_{\mathrm{total}}} = 12.17 \times 10^{-4}$ M, $c_{\mathrm{Fe(II)}_{\mathrm{total}}} = 4.48 \times 10^{-4}$ M and $c_{\mathrm{SO_4^{2-}}_{\mathrm{total}}}$ = 0.059 to 1.089×10^{-3} M. The authors' Figure 1 suggests that similar concentrations were used throughout). The ionic strength was maintained at I = 0.5 M ($NaClO_4$). The values reported for K_{1c} (75 and 211 M^{-1} for 0 and 25 °C, respectively) were obtained from extrapolations against the HSO_4^- to H^+ ratio. Values of K_{2c} from the same calculations were reported to be similar to those found by Mattoo [1959MAT].

An extended Debye-Hückel method was used to estimate a value of (25.9 ± 1.3) kJ·mol^{-1} ((6.2 ± 0.3) kcal·mol^{-1}) for $\Delta_r H_1^\circ$ at 25 °C, and 1.41×10^{-4} M^{-1} for K_1°.

Based on a study of the kinetics of the Fe(III)-Fe(II) exchange reaction, further values of 68 and 198 M^{-1} were obtained for K_{1c} at 0 and 25 °C, respectively (I = 0.5 M).

In all their experiments the authors assumed that only negligible concentrations of $FeHSO_4^{2+}$ were formed. The reported "molar" concentrations at all temperatures were probably the room-temperature molar concentrations. The authors reported use of values of 0.084, 0.064 and 0.042 M for 0, 11 and 25 °C and I equal to 0.5 M for $K^{-1}_{c1,1(\mathrm{HSO_4^-})}$, the deprotonation constant of HSO_4^- (the notation in the original paper was K_a); however, the values used for 1 and 22 °C were not specifically noted.

The original results have been converted to the molal scale and recalculated with $K_{m1,1(\mathrm{HSO_4^-})}$ as redetermined using TDB auxiliary data. The values of $K_{1\mathrm{FeSO_4^+}}$ and $K_{2\mathrm{Fe(SO_4)_2^-}}$ at 25 °C from this paper have been included in the set of the values used for the SIT optimization of the K_n° and $\Delta\varepsilon$ values.

A list of potential differences between the two half cells described above, as a function of the sulfate molarity, is given in the original paper (Table 2, p.1321). The method of calculation used was that described above in the Appendix A entry for the paper of Mattoo [1959MAT]. A value of (19.6 ± 2.7) mol^{-1}·kg was derived for $K_{m1,1(\mathrm{HSO_4^-})}$ using the SIT, in contrast to the value of 23.8 mol^{-1}·dm^3 in the original paper.

The values of $[\mathrm{SO_4^{2-}}] \times 10^2$ M given in Table 2 of the original paper are not free sulfate ion concentrations but total sulfate concentrations. The recalculation of $K_{1\mathrm{FeSO_4^+}}$ and $K_{2\mathrm{Fe(SO_4)_2^-}}$ by the SIT method, taking into account the $\mathrm{Fe^{2+}/SO_4^{2-}}$

association, and using 6 kg·mol^{-1} for $K_{1m\mathrm{FeHSO_4^{2+}}}$, produces: $K_{1m\mathrm{FeSO_4^+}}$ = (275 ± 30) kg·mol^{-1} and $K_{2m\mathrm{Fe(SO_4)_2^-}}$ = (12 ± 1) kg^2·mol^{-2} (I_m = 0.5).

The $K_{1m\mathrm{FeSO_4^+}}$ value obtained by potentiometry is greater than the original one, and rather high when compared to other literature values at the same ionic strength. One reason for that might have been the junction potential which would have varied upon addition of Na_2SO_4 in the working compartment of the cell. The free acidity $m_{\mathrm{H^+}}$ was 0.125 mol·kg^{-1} at the beginning of the additions and 0.05 mol·kg^{-1} at the end. In the original paper the $K_{1c\mathrm{FeSO_4^+}}$ value from potentiometry is close to the values from spectrophotometry and kinetics. This could have been fortuitous because not accounting for the $\mathrm{Fe^{2+}}$-$\mathrm{SO_4^{2-}}$ association would have led to assignment of a lower constant, and neglecting the junction potentials, mainly due to differences of acidity in the two half cells would have increased it. A very rough estimate, supposing that the junction potential was mainly due to these differences in $m_{\mathrm{H^+}}$, indicates that the potential of the cell used would have varied by +23 mV between the beginning and end of the experiment. Therefore, the recalculated potentiometric $K_{1\mathrm{HSO_4^-}}$ value was not used for the overall optimization in the present review.

The values of $K_{m1,1(\mathrm{HSO_4^-})}$ for re-analysis of the kinetic and spectrophotometric data were obtained using the SIT and the value of $K^{\circ}_{1,1(\mathrm{HSO_4^-})}$ from Chapter IV. For 25 °C and I_c equal to 0.5 mol·dm^{-3}, $K_{c1,1(\mathrm{HSO_4^-})}$ is 23.8 mol^{-1}·dm^3 in the original paper, but $K_{m1,1(\mathrm{HSO_4^-})}$ is 19.6 mol^{-1}·kg based on the TDB auxilliary data values. In addition the value of the formation constant of $\mathrm{FeSO_4^+}$ from spectrophotometry at 22 °C in the original paper has been corrected to obtain the 25 °C value in the same manner described in other Appendix A synopses (*e.g.*, for [1953WHI/DAV]).

The spectrophotometric data of Willix at several temperatures were treated by the SIT formulation to get a value of $\Delta_{\mathrm{r}}H_{1m}$ by applying the van't Hoff formula:

$$\mathrm{d}(\ln K_{1m})/\mathrm{d}(1/T) = -\Delta_{\mathrm{r}}H_{1m}/R \qquad \text{(A.61)}$$

With $K_{1m\mathrm{FeSO_4^+}}$ values of (76 ± 7) kg·mol^{-1} at 274.15 K, (113 ± 10) kg·mol^{-1} at 284.15 K and (175 ± 20) kg·mol^{-1} at 295.15 K, a value of (26.7 ± 2) kJ·mol^{-1} is calculated for $\Delta_{\mathrm{r}}H_{1m}$.

[1964BAR]

Solid-state cell-potential measurements are reported for five cells, three of which provide measurements of the Fe-wüstite-Fe_3O_4 eutectoid temperature, T_c (the other two were designed to measure the potential of the W-WO_2 couple). A change in slope of the potential-difference *vs*. T plots marks a change in composition of one of the electrodes from [Fe + Fe_3O_4] below T_c to either [Fe + wüstite] or [wüstite + Fe_3O_4] above T_c (depending on the overall electrode composition). These two electrode types are here denoted Fe-O(I) and Fe-O(II). The following results were obtained, E values being estimated from the figures with an experimental uncertainty of at least 3 mV.

Cell [1], Ni-NiO *vs*. Fe-O(I): $T_c = 842$ K, $E = 232.4$ mV

Cell [2], Ni-NiO *vs*. Fe-O(II): $T_c = 850$ K, $E = 233.8$ mV

Cell [5], Mo-MoO_2 *vs*. Fe-O(II): $T_c = 845$ K, E = 30.6 mV

The values of T_c are discussed further in Section VII.2.8.3. Because of the likelihood of mixed (three-oxide) potentials in the vicinity of T_c, potential data obtained below T_c were not included in the discussion of $\Delta_f H_m^o$ (Fe_3O_4, cr, 298.15 K) in Section VII.2.7.2.3. The cell-potential values at T_c for Cells [1] and [2] are about 9 mV lower than expected from more recent, high-precision measurements (*e.g.*, [1986HOL/NEI]).

Note the similar study of the wüstite eutectoid by Birks [1966BIR].

[1964BAR2]

Sixteen solid-state cell-potential measurements are tabulated for wüstite of variable composition ($Fe_{0.899}O$ to $Fe_{0.953}O$) *vs*. the Fe-wüstite buffer at 973 to 1173 K, and more data are depicted in figures. The eutectoid point is estimated to be $Fe_{0.939}O$ at 842 K. The study is largely beyond the scope of the current review, except that a slightly non-linear relationship was observed between composition (expressed as O/Fe) and potential-difference values, and hence oxygen chemical potential. Note the critique of this study by Giddings and Gordon [1973GID/GOR], who point out the difficulty of obtaining reliable data at extremely low oxygen chemical potentials with an open cell design employing flowing inert gas.

[1964BRA/ROB]

This paper deals with an X-ray diffraction and a UV-visible spectrophotometry study of aqueous iron(III) chloride solutions. It was found that the Fe(III) species in concentrated solutions of $FeCl_3$ (5 M) depends on the pH. At low pH, polymers built of tetrahedral $FeCl_4^-$ and octahedral $FeCl_4(H_2O)_2^-$ units sharing chloride ions were observed in almost equal quantities. In unacidified solutions the octahedral $FeCl_4(H_2O)_2^-$ species was largely dominant.

The data are not sufficiently precise to support the conclusions in unacidified solutions. In particular the charge balance cannot be understood in terms of the measured pH (≈ 2) which would have precluded the occurrence of any extensive hydrolysis. Such pH measurements in very highly concentrated solutions are questionable.

[1964DAU/DAU]

The authors summarised literature values of the solubility of $Fe(OH)_2$(s) and of Fe(II) hydrolysis constants [1963DAU/DAU]. Later on they reported additional measurements [1963DAU/DAU2]. In this paper $FeCl_2$ solutions were titrated with $Ba(OH)_2$ in aqueous solutions of $BaCl_2$, leading to precipitate formation (the solid was presumed to be $Fe(OH)_2$) at 20 °C. The total concentration of Fe^{2+} and the pH were monitored as a function of the amount of added $Ba(OH)_2$. The solid was not analysed, the method of pH calibration was not described, and attainment of equilibrium was not checked. Evaluation of the results is difficult because there are many unknowns in the system: $K_{s,0}$ ($Fe(OH)_2(s)$), ${}^*\beta_1$ ($FeOH^+$), K_1($FeCl^+$); furthermore, values for ${}^*\beta_1$ ($BaOH^+$) and K_1($BaCl^+$) are required as auxiliary data. Values of the solubility product $c_{Fe^{2+}} c^2_{OH^-}$ were determined to be $(0.76; 0.88; 0.94) \times 10^{-16}$ at $I = (0.015; 0.03; 0.15$ M) at 20 °C. Values of the formation constants of the assumed $FeCl_n^{2-n}$ complexes were calculated from then 'known' values of $K_{s,0}$ ($Fe(OH)_2(s)$). The reported formation constants for $FeCl^+$ (β_1($c_{FeCl^+} / (c_{Fe^{2+}} c_{Cl^-})$)) = 288 to 625 M^{-1}) are unreasonably high. The authors' Equation (1) is unclear (as there is no term involving the concentration of $FeOH^+$). The estimated concentration of the 1:1 complex based on values given for c_{Cl^-}, $c_{Fe^{2+}}$ and β_1 exceeds the total iron concentration in solution. Hence, the reported evaluation leads to incorrect conclusions concerning the value of β_1. The results from this study are not used further in the present review.

[1964FER]

This paper describes the measurement of heats of solution (and hence, of dehydration) of synthetic goethite, as well as two specimens that were partly dehydrated and one essentially fully dehydrated to hematite. The goethite was prepared from a hydrated iron(III) oxide gel according to published procedures [1934FRI/ACK]. The only detected impurities were "traces" of Ca, Al, and Mg. Phase identification was by XRD, and the weight loss near 220 °C corresponded to conversion of FeOOH to Fe_2O_3 (theor. 10.14%) (but not to the tabulated total moisture content of 15.2 weight-%).

All calorimetric experiments were made by dissolving 2.0444 g of the overall composition (with adjusted water content) $Fe_2O_3 \cdot 1.35H_2O$ in (697.0 ± 0.5) g of aqueous HCl containing a small quantity of dissolved $FeCl_3$ (20.68 weight-% Cl, 0.178 weight-% Fe(III)) at 71 °C. Measured temperature increases were of the order of 0.1 °C. The pseudo-adiabatic, graphite calorimeter was described elsewhere [1963FER].

Twenty measurements were made altogether on four specimens: (A) as-prepared, and heated for (B) 80 minutes and (C) 50 hours at 300 °C and (D) for 2 hours at 990 °C; these specimens were analysed for water content and the crystallite size was measured by XRD, and the following calorimetric results (± 2σ) were reported.

Table A-19: Enthalpy of dissolution for goethite and hematite of different crystallite size and water content.

Specimen	$H_2O : Fe_2O_3$ (mass)	$\Delta H_{dissolution}(Fe_2O_3)$/kJ·mol^{-1}	Crystallite size (Å)	Phase identification
A	15.2	− 33.10 ± 0.46	240	α-FeOOH
B	7.9	− 47.03 ± 1.21	73	α-Fe_2O_3
C	3.9	− 46.07 ± 1.21	94	α-Fe_2O_3
D	0.3	− 38.07 ± 1.13	≥170	α-Fe_2O_3

The difference between results for specimens A and D yields: $\Delta_r H^\circ_m$ (2α-FeOOH $\rightleftharpoons$ α-Fe_2O_3 + H_2O(l)) = (5.0 ± 1.3) kJ·mol^{-1}.

The differences between specimens B, C, and D are discussed in terms of particle size and surface enthalpy (as further discussed, for example, by Diakonov *et al.* [1994DIA/KHO]).

The heat of dehydration stated above seems to be a good measure for the conversion of fairly well-crystallized goethite to a comparably well- (or better-) crystallized hematite. This value is retained for further evaluation in the current (OECD/NEA) assessment. Interpretation of the remaining data (for specimens B and C) in terms of particle size alone, however, does not seem justified. There are likely to be significant internal as well as surface-energy contributions, *e.g.*, from crystallographic defects and/or metastable solid solutions of FeOOH in Fe_2O_3 ("protohematite"; see [1991WAY], [1999GUA/VEN]).

[1964HOR/MYE]

The effect of pressure on the complexation of iron(III) by chloride was investigated by conductivity. The conductivity of aqueous Fe(III),Cl^- solutions increases much more with pressure than the conductivity of the corresponding perchlorate or nitrate solutions. This has been attributed to the dissociation of the chlorido complexes under pressure because the complex formation equilibrium is shifted towards the formation of hydrated cations and anions. Increased pressure favors the hydration reactions. Here dissociation of the chlorido complex increases with increasing pressure because the hexaaquo iron(III) ion is formed.

[1964KEL]

Available literature data on high-temperature equilibrium reactions (793 to 997 K) between $Fe_2(SO_4)_3$(cr) and SO_3(g), SO_2(g) and O_2 were reviewed. The equation

$$\Delta_r G^\circ_m/\text{kJ·mol}^{-1} = 609.90 + 0.102311(T/\text{K})\ \log_{10}(T/\text{K}) - 0.89157(T/\text{K})$$

for the reaction

$$Fe_2(SO_4)_3(cr) \rightleftharpoons Fe_2O_3(cr) + 3\,SO_3(g)$$

was fitted to the results of Grünzweig [1913GRU], Neumann and Heintke [1937NEU/HEI], Blanks [1961BLA], Warner and Ingraham [1960WAR/ING], and Ingraham [1963ING]. Several of these papers were unavailable to the present reviewer. The second-law entropy of $Fe_2(SO_4)_3$(cr, 298.15 K) calculated by Kellogg, 261.7 J·K^{-1}·mol^{-1}, is much lower than has been found experimentally [2005MAJ/NAV], and therefore, even though a reasonable value was assumed for the average heat capacity of reaction from 800 to 298.15 K (– 44 J·K^{-1}·mol^{-1}), Kellogg's calculated value of $\Delta_f H^\circ_m$ ($Fe_2(SO_4)_3$,cr), – 2603.4 kJ·mol^{-1}, is probably too negative. A third-law analysis using the entropy value (305.6 J·K^{-1}·mol^{-1}) from Majzlan *et al.* [2005MAJ/NAV], which properly incorporates the magnetic contribution, gives

– 2578 kJ·mol^{-1} for $\Delta_f H_m^o$ ($Fe_2(SO_4)_3$, cr, 298.15 K) based on $\Delta_r G_m$ (900 K), and – 2581 kJ·mol^{-1} based on $\Delta_r G_m$ (800 K). The author used thermodynamic quantities for SO_3(g) and SO_2(g) based on assessed values of $\Delta_f H_m^o$, S_m^o and $C_{p,m}^o$ from Evans and Wagman [1952EVA/WAG]. These are similar to the values reported by Gurvich *et al.* [1989GUR/VEY], and differences affect the calculated value of $\Delta_f H_m^o$ ($Fe_2(SO_4)_3$, cr, 298.15 K) by < 1 kJ·mol^{-1}.

[1964KOH/ZAS2]

Kohler and Zäske carried out closed system measurements of water pressures over $FeSO_4{\cdot}7H_2O$ and its dehydration products at 20 torr (2.7 kPa) as a function of temperature. X-ray diffraction patterns were reported for the monohydrate, tetrahydrate and heptahydrate of $FeSO_4$, and the sequential dehydration produced mixtures of the heptahydrate with the tetrahydrate, and the tetrahydrate with the monohydrate. Above 56 °C, the vapour pressure over the saturated solution is lower than over either salt pair, suggesting that neither the heptahydrate nor the tetrahydrate are stable, and that the heptahydrate is stable with respect to the monohydrate to at least 58 °C (as the vapour pressure over the 7/4 pair is lower than the vapour pressure over the 4/1 pair). Dehydration of the monohydrate required temperatures greater than 190 °C, and resulted in oxidation of the iron and partial decomposition. The original pressure data were not published, only simple linear equations summarizing the results between 40 and 54 °C (the average $\Delta_r G_m$ for dehydration from the heptahydrate to the tetrahydrate was 156.2 kJ·mol^{-1}). Therefore, although the results are extremely useful in assisting with interpretation of the results from other papers (*e.g.*, [1923SCH], [1935BON/BUR]), they are not used in this review for the calculation of the enthalpy and Gibbs energy of dehydration of $FeSO_4{\cdot}7H_2O$(cr) at 298.15 K.

[1964KOS]

Kostryukova reported measurements of the specific heats of $FeCl_2$(cr) for temperatures between 1.8 and 4.0 K. The experimental results were not tabulated in the paper, but could be retrieved from the plots of $T^2C_{p,m}^o$ *vs.* T^5 [1964KOS], [1969KOS], and $C_{p,m}^o$ *vs.* T [1969KOS] (the author used the symbol C for $C_{p,m}^o$). The plot of $T^2C_{p,m}^o$ *vs.* T^5 is linear, but does not extrapolate to 0 J·K·mol^{-1} at T = 0 K. The author fitted an equation of the form

$$C_{p,m}^o\,/\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}} = \mathrm{A}\,(T/\mathrm{K})^3 + \mathrm{B}\,(T/\mathrm{K})^{-2}$$

to her results, and suggested that this indicated another heat-capacity anomaly at even lower temperatures, below 1.8 K. Although the low-temperature behaviour of $FeCl_2$(cr) in a magnetic field is complex [1972BIR/YEL], no further evidence for such a low-temperature heat-capacity transition seems to have been reported in the absence of an applied magnetic field. Unless there is a major undetected anomaly, the contribution from 0 to 4 K to the value of S_m^o ($FeCl_2$, cr, 298.15 K) is (0.05 ± 0.02) J·K^{-1}·mol^{-1}.

[1964KOS/KAL]

The authors reported measurements of the heat capacity of a natural sample of siderite (97% $FeCO_3$, but the composition of the other components was not reported), from ~ 80 to 294 K. The integrated value of the contribution to S°_{m} from 70 to 298.15 K is reported as 79.3 $J \cdot K^{-1} \cdot mol^{-1}$.

The rather sparse heat-capacity values, were recovered from the authors' figure, and second- and third-order polynomials were fitted to the C_p / T values. The functions were integrated, and a similar value for the entropy contribution, 79.0 $J \cdot K^{-1} \cdot mol^{-1}$, was obtained.

Extrapolation of the values of $C_p(T)$ from 202 to 294 K leads to a value of C_p ($FeCO_3$, cr, 298.15 K) of 87.5 $J \cdot K^{-1} \cdot mol^{-1}$.[1]

Because detailed analytical results and the numerical values of C_p were not reported, the values in this paper (and the earlier paper with results for the same sample at lower temperatures [1963KAL]) are not used in the estimation of S°_{m} ($FeCO_3$, cr) in the present review.

[1964PLA]

The author used turbidimetry to detect the onset of precipitation of "$Fe(OH)_3$" during titration of acidic iron(III) sulfate and chloride solutions with NaOH or "NH_4OH" at (25.0 ± 0.3) °C. Results were corrected for complexation of Fe^{3+} with hydroxide (only mononuclear species were considered despite $c_{Fe_{total}}$ as high as 10^{-2} M), chloride, and sulfate, and an activity correction was applied to the resulting free Fe^{3+} concentration. There was also no discussion of how the pH meter was calibrated or what value of pK_w was used with no supporting electrolyte added at maintain a constant ionic strength. The activity product, obtained from 14 measurements at pH values between 2.05 and 3.05, was $a_{Fe^{3+}} \cdot (a_{OH^-})^3 = 10^{-(38.6 \pm 0.4)}$.

The exact nature of the precipitate is unknown, but it is probably best treated as a 2-line ferrihydrite (see [1998JAM/DUT], [2000JAN/COW], [2004MAJ/NAV], and references therein). While every effort seems to have been made to correct for hydrolysis and complexation in order to extract an activity product from the titration/turbidimetry data, the description of the procedure is terse and the tabulated data do not include all the values required for a recalculation of activity coefficients

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[1] The difference between the values of C_p ($FeCO_3$, cr) and C_p ($NiCO_3$, cr) from [2005GAM/BUG] based on the same source [1964KOS/KAL] is inconsistent with the heat-capacity differences between several other pairs of Fe(II) and Ni salts. Yet the difference between the heat capacities (298.15 K) for the Fe(II) and Mn(II) carbonates [1964KOS/KAL] seems to be reasonably consistent with the heat-capacity differences between several other Fe(II) and Mn(II) salts [1982WAG/EVA], [1995ROB/HEM]. This suggests that the TDB value for C_p ($NiCO_3$, cr, 298.15 K) may need to be treated with caution.

with more modern methods (for example, sulfate concentrations and hydroxide titres are not given, so exact ion concentrations are not known).

The measured solubility product appears to represent a supersaturation limit for formation of ferrihydrite, rather than a true equilibrium solubility; this is not necessarily a pH-independent constant. While it therefore may not represent a thermodynamic value, even for a poorly crystalline solid such as 2-line ferrihydrite, the activity product obtained in this study has practical use in defining the concentration limit to *kinetic* stability (supersaturation) of iron(III) solutions over the pH range studied.

[1964TAY/SCH]

The authors reported 196.2, 189.5 and 182.4 $\text{kJ}\cdot\text{mol}^{-1}$ (46.9, 45.3 and 43.6 $\text{kcal}\cdot\text{mol}^{-1}$) for the Gibbs energies of reaction at 1173, 1273 and 1373 K for

$$\text{Fe(cr)} + \tfrac{1}{2}\,\text{SiO}_2\text{(cr)} + \tfrac{1}{2}\,\text{O}_2\text{(g)} \rightleftharpoons \tfrac{1}{2}\,\alpha\text{-Fe}_2\text{SiO}_4,$$

based on potential-difference measurements from the cell

$$\text{Pt, O}_2\text{(g)|Fe, Fe}_2\text{SiO}_4\text{, SiO}_2\text{|ZrO}_2\text{ (+CaO, MgO)|“FeO”, Fe|Pt.}$$

The form of the SiO_2 was not reported. O’Neill [1987NEI2] has shown that the results are reasonably consistent with other studies carried out in the same temperature range. To calculate $\Delta_f H_m^\circ$ (Fe_2SiO_4, α, 298.15 K), the reported enthalpies of reaction are used, along with consistent auxiliary data for quartz ([1989COX/WAG], [1998CAR/SAL]) and oxygen [1989GUR/VEY], and with the values selected in this review for the heat capacity and entropy of α-Fe_2SiO_4 (Section X.2.1.1.1) and Fe(cr) (Section V.2). Values of − 1473.3, − 1474.6 and − 1474.8 $\text{kJ}\cdot\text{mol}^{-1}$ are obtained for 1173, 1273 and 1373 K (assuming the initial SiO_2 to be cristobalite [1982RIC/BOT] rather than quartz would lead to slightly more negative values, − 1473.5, − 1474.9 and − 1475.3 $\text{kJ}\cdot\text{mol}^{-1}$). If the reference electrode values from O’Neill [1987NEI2] are used, values of − 1474.1, − 1475.1 and − 1475.2 $\text{kJ}\cdot\text{mol}^{-1}$ are obtained for $\Delta_f H_m^\circ$ (Fe_2SiO_4, α, 298.15 K) from the data for 1173, 1273 and 1373 K. In this review the 2σ uncertainty of the average value is estimated as ± 1.5 $\text{kJ}\cdot\text{mol}^{-1}$.

[1964VAL/CAR]

A thermodynamic treatment is developed to derive the properties of Fe_3O_4 from oxygen potential and composition data for the wüstite field, obtained by detailed studies in CO-CO_2 atmospheres. The treatment includes “internal boundaries”, *i.e.*, second- or higher-order phase transitions, between three postulated modifications of wüstite (see Section VII.2.8). In the current review, this paper is cited only for the experimental values of the “external” Fe-wüstite and wüstite-Fe_3O_4 boundaries (see Section VII.2.7.2.3). The unusually high eutectoid (Fe-wüstite-Fe_3O_4) temperature of 890 K is discussed under [1965VAL/RAC].

[1964VAL/RAC]

The authors report the following p_{O_2}-T relationships for the Fe-wüstite (p_0) and wüstite-magnetite (p_1) equilibria, based on a combination of thermogravimetric and conductimetric measurements:

$$\log_{10} p_0 = \{6.668 - 27330/T\} \pm 0.069 \text{ (based on 18 data points);} \qquad \text{(A.62)}$$

$$\log_{10} p_1 = \{13.590 - 33495/T\} \pm 0.063 \text{ (based on 10 data points).} \qquad \text{(A.63)}$$

The experimental methods are apparently described elsewhere; the partial pressures are presumably relative to one atmosphere (101.3 kPa).

When the authors pooled their data with those of Darken and Gurry [1945DAR/GUR], they obtained the following variants of the above equations:

$$\log_{10} p_0 = \{6.774 - 27504/T\} \pm 0.100; \qquad \text{(A.64)}$$

$$\log_{10} p_1 = \{13.552 - 33384/T\} \pm 0.170. \qquad \text{(A.65)}$$

Much of the paper is devoted to a discussion of three subphases, denoted W_1, W_2, and W_3, purported to exist within the wüstite field [1963VAL/KLE].

The intersection of Eqs (A.62) and (A.63) yields an Fe-wüstite-magnetite triple point of 890 K, which is significantly higher than most reported estimates, including the value of (847 ± 7) K assessed by Grønvold *et al.* [1993GRO/STO]. The question of wüstite subphases is beyond the scope of the NEA review.

A comprehensive paper on this and related studies was published by Vallet and Raccah [1965VAL/RAC], and is reviewed in more detail.

[1965ALC/SUD]

Alcock *et al.* carried out differential thermal analysis and gravimetric studies of the behaviour of $FeSO_4$(cr), $Fe_2(SO_4)_3$ and Fe_2O_3(cr) in mixtures of SO_2(g), O_2(g) and N_2(g), primarily near 900 K. Equations are presented for the temperature dependence of $\Delta_r G$ for the equilibria:

$$Fe_2O_3\cdot SO_3(cr) + 2\,SO_2(g) + O_2(g) \rightleftharpoons Fe_2O_3\cdot 3SO_3(cr)$$

and

$$2\,Fe_2O_3(cr) + 2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,Fe_2O_3\cdot SO_3(cr).$$

The authors regarded their results as preliminary, and no additional analytical data were presented to corroborate the formation of the two basic iron(III) sulfates. Kellogg [1964KEL] indicated that there was no credible evidence for formation of such basic anhydrous sulfates. This was confirmed by Jacob and Iyengar [1986JAC/IYE], and the results from the study of Alcock *et al.* are not used further in the present review.

[1965BAR]

The heat of formation of goethite was determined from its heat of dissolution, using a natural sample. Results were corrected in accordance with the following chemical analysis (weight-%): 95.12% FeOOH, 1.73% SiO_2, 1.62% H_2O, 0.81% Mn_2O_3, 0.54% Al_2O_3, 0.18% MgO. The heats of dissolution in aqueous HF (20.1 weight-%) were measured for this material (6 measurements) and a reagent-grade hematite powder reference material (5 measurements; dried at 500 °C and containing 0.32 weight-% H_2O). The calorimeter operated at 73.7 °C, and specimens were introduced at a temperature of 25 °C, *i.e.*, heat measurements corresponded to the conversion of pure substances at 25 °C to solution products at 73.7 °C. Specimens were introduced in gelatin capsules or (for goethite) Pt capsules using $KHSO_4$ as a soluble sealant. Measurements were corrected for the heat effects of the capsules, and a previously measured heat of dilution of water under similar conditions was used to derive the heat of reaction given below.

Results yielded $\Delta_r H_m^\circ = -(940 \pm 90)\ \text{cal}\cdot\text{mol}^{-1} = -(3930 \pm 380)\ \text{J}\cdot\text{mol}^{-1}$ for the reaction: $\frac{1}{2}\,\alpha\text{-}Fe_2O_3 + \frac{1}{2}\,H_2O(l) \rightarrow \alpha\text{-}FeOOH$.

This appears to be a careful measurement, which is widely cited in the literature, though perhaps superseded in recent years (see, in particular, [2003MAJ/GRE], [2005MAZ/NAV]). The heat of reaction (rather than the derived heat of formation) is retained for inclusion in the current (OECD/NEA) assessment. The two main drawbacks to this measurement are the relatively high impurity content of the goethite, and the fact that complete dissolution of hematite is often difficult to achieve.

[1965BAR/ADA]

Barany and Adami [1965BAR/ADA] measured the enthalpies of solution of iron(III) sulfate, and aqueous sulfuric acid ($H_2SO_4\cdot14.855H_2O$) at 25 °C into a hydrofluoric acid solution (20.10 weight-% HF) at 73.7 °C (also see [1948TOR/SAH]). From these results and earlier measurements of the heats of solution of hematite [1965BAR] and water [1962BAR] into similar HF solutions, and literature values for the enthalpies of formation of $H_2O(l)$, $H_2SO_4\cdot14.855H_2O(l)$ and hematite (α-Fe_2O_3), a value of $-(2575.59 \pm 2.55)\ \text{kJ}\cdot\text{mol}^{-1}$ was calculated for the enthalpy of formation of $Fe_2(SO_4)_3$ at 298.15 K. In the present review, a recalculation was done using enthalpy of formation data for sulfuric acid solutions from Wagman *et al.* [1982WAG/EVA], adjusted to the CODATA value [1989COX/WAG] for the sulfate ion (hence, $\Delta_f H_m^\circ(H_2SO_4\cdot14.855H_2O, \text{cr}, 298.15\ \text{K}) = -5129.64\ \text{kJ}\cdot\text{mol}^{-1}$), and the selected value (Section VII.2.2.1) for the enthalpy of formation of hematite ($\Delta_f H_m^\circ(Fe_2O_3, \alpha, 298.15\ \text{K}) = -(826.29 \pm 2.63)\ \text{kJ}\cdot\text{mol}^{-1}$). From these, $\Delta_f H_m^\circ(Fe_2(SO_4)_3, \text{cr}, 298.15\ \text{K}) = -(2584.02 \pm 5.00)\ \text{kJ}\cdot\text{mol}^{-1}$), where the uncertainty is estimated in this review. As discussed by Majzlan *et al.* [2005MAJ/NAV], it is not clear whether this value is for the monoclinic or the trigonal form of the solid. The report claims that the X-ray diffraction pattern "agreed with the one given in the ASTM Catalog of X-ray Powder data";

(probably pattern 14-253, source unknown, which apparently was deleted from the ASTM records when later patterns became available). Posnjak and Merwin [1922POS/MER] found both forms in their syntheses.

[1965BIZ/MAI]

This short paper presents a plot of the molar heat capacity of FeF_3(cr) for temperatures between 102 and 445 K. The method used for the measurements is not mentioned; the synthesis is described, but no analytical information is provided. A small thermal anomaly was found at 367 K.

The information in the authors' figure was digitized. A polynomial fit to the values for temperatures from 250 K to 320 K leads to a value of 91.33 $J\cdot K^{-1}\cdot mol^{-1}$ for $C^{o}_{p,m}$ (FeF_3, cr, 298.15 K). Because experimental details are lacking, the uncertainty in this value is estimated in the present review as ± 2.00 $J\cdot K^{-1}\cdot mol^{-1}$. Based on integration of arbitrary functions of C_p/T, the calculated contribution to S^{o}_{m} (FeF_3, cr) from the heat-capacity anomaly at 367 K is ~ 2 $J\cdot K^{-1}\cdot mol^{-1}$ for temperatures above 400 K. This estimate is likely a lower limit, as the anomaly is rather broad, extending below 300 K.

[1965FER]

This paper describes an extension of the work presented by the same author in [1964FER], and presents the measured heats of solution at 70 °C (and hence the relative enthalpies) of a series of goethite/hematite specimens, obtained by calcining synthetic goethite at temperatures from 90 to 990 °C.

All calorimetric experiments correspond to the conversion: [$360\,HCl + 2736\,H_2O + 2\,FeCl_3$](solution) + [$Fe_2O_3\cdot 1.8H_2O$](condensed) $\rightarrow$ [$354\,HCl + 2740.8\,H_2O + 4\,FeCl_3$](solution).

Here, [$Fe_2O_3\cdot 1.8H_2O$](condensed) represents a mixture of any given goethite/hematite specimen and sufficient water to give a constant overall compositon. The pseudo-adiabatic, graphite calorimeter was described elsewhere [1963FER].

Fourteen specimens were studied, and data from 11 phase-pure goethite or hematite specimens (as determined by XRD) were plotted as a function of BET surface area, yielding the estimated surface enthalpies:

$$\Delta H^{o}_{m}\,(\text{surface, }\alpha\text{-FeOOH}) = 0.28\ \text{cal}\cdot\text{m}^{-2} = 1.17\ \text{J}\cdot\text{m}^{-2}\,;$$

$$\Delta H^{o}_{m}\,(\text{surface, }\alpha\text{-Fe}_2\text{O}_3) = 0.18\ \text{cal}\cdot\text{m}^{-2} = 0.75\ \text{J}\cdot\text{m}^{-2}.$$

Extrapolation of the data to zero surface area yields, for well-crystallized goethite and hematite: $\Delta_r H^{o}_{m}$ (2α-FeOOH $\rightarrow$ α-$Fe_2O_3 + H_2O$(l), 343 K) = 3.06 $kcal\cdot mol^{-1}$ = 12.8 $kJ\cdot mol^{-1}$ (see also the discussion by Diakonov *et al.*, based on a slightly different data selection [1994DIA/KHO]) which is significantly higher than the value of (5.0 ± 1.3) $kJ\cdot mol^{-1}$ obtained in [1964FER]. No uncertainty estimate is given for the new value, but it is probably at least ± 5 kJ·mol^{-1}, because there are few data for goethite, especially for coarse-grained material.

While the heats of dissolution seem to be a good measure of the relative enthalpies of the various specimens, interpretation of the data in terms of particle size alone does not seem to be justified. There are likely to be significant internal as well as surface-energy contributions, *e.g.*, from crystallographic defects and/or metastable solid solutions of FeOOH in Fe_2O_3 ("protohematite"; see [1991WAY], [1999GUA/VEN]).

Note that a more detailed account of this work is given in [1966FER].

[1965GER/DOD]

This study of oxygen chemical potential within the wüstite field, derived from measurements in CO-CO_2 atmospheres at 1073 K, is used here only as one of many sources of values for wüstite boundary compositions.

[1965JAM/BRO]

Values of the heats of solution of $FeSO_4{\cdot}7H_2O$ (18.7 kJ·mol^{-1}), and a series of partially dehydrated solids were obtained by dissolution of samples (0.2 to 0.5 g) in 1 L of water 302.15 K (29.0 °C).

The partially dehydrated solids were prepared in three different ways—heating to 100 °C, equilibration over concentrated H_2SO_4 and vacuum dehydration—and the enthalpies of solution of solids appeared to be very much dependent on the mode of preparation. The heats of solution of samples prepared by the last method were much more exothermic (> 30 kJ·mol^{-1} for solid compositions near $FeSO_4{\cdot}4H_2O$) than those prepared by the first two methods. Unfortunately there are no detailed analyses of the solids (aside from water content).

Based on the authors' equation for the samples that were not prepared by vacuum hydration, the enthalpy differences between compositions close to those for the heptahydrate (18.9 kJ·mol^{-1}), tetrahydrate (– 6.8 kJ·mol^{-1}) and monohydrate (– 32.4 kJ·mol^{-1}) are similar to those reported by de Forcrand [1914FOR] at 286.65 K and by Larson [1968LAR] at 298.15 K. However, the value reported by Jamieson *et al.* for the heat of solution of the heptahydrate does seem to be 5 – 6 kJ·mol^{-1} more positive than might be expected for such a low final molality (~ 0.002 m). The details reported are inadequate to allow a direct quantitative comparison of the results.

[1965PAO]

The heat of solution of $FeBr_2$(cr) in water was reported as – 26.16 kcal·mol^{-1}. There was a typographical error in this value, and the corrected value, equivalent to – (84.35 ± 0.25) kJ·mol^{-1}, was published in a correction [1966PAO]. Experimental details are sparse. The reported value is the average of "at least two determinations". Although not stated explicitly, it can be assumed from other papers from the same group that the values are for 298.15 K and a final salt to water ratio of approximately 1:2000

[1964PAO/VAC], [1965PAO/SAB]. Thus, the value for $FeBr_2$ should be comparable to those from Hieber *et al.* [1934HIE/APP] and Li and Gregory [1952LI/GRE]. A limiting-law correction of 1.3 to 1.5 $kJ \cdot mol^{-1}$ can be applied, leading to – 85.7 $kJ \cdot mol^{-1}$, though the final concentration is sufficiently high that it is unlikely that the limiting-law correction is sufficient. Therefore, in the present review, the uncertainty in the enthalpy of solution is estimated as ± 2.0 $kJ \cdot mol^{-1}$.

[1965PAO/SAB]

The heat of solution of $FeI_2(cr)$ in water containing 0.028 m *n*-propyl iodide and "a small quantity of HI" was reported as – (81.42 ± 0.13) $kJ \cdot mol^{-1}$. Experimental details are sparse. The reported value is the average of "at least two determinations", probably at or near 298 K. The final FeI_2 to water molar ratio was approximately 1:4000 [1965PAO/SAB]. A limiting-law correction of 1.1 $kJ \cdot mol^{-1}$ can be applied, leading to – 82.5 $kJ \cdot mol^{-1}$ at infinite dilution, though the final concentration is sufficiently high that it is unlikely that the limiting-law correction is sufficient. Therefore, in the present review, the uncertainty in the enthalpy of solution is estimated as ± 3.0 $kJ \cdot mol^{-1}$. Using our selected value of $\Delta_f H_m^o$ (Fe^{2+}, 298.15 K), – (90.00 ± 0.50) $kJ \cdot mol^{-1}$, $\Delta_f H_m^o$ (FeI_2, cr, 298.15 K) is – (121.1 ± 3.0) $J \cdot K^{-1} \cdot mol^{-1}$.

[1965VAL/RAC]

This paper presents a detailed compilation and interpretation of the results of a major study of wüstite in CO-CO_2 atmospheres. Data are tabulated as $\log_{10} p_{O_2}$ values, and values from [1921CHA], [1945DAR/GUR] and a few other sources are also compiled. A correction of -0.032 to the $\log_{10} p_{O_2}$ values is necessary for consistency with CODATA thermodynamic values for CO and CO_2.

Altogether, 18 measurements are given for the Fe-wüstite boundary at 1053 to 1595 K, 10 for wüstite-Fe_3O_4 at 1073 to 1523 K, and 185 for single-phase wüstite compositions from $FeO_{1.0511}$ to $FeO_{1.1530}$ —essentially the entire composition range— at 1073 to 1523 K. Plots of $\log_{10} p_{O_2}$ *vs.* x in FeO_x were linear at 1193 to 1523 K, but showed "capricious" non-linear behaviour at 1073 to 1173 K.

An unusually high value of 890 K for the Fe-wüstite-Fe_3O_4 eutectoid temperature appears to reflect linear fitting of $\log_{10} p_{O_2}$ *vs.* $1/T$ for the wüstite boundaries over an excessively long T range, and does not indicate poor data quality.

The wüstite phase-boundary data are included in the compilations depicted in Section VII.2.7.2.3 and in the estimate of boundary compositions. They are not included in the estimation of phase-boundary oxygen chemical potentials, because they are superseded by more recent, high-quality cell-potential data such as those of [1988NEI] and [1981JAC/ROS].

[1966BER/SHA]

Equilibrium constants for the reaction

$$\alpha\text{-}Fe_2SiO_4 + 2\,H_2(g) \rightleftharpoons 2\,Fe(cr) + SiO_2(\alpha\text{-quartz}) + 2\,H_2O(g)$$

were reported for temperatures between 1033 and 1403 K, with experiments approaching equilibrium both by reduction and oxidation. The form of the SiO_2 after the experiments was reported to be quartz. The equilibrium constants, when combined with consistent auxiliary data for quartz ([1989COX/WAG], [1998CAR/SAL]) hydrogen and water [1989GUR/VEY]), and with the values selected in this review for the heat capacity and entropy of α-Fe_2SiO_4 (Section X.2.1.1.1) and Fe(cr) (Section V.2) lead to values of $\Delta_f H_m^\circ$ (Fe_2SiO_4, α, 298.15 K) scattered between -1481.3 and -1489.6 $kJ\cdot mol^{-1}$. There are no systematic trends with temperature, nor marked dependence on whether equilibrium was approached by reduction or oxidation. The average value is $-(1486.0 \pm 1.4)$ $kJ\cdot mol^{-1}$ (95% confidence limit), markedly more negative than most other values. The results are not used further in the present review except for comparison purposes.

[1966BIE/CHO]

Experiments were performed at 25 °C with a cell with a liquid junction containing a glass electrode and an Ag,AgCl reference electrode in 0.5 $mol\cdot dm^{-3}$ (NaCl) solutions. The iron(III) concentration was varied from 0.001 to 0.025 $mol\cdot dm^{-3}$ while maintaining a Fe(III)/Fe(II) ratio of 0.3 to 3. In 60 experiments the authors claim to have reached a steady-state pseudo-equilibrium after about three weeks with the precipitation of a fine solid phase that corresponds to the following reaction:

$$Fe^{3+} + n\,H_2O(l) + (3-n)\,Cl^- \rightleftharpoons Fe(OH)_nCl_{(3-n)}(s) + n\,H^+.$$

From a plot of $\log_{10}[Fe^{3+}]$ *vs.* $\log_{10}[H^+]$ over a range of the latter from -1.8 to -3.0 an excellent straight line was drawn: $\log_{10}[Fe^{3+}] - n\log_{10}[H^+] = 3.04$, such that $\log_{10}{}^*K = -(3.04 \pm 0.05)$ and $n = (2.7 \pm 0.02)$ in 0.5 $mol\cdot dm^{-3}$ (NaCl). Furthermore, they used an indirect light-scattering technique to convince themselves that no hydrolyzed Fe(III) existed in solution under their experimental conditions. They were unable to isolate and hence analyze the solid, although XRD data for some of the precipitates were obtained and published elsewhere.

The assumption was made based on previous literature values for the formation of chlorido complexes that the dominant Fe species in solution would be $FeCl^{2+}$, $FeCl_2^+$ and $FeCl^+$. This is certainly an overestimation in the latter case and involves serious uncertainties with the estimation of activity coefficients *vs.* mass action considerations in this chloride medium. These formation constants were not given and without varying the chloride concentration, no check could be made of the chloride composition of the solid. However, the weakest aspect of this report is the claim that Fe^{3+} does not hydrolyze in these solutions with $\log_{10}[H^+]$ as low as -3, an assumption that is at odds with copious data in the literature on Fe^{3+} hydrolysis. Therefore, the results of this study are not retained by this review.

[1966BIR]

Solid-state cell-potential measurements are reported for Fe-wüstite (at ~913 to 1143 K) and Fe-Fe_3O_4 (at ~703 to 833 K) *vs*. Ni-NiO, and for Fe-wüstite *vs*. wüstite-Fe_3O_4 at ~ 873 to 1073 K, all using a CaO-stabilized ZrO_2 electrolyte. The author was able to extend measurements to such low temperatures by using a high-density electrolyte fired at about 1870 K. A Fe-wüstite-Fe_3O_4 eutectoid temperature of 833 K was obtained. Data are depicted but not tabulated. Measurement of the positions of data points in Fig. 1 of this paper yields values for $\Delta_f G_m^o$ (Fe_3O_4, cr, T), and hence of $\Delta_f H_m^o$ (Fe_3O_4, cr, 298.15 K), that average 3.8 $kJ \cdot mol^{-1}$ more negative than values obtained from O'Neill's oxygen chemical potential expression [1988NEI].

Measurements extend to lower temperatures than usual for similar cell-potential studies, there is relatively large experimental scatter as compared with [1988NEI], and there is some additional uncertainty about the Ni-NiO reference electrode potential. For these reasons, data from this study are not used in the final assessment of $\Delta_f H_m^o$ (Fe_3O_4, cr, 298.15 K).

[1966FER]

The surface enthalpies of hematite and goethite were estimated by measuring the heats of dissolution and surface areas (BET method) of finely divided specimens of both phases, as well as estimating their crystallite size by XRD. A combination of four low-temperature goethite syntheses and up to 6 subsequent heat treatments yielded 5 goethite and 8 hematite specimens, plus mixtures in a few cases. Solids were analysed for H_2O content and water was added to each dissolution sample to give a constant overall composition $Fe_2O_3 \cdot 1.8H_2O$, thus avoiding the need to correct for the enthalpy of dilution. Heats of dissolution at 343 K were measured (5 runs per specimen) with 2.134 g of specimen and 697 g of solvent (aqueous HCl containing a small quantity of $FeCl_3$) according to the overall stoichiometry:

$$[360HCl \cdot 2736H_2O \cdot 2FeCl_3](l) + [Fe_2O_3 \cdot 1.8H_2O](s{+}l) \rightleftharpoons$$
$$[354HCl \cdot 2740.8H_2O \cdot 4FeCl_3](l).$$

To interpret the results, Ferrier hypothesized that: (i) the heats of formation and disappearance of solid surfaces are equal, and constant for a given material; (ii) surface enthalpy is the principal term responsible for the observed differences in heats of dissolution (for different specimens of each phase); (iii) the surface area measured by the BET method at 77 K is unchanged at the dissolution temperature of 343 K.

There was relatively poor agreement between XRD crystallite size and BET surface area, partly due to the inability to correct for instrumental broadening of the XRD lines for the coarser-grained specimens. The BET measurements were therefore preferred for estimating surface enthalpy. Linear regression of $\Delta_{\mathrm{diss}}H^{\circ}_{\mathrm{m}}$ *vs.* BET surface area for each solid yielded the relationship:

$$2\,\alpha\text{-FeOOH} + 0.8\,\mathrm{H_2O(ads + l)} \rightleftharpoons \alpha\text{-Fe}_2\mathrm{O}_3 + 1.8\,\mathrm{H_2O(ads + l)}$$

$$\Delta_{\mathrm{r}}H^{\circ}_{\mathrm{m}}/\mathrm{kJ\cdot mol^{-1}} = 14.40 + 0.7732\varepsilon_2 - 1.2477\varepsilon_1 = 14.40 + \frac{1431}{l_2} + \frac{3025}{l_1}$$

where ε_2 and ε_1 are the molar surface areas (in thousands of $\mathrm{m^2\cdot mol^{-1}}$) for 2FeOOH and $\mathrm{Fe_2O_3}$, and l_2 and l_1 are the equivalent cubic particle dimensions in Å (note that the usual fine needle habit of goethite is not well represented by a cubic approximation). The uncertainty of individual enthalpy measurements was estimated to be about ± 1 $\mathrm{kJ\cdot mol^{-1}}$, but the uncertainty in surface area dominated the linear regression.

The implied value of 14.40 $\mathrm{kJ\cdot mol^{-1}}$ for the enthalpy of conversion of coarse-grained goethite to hematite + water at 343 K is retained for further discussion in Section VII.2.9. Reanalysis of Ferrier's data by [1994DIA/KHO] yielded a 298 K value of (13.7 ± 2.4) $\mathrm{kJ\cdot mol^{-1}}$.

While the extrapolation to zero surface area gives a reasonable enthalpy value for the interconversion of coarsely crystalline phases, the derived surface enthalpies are much less reliable. It is likely that the dehydration of goethite at temperatures as low as 300 °C, as used by Ferrier, yielded a poorly crystalline (defective) hematite, *i.e.*, with a significant internal excess enthalpy in addition to the surface enthalpy. In other words, the second of Ferrier's three hypotheses, cited above, is probably not valid.

Note that Ferrier also published two preliminary communications and a later summary of this work ([1964FER], [1965FER], [1968FER]).

[1966LOF/MCI]

Lofgren and McIver carried out measurements of the potentials of the cells $\mathrm{Ni,NiF_2\,|\,CaF_2\,|\,FeF_2,\ Fe}$ and $\mathrm{Ni,NiF_2\,|\,CaF_2,\ (YF_3,\ 3\%\ by\ weight)\,|\,FeF_2,Fe}$ at temperatures from 873 to 1003 K.

Although the results were not tabulated, a good plot was provided, and Bagshaw [1972BAG] reported a linear equation that was an excellent fit to the data:

$$E(\mathrm{A.66})/\mathrm{mV} = 278.3_8 + 0.1_1\,(T/\mathrm{K})$$

$$\mathrm{NiF_2(cr) + Fe(cr) \rightleftharpoons FeF_2(cr) + Ni(cr)} \qquad (\mathrm{A.66})$$

A third-law analysis of the results was done using auxiliary values from the present review, and thermodynamic quantities for Ni(cr) and $\mathrm{NiF_2(cr)}$ from Gamsjäger *et al.* [2005GAM/BUG]. This leads to values of -712.4 and -712.0 $\mathrm{kJ\cdot mol^{-1}}$ for $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($\mathrm{FeF_2}$, cr, 298.15 K) based on the potentials (from the Bagshaw equation) at 873 and 1003 K.

[1966PAO]

This note corrects a typographical error in [1965PAO].

[1966SCH/MUA]

Equilibrium constants of the reduction reaction

$$\alpha\text{-}Fe_2SiO_4 + 2\,CO(g) \rightleftharpoons 2\,Fe(cr) + SiO_2(cr) + 2\,CO_2(g)$$

were reported for 1273, 1373 and 1423 K. These equilibrium constants, when combined with consistent auxiliary data for quartz ([1989COX/WAG], [1998CAR/SAL]) and carbon dioxide and carbon monoxide [1989GUR/VEY]), and with the values selected in this review for the heat capacity and entropy of α-Fe_2SiO_4 (Section X.2.1.1.1) and Fe(cr) (Section V.2) led to values of $\Delta_f H_m^\circ$ (Fe_2SiO_4, α, 298.15 K) of -1477.5, -1478.0 and -1476.8 kJ·mol^{-1}. The form of the product SiO_2 was not explicitly stated. In the present review, the 2σ uncertainty in the average value is estimated as ± 1.5 kJ·mol^{-1}.

[1966SZY/BUR]

This paper describes magnetic susceptibility measurements on natural and synthetic goethite (α-FeOOH) specimens, with emphasis on variations in the Néel transition at ~ 320 - 370 K. Previous Mössbauer studies are also discussed.

[1966TRA]

Heats of solution of powder samples of α-, γ-, and ε-Fe_2O_3 in aqueous HCl (density 1.19 g·cm^{-3}) were measured at 25 °C. The results, corrected for excess water content and heats of wetting, yield the following transformation enthalpies.

$$\Delta_{trs} H_m^\circ (Fe_2O_3, \gamma\rightarrow\alpha, 298.15\ K) = -(19.5 \pm 6.5)\ kJ\cdot mol^{-1}$$

$$\Delta_{trs} H_m^\circ (Fe_2O_3, \varepsilon\rightarrow\alpha, 298.15\ K) = -(28.2 \pm 6.5)\ kJ\cdot mol^{-1}$$

Guinier-type XRD photographs are reproduced in the paper, but no particle size or surface-area data are given. Based on the XRD pattern, the ε-Fe_2O_3 specimen was evidently much more poorly crystalline than the other two polymorphs. The α-Fe_2O_3 specimen was prepared by heating "amorphous ferric hydroxide" in air at 400 °C for 48 hours. The fact that the heat of dissolution could be measured at 25 °C indicates that this specimen was more reactive than most hematite samples, which is consistent with the relatively low synthesis temperature.

The result for ε-Fe_2O_3 remains the only thermodynamic measurement for this polymorph, but that for γ-Fe_2O_3 has been superseded by [2003MAJ/GRE]; see Sections VII.2.4.2 and VII.2.6.

[1966ZAU/GRE]

Zaugg and Gregory carried out transpiration experiments on the equilibrium

$$Fe(cr) + I_2(g) \rightleftharpoons FeI_2(cr) \qquad (A.67)$$

for temperatures between 771 and 858 K. A flow of argon was passed over FeI_2(cr), and the resulting mixture of FeI_2(g) and decomposition products including I_2(g) were equilibrated with FeI_2(cr) and FeI_2(cr)-Fe(cr) mixtures. Different amounts of I_2(g) were also added to the gas stream. The equilibrated gas stream was passed through a cooler section to condense FeI_2, and then through a cold trap to collect the more-volatile iodine-containing species. The argon was collected in a second trap. After correction for iron(III) species and the equilibrium between I_2(g) and I(g), the calculated partial pressure of I_2(g) was used to calculate the equilibrium constant for Reaction (A.67). From a second-law and attempted third-law analysis, the authors proposed – (24 ± 1) kcal·mol^{-1} (*i.e.*, – (100.4 ± 4.2) kJ·mol^{-1}) for $\Delta_f H_m^o$ (FeI_2, cr, 298.15 K).

This value was used as a major component in the selection of – (104.6 ± 8.4) kJ·mol^{-1} by JANAF [1971STU/PRO], [1998CHA] in 1966, but does not compare well with much more negative values (~ – 120 kJ·mol^{-1}) based on solution calorimetry [1934HIE/WOE], [1990EFI/EVD].

Bartovská *et al.* [1968BAR/BAR] pointed out that partial pressures as determined from many of the vapour-equilibration studies agree fairly well, but that extrapolations based on the narrow ranges of experimental temperatures lead to inaccurate (and hence inconsistent) values for $\Delta_f H_m^o$ (FeI_2, cr, 298.15 K) and S_m^o (FeI_2, cr, 298.15 K). However, the pressure measurements are not inconsistent with values from later mass-spectrometric and torsion-balance studies [1984GRA/ROS], [1985HIL/VIS], [1996SCA/PIA], and the lack of agreement in the derived enthalpy of formation values for FeI_2(cr) at 298.15 K remains unresolved.

[1967BAL]

This paper deals with the hydrolysis of Fe(III) in concentrated iron(III) trichloride solutions. The author reported information that provides a better understanding of the observations of Brady *et al.* [1964BRA/ROB]. Several techniques were used in parallel: pH measurements, ir spectrophotometry in the OH stretching region (see Table A-20), UV-visible spectrophotometry in the d-d transition region (see Table A-21), and transport measurements of migration of species in an electric field.

Table A-20: Position of ir bands in the O–H stretching region.

Compound	Maxima (cm^{-1})			
$FeCl_3(H_2O)_6$ melt at 20 °C	3570	3448 (1.1)	3311 (1.05)	3155 (0.95)
$FeCl_3(H_2O)_6$ sat. with HCl(g)	3570	3435 (0.7)	3300 (0.65)	3125 (0.6)
$FeCl_3(H_2O)_{15}$	3560	3424 (1.4)	3280 (1.4)	3141 (1.30
$FeCl_3(H_2O)_{7.7}(HCl)_{1.35}$	3560	3448 (1.1)	3311 (1.1)	3164 (1.05)
12 M HCl in water		3435	3226 (0.4)	3125 (0.6)

Table A-21: Decadic molar absorption coefficients of the tetrahedral $FeCl_4^-$ at three maxima.

λ/nm	ε/m^2·mol^{-1}	
	$[Et_4N]FeCl_4$	$FeCl_3(H_2O)_6$ sat. with HCl(g)
533	0.130	0.132
622	0.0360	0.0420
685	0.0550	0.0560

Considerable hydrolysis occurs in concentrated unacidified solutions of $FeCl_3$ ($FeCl_3·6H_2O$ to $FeCl_3·40H_2O$), as indicated by measured pH values close to 0 and lower. The ir band in the region of 3125 cm^{-1}, as found for pure aqueous solutions of HCl, and attributable to H_3O^+ stretching, was found for the $FeCl_3$ solutions. The transport experiments showed that Fe(III) transport can account only partially for the total current and that other cations participate to the delivered current.

The d-d transition bands of tetrahedral $FeCl_4^-$ (600, 620, 685 and 730 nm) were observed as well as the very weak 920 nm band attributed to the octahedral Fe^{3+} species.

This qualitative investigation complements that of Brady *et al.* [1964BRA/ROB] in which the charge balance did not correspond to the claimed species. Consideration of hydrolysis permits a credible charge balance to be proposed. The negative charge of the anionic $FeCl_4^-$ complex is balanced by the positive charge of cations such as H_3O^+ and cationic hydroxido-iron complexes. The occurrence of these species is in accord with the low pH of the solution, much lower than those measured by Brady *et al.* [1964BRA/ROB], 0 instead of 2. The migration and ir data reinforce this interpretation. However, there are no thermodynamic results reported in this paper.

[1967BER2]

Solubility equilibrium constants in aqueous solutions saturated with 1 atm H_2S at 25 °C have been determined for synthetic mackinawite (tetragonal FeS), greigite (cubic Fe_3S_4) and freshly precipitated FeS by means of pH measurements combined with analysis for dissolved Fe(II) ion. Equilibrium with mackinawite and greigite was approached both from undersaturation and supersaturation. In undersaturation experiments, precipitates were obtained from $FeSO_4$ solution and separated using a 0.45 μm Millipore filter. The nature of the precipitates was checked by X-ray diffraction. The fresh precipitate, mackinawite and greigite were obtained by bubbling H_2S through a $FeSO_4$ solution at room temperature, 60 °C and 80 - 90 °C, respectively, and then the solutions were cooled. In oversaturation experiments, the solubilities in distilled H_2O or 0.01 m KCl solution were measured. The equilibrium constants were reported for the reactions $FeS(s) \rightleftharpoons Fe^{2+} + S^{2-}$ and $\frac{1}{3}\,Fe_3S_4(s) \rightleftharpoons Fe^{2+} + S^{2-} + \frac{1}{3}\,S(\text{rhombic})$. The equilibrium constants for the reactions with predominating species can be calculated with the author's relevant constants for the $H_2S(g) \rightleftharpoons H_2S(aq)$ reaction and dissociation constants for H_2S to be $\log_{10} K = 4.04$ for $FeS(\text{fresh ppt}) + 2H^+ \rightleftharpoons Fe^{2+} + H_2S(aq)$, $\log_{10} K = 3.37$ for $FeS(\text{mackinawite}) + 2H^+ \rightleftharpoons Fe^{2+} + H_2S(aq)$, and $\log_{10} K = 2.68$ for $\frac{1}{3} Fe_3S_4(\text{greigite}) \rightleftharpoons Fe^{2+} + S^{2-} + \frac{1}{3} S(\text{rhombic})$, respectively. In the case of greigite, the measured Eh values (Section II.1.7.5, pp. 20) of the solution were near 0.0, close to the calculated Eh for the reaction $H_2S(aq) \rightleftharpoons 2H^+ + S(\text{rhombic}) + 2e^-$, thus justifying the proposed reaction. Activity coefficients were calculated with using a Debye-Hückel equation (ionic strengths were less than 0.01 m). Although the experiments were carried out appropriately, the values were obtained for the fixed pH values which were attained as a result of precipitation or dissolution. As for the attainment of the equilibrium condition, equilibrium pH values were 3.60 to 3.98 for fresh precipitate, 3.96 to 4.26 (undersaturation) and 3.30 (oversaturation) for mackinawite, and 2.92 to 2.99 (undersaturation) and 4.01 to 4.04 (oversaturation) for greigite. The differences between $\log_{10} K$ values obtained by undersaturation and by oversaturation were 0.09 for mackinawite and 0.26 for greigite. Therefore, in the case of greigite, it is uncertain whether the dissolution equilibrium was attained or not. As for the freshly precipitated FeS and mackinawite, the freshly precipitated FeS claimed by the author is also considered to be nanoparticulate mackinawite. Therefore the values reported for the freshly precipitated FeS and mackinawite are both considered to refer to nanoparticulate mackinawite. The difference between them is considered due to the difference in ageing conditions. Considering the uncertainty in the pH measurements and activity corrections, this review takes the mean of the values reported for the freshly precipitated FeS and mackinawite, assigns a fairly large uncertainty, and obtains $\log_{10} K = (3.7 \pm 0.5)$ for $FeS(\text{mackinawite}) + 2H^+ \rightleftharpoons Fe^{2+} + H_2S(aq)$.

[1967BOH]

This study involved measurements of the total iron(III) concentration in 0.01 and 0.1 M $CaCl_2$ solutions at 25 °C containing suspensions of seven acid soils at solid to liquid ratios of 1:10 to 1:1000. The clay content of the soils ranged from 4.8 to 49.3% and 20 g samples of each soil were prewashed with 500 mL of the appropriate $CaCl_2$ solution. The equilibrating mixtures, which were continuously purged with water-saturated air, were sampled after 4 - 6, 19, 50 - 59 and 139 - 153 days. Dissolved iron was extracted into an organic solvent and analysed spectrophotometrically. These procedures were carried out with considerable care. The pH of the aqueous supernatant solutions was measured presumably with calibration *vs.* standard buffer solutions. After generally decreasing over time, by 139 days the average molar ion product, $c_{\text{Fe(III)}} c_{\text{OH}^-}{}^3$ was reported as $(1.1 \pm 0.5) \times 10^{-39}$ for six of the seven soils tested. This value was independent of the prevailing $CaCl_2$ concentration and the solid to liquid ratios employed.

This study involves an uncharacterized amorphous iron(III) solid phase, or phases, such that the results provide no meaningful thermodynamic data, but they give an internally consistent estimate of the solubility of amorphous iron(III) hydroxide/oxide. These results are consistent with previous results for amorphous material, prior to the onset of the formation of microcrystalline goethite.

[1967ERE/FIL]

Galvanic potentials were measured for the cells

$$\mathrm{Pt|``FeO", Fe_3O_4|(CaO)ZrO_2|Fe_2SiO_4, SiO_2, Fe|Pt}$$

$$\mathrm{Pt|``FeO", Fe_3O_4|(CaO)ZrO_2|Fe, ``FeO"|Pt}$$

to determine the Gibbs energy of formation of α-Fe_2SiO_4. The results are reported only as equations and on a very small graph. The authors' equation (6), when combined with consistent auxiliary data for quartz ([1989COX/WAG], [1998CAR/SAL]) and oxygen [1989GUR/VEY], and with the values selected in this review for the heat capacity and entropy of α-Fe_2SiO_4 (Section X.2.1.1.1) and Fe(cr) (Section V.2) leads to values for $\Delta_f H_m^o$ (Fe_2SiO_4, α, 298.15 K) that are 5 to 20 $kJ\cdot mol^{-1}$ more negative than values from other sources. The data presentation is not sufficient to allow a proper re-evaluation of the information in this paper.

[1967FER]

The heats of dissolution of maghemite (γ-Fe_2O_3) and hematite (α-Fe_2O_3) in aqueous HCl (containing a small quantity of $FeCl_3$) at 343 K were compared. The specific surface area of the maghemite was 2420 $m^2\cdot mol^{-1}$, and that of the hematite was "the same". In all cases the solid composition was adjusted by adding a small quantity of water, so that the overall dissolution reaction was:

$[360\,HCl + 2736\,H_2O + 2\,FeCl_3](sln) + Fe_2O_3\cdot 1.8\,H_2O(s + ads + sln) = [354\,HCl + 2740.8\,H_2O + 4\,FeCl_3](sln)$

The purity of the maghemite was estimated at 90% by magnetic measurements. Impurities included 2% volatiles (presumably mainly H_2O), no more than 1.5% non-volatile non-ferrous inorganics (Mn, Si, Mg, Al, Ca), the remainder being other iron oxides and oxyhydroxides (α-Fe_2O_3, β-FeOOH, γ-FeOOH).

Four runs yielded $\Delta_f H_m^o = -(54.7 \pm 0.4)$ $kJ\cdot mol^{-1}$ for the impure maghemite, and the author cites a value of $-(42.3 \pm 2.1)$ $kJ\cdot mol^{-1}$ for a matched hematite sample. The author's value of $\Delta_{trs} H_m^o$ Fe_2O_3, $\gamma\rightarrow\alpha$, 343 K) = $-(13.8 \pm 2.5)$ $kJ\cdot mol^{-1}$, however, is not fully corrected for impurities nor adjusted to 298.15 K. This correction is difficult and imprecise, because of uncertainties in the solid analysis and surface-area effects, but Diakonov's recalculated value of $\Delta_{trs} H_m^o$ (Fe_2O_3, $\gamma\rightarrow\alpha$, 298.15 K) = $-(15.6 \pm 3.5)$ $kJ\cdot mol^{-1}$ is preferred [1998DIA].

[1967KOM/OLE]

The oxygen chemical potential of hematite, as a function of composition, was measured electrochemically at 1173 to 1273 K and manometrically at 1526 to 1657 K. Most of the data are beyond the scope of this review (see synopsis of [1961SAL]), except the following values of the equilibrium p_{O_2} /bar for magnetite + hematite: 4.24×10^{-8} at 1173 K; 2.42×10^{-6} at 1273 K.

The solubility (mol-%) of Fe_3O_4 in α-Fe_2O_3 was estimated to increase from 0.48 at 1173 K to 4.3 at 1657 K.

[1967MAR/BON]

The potential difference for the cell Fe, FeF_2 | CaF_2 | NiF_2, Ni was reported as − 0.374 V at 600 °C. This is undoubtedly the same measurement reported by Markin [1968MAR] as (0.374 ± 0.003) V at 600 °C for the cell Ni, NiF_2 | CaF_2 | FeF_2, Fe. It is essentially identical to the one reported by Lofgren and McIvor [1966LOF/MCI] (and may be the same measurement).

[1967MAS]

This paper is a report on a spectroscopic study (220 to 370 nm) of complexation of sulfate with iron(III) at 20 °C. All solutions contained 0.2 M $HClO_4$ to inhibit hydrolysis, and a constant ionic strength of 1.2 M was maintained with $NaClO_4$. The total iron(III) perchlorate concentration was between 1.3×10^{-4} and 1.3×10^{-3} M, and the sulfate concentration was varied between 1.3×10^{-3} and 1.3 M (sulfate added as Na_2SO_4). The reported value of the first Fe(III)-sulfato complexation constant (20 °C, I_c = 1.2 M) was (115 ± 3) M^{-1}. It is assumed that results from solutions with higher sulfate concentrations (such that the total ionic strength would have been > 1.2 M) were omitted from the calculations. Formation constants for $FeBr^{2+}$ (K_1 = (0.70 ± 0.02) M^{-1}) and the mixed complex $FeBrSO_4(aq)$ (K_{11} = (319 ± 10) M^{-2}) were also reported for the same conditions.

The main importance of this paper is the spectroscopic evidence for the existence of Fe(III) mixed bromidosulfato complexes. The reported $K_{1FeSO_4^+}$ value is in line with the other selected values, but it has not been used further in the present review because of the lack of information concerning the solution compositions.

[1967NAF/MUA]

Pellets containing SiO_2 (from decomposition of "silicic acid") and "FeO" from reduction of Fe_2O_3 (SiO_2:"FeO" equal to 0.5) were prepared. At 1423 and 1449 K, oxygen partial pressures were set using mixtures of H_2 and CO_2 so that the oxygen partial pressure at which metallic iron began to form from the fayalite/silica mixtures could be determined. The oxygen partial pressures were decreased to precipitate the iron, and then increased until analysis of other samples showed that the iron was re-oxidized. The samples were quenched, and the components present were confirmed by X-ray diffraction. The transition oxygen pressures, when combined with consistent auxiliary data for quartz ([1989COX/WAG], [1998CAR/SAL]), and with the values selected in this review for the heat capacity and entropy of α-Fe_2SiO_4 (Section X.2.1.1.1) and Fe(cr) (Section V.2) lead to values of $\Delta_f H_m^\circ$ (Fe_2SiO_4, α, 298.15 K) of − 1459.6 and − 1463.1 kJ·mol^{-1} —10 to 15 kJ·mol^{-1} less negative than found in most other studies [1987NEI2], [1989JAC/KAL]. The results from this study are not used further in the present review.

[1967SWI/TUR]

Experiments were performed on zone-refined Fe with a total impurity level of about 30 ppm. Oxygen solubilities were measured by prolonged exposure (18 hours at 1623 K, 1 week at 1154 K) to H_2-H_2O gas mixtures with compositions corresponding to oxygen potentials just outside the wüstite stability field. The resulting oxygen content of the Fe was analysed by a vacuum fusion method, corrected for blank measurements. The authors conclude that the solubility of O in α-Fe is about 2 to 3 ppm (atomic fraction $x_O \sim 9 \times 10^{-6}$) at 1154 K, declining to even smaller values at lower temperatures, and rising to about 25 ppm ($x_O \sim 9 \times 10^{-5}$) in γ-Fe at 1623 K. Some early studies that suggested much higher oxygen solubilities, *e.g.*, 18 mol-% at 1045 K [1924EAS/EVA], were evidently in error.

This paper complements an earlier study from the same laboratory [1966HEP/SMI]. The combined results, as summarized in this paper, demonstrate that the equilibrium solubility of O in Fe is sufficiently low that the activity of Fe at the Fe-Fe_3O_4 and Fe-wüstite phase boundaries is not significantly different from 1 for the purposes of the current review.

[1967TAK/POS]

This paper describes a novel approach in which metallic iron was dissolved galvanostatically into a solution (0.5 M NaCl), the pH of which was controlled with a pH-stat electrochemically at 25, 50 and 75 °C. It is not clear how the pH was calibrated, although pH appears to be based on the conventional activity scale rather than on a calibrated concentration scale (pH_c). The values of $\log_{10}{}^*K^{\circ}_{1,1}$ are given as -9.5, -9.0 and -8.5, respectively, in molar units utilizing an apparent Debye-Hückel-based activity coefficient model. The coulombs of charge passed at each pH to reach a steady-state condition provided the results which are only represented on a small plot of $|i_\infty|/i_c$ *vs.* pH. Two titrations were conducted at 25 °C, and were evaluated according to the following equation:

$$|i_\infty|/i_c = 2e^{\mathrm{pH}}/\{1+(\gamma_{\mathrm{FeOH^+}}/\gamma_{\mathrm{Fe^{2+}}}\,{}^*K_{1,1})\}.$$

However, this reviewer could not reproduce this relationship. The points for the two 25 °C titrations (the points at 50 and 75 °C could not be defined clearly) were digitized to provide a data set for the following analysis.

$$\begin{aligned}
{}^*K_{1,1} &= c_{\mathrm{FeOH^+}}c_{\mathrm{H^+}}/c_{\mathrm{Fe^{2+}}}\\
c_{\mathrm{FeOH^+}} &= -i_\infty t/FV;\ c_{\mathrm{Fe^{2+}}} = i_c t/2FV + i_\infty t/FV\\
{}^*K_{1,1} &= \{-i_\infty t/FV\}c_{\mathrm{H^+}}/\{i_c t/2FV + i_\infty t/FV\}\\
{}^*K_{1,1}i_c/2 + {}^*K_{1,1}i_\infty &= -i_\infty c_{\mathrm{H^+}}
\end{aligned}$$

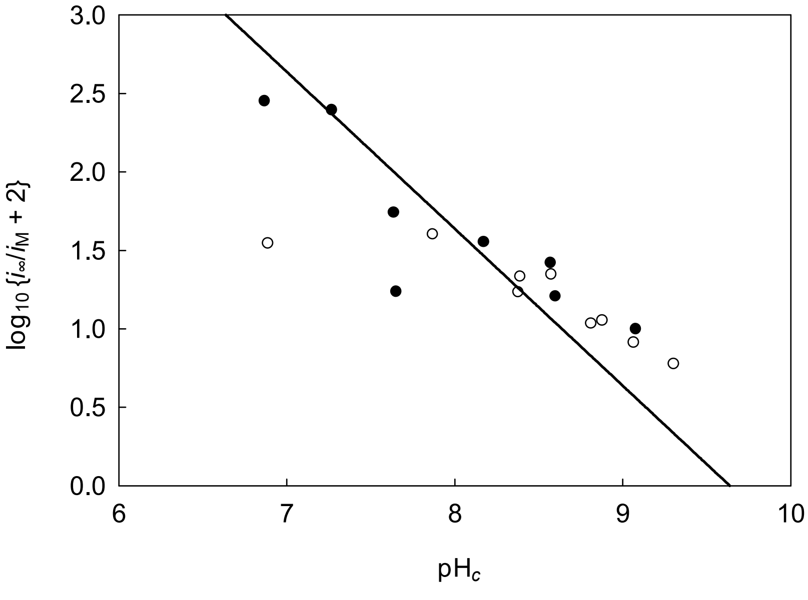
$$\begin{aligned} i_c / i_\infty &= -2\{c_{\mathrm{H}^+} / {}^*K_{1,1} + 1\} \\ \log_{10}\{i_c / i_\infty + 2\} &= \log_{10}\{2 / {}^*K_{1,1}\} - \mathrm{pH}_c \\ &= \log_{10}\{2 / {}^*K_{1,1}\} - \{\mathrm{pH} + \log_{10}(\gamma_{\pm\mathrm{HCl}})\} \end{aligned} \qquad (A.68)$$

A plot of the LHS of Equation (A.68) *vs.* pH$_c$ (Figure A-14) yielded:

$\log_{10}\{2 / {}^*K_{1,1}\} = (9.367 \pm 0.107)$

$\log_{10} {}^*K_{1,1} = -(9.3 \pm 0.3)$ (the statistical uncertainty was tripled by this review) at 0.513 molal ionic strength (NaCl).

Figure A-14: Plot of the LHS of Eq. (A.68) *vs.* pH$_c$ for two titrations carried out at 25 °C where the open and closed symbols represent results of titrations 1 and 2, respectively.



Baes and Mesmer [1976BAE/MES] quote the $\log_{10} {}^*K^{\circ}_{1,1}$ value of −9.5 as providing confirmation of the [1971MES] value, but considering the undisclosed details of this study by Tagashi and Posey, including the activity coefficient calculations which appear not to have been implemented, and the uncertainty as to the validity of the fitting equation quoted by these authors, this review considers the value of pK_{11} = −(9.3 ± 0.3) as tentative at best and is not used further in this review.

[1967VAS/LOB2]

In this paper calorimetric measurements of the heat of formation of $FeCl^{2+}$ in aqueous solutions as a function of temperature and ionic strength (2 to 8 M) were reported. The chemical conditions were chosen to get only the $FeCl^{2+}$ complex in solution.

The formation constant of $FeCl^{2+}$ as a function of the ionic strength at 25 °C was deduced from an analysis of the literature available at that time [1964SIL/MAR], [1959COL/NAU]. Extrapolation of the experimental values of ΔH_1 to zero ionic strength was carried out for six temperatures (10 to 55 °C) using an equation established by one of the authors [1967VAS]. The authors discarded the experimental values from 7 and 8 M $HClO_4$ when doing their fit. At a fixed ionic strength the value of ΔH_1 was found to depend on the temperature according to Eq. (A.69).

$$\Delta H_1 = a + b \log_{10}(T/\mathrm{K}) \qquad \text{(A.69)}$$

The coefficients a and b are linear functions of the molal ionic strengths between 2.3 and 6.3 (molal concentrations were also documented by the authors).

Thus, a general Eq. (A.70) giving ΔH_1 as a function of the temperature and the ionic strength in the molal scale was derived.

$$\Delta H_1 = 6303\, I_m - 78640 + 33744 \log_{10}(T/\mathrm{K}) - 271.95\, I_m \log_{10}(T/\mathrm{K}). \qquad \text{(A.70)}$$

where I_m is the ionic strength between 2.3 and 6.3.

This work allowed a set of thermodynamic constants for formation of $FeCl^{2+}$ as a function of the temperature and the ionic strength to be proposed. At 25 °C and $I = 0$, $\Delta_r H_1^\circ = (23.43 \pm 0.84)\ \mathrm{kJ \cdot mol^{-1}}$, $\Delta_r G_1^\circ = -(7.88 \pm 0.11)\ \mathrm{kJ \cdot mol^{-1}}$, $\Delta_r S_1^\circ = (105 \pm 4)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ and $\Delta_r C_{p1}^\circ = (242.7 \pm 12.5)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. Using these values and the values of $\Delta_f H^\circ$, $\Delta_f G^\circ$ and S° of Fe^{3+} and Cl^- found in the literature at that time they found: $\Delta_f H^\circ(FeCl^{2+}) = -191.04\ \mathrm{kJ \cdot mol^{-1}}$, $\Delta_f G^\circ(FeCl^{2+}) = -149.66\ \mathrm{kJ \cdot mol^{-1}}$, and $S^\circ(FeCl^{2+}) = -131.8\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. These numbers are roughly within the range of values recommended in this review. A rather significant difference is the value adopted for $\log_{10} \beta_1^\circ$: (1.38 ± 0.08) in the paper and (1.53 ± 0.10) in this review. The value of $\Delta_r H_1^\circ = (23.43 \pm 0.84)\ \mathrm{kJ \cdot mol^{-1}}$ resulting from the extrapolation of $\Delta_r H$ values to zero ionic strength was revised by Tagirov *et al.* [2000TAG/DIA], who used another equation proposed by Khodakovsky [1975KHO]. However, even if the equation of Khodakovsky is based on more fundamental thermodynamic criteria, the difference between the results is smaller than the uncertainties. The equation of Khodakovsky applied to the data of Vasil'ev and Lobanov for the extrapolation of $\Delta_r H_1$ to zero ionic strength yielded $\Delta_r H_1^\circ = (22.47 \pm 2.10)\ \mathrm{kJ \cdot mol^{-1}}$.

[1967WEL/SAL]

The acceleration of the Fe(II)-H_2O_2 oxidation reaction by different halide ions (and by PF_6^-) at various temperatures (0 to 45 °C) in $(Na,H)ClO_4/X^-$ solutions (I = 1 to 4 M) was investigated. Acceleration of this reaction was attributed to the formation of

$Fe(II)X_n^{2-n}$ with X^- = Cl^-, Br^-, F^-, PF_6^- and more rapid reaction of these complex ions than the simple aquated ion Fe^{2+}. Most solutions contained only a small amount of $HClO_4$ (0.004 M), although a few experiments were carried out at higher acid concentrations.

The authors' Table 2 seems to contain only some of the results from this work, and the β values in Table 2 seem to be the results from extrapolation to c_{X^-} = 0 at each temperature, at least in some cases regardless of total ionic strength. The extrapolations in their Figures 3, 4, 6, 7 and 8 show various other experimental values, primarily at low values of c_{X^-}, but no $\log_{10}\beta$ values for these experiments are provided in Figure 5. At 25 °C, the reported formation constants are 198 M^{-2} for $FeF_2(aq)$, 0.54 M^{-1} for $FeBr^+$ and 5.54 M^{-1} and 9.80 M^{-1} for $FeCl^+$. As noted by Po and Sutin [1968PO/SUT], the later value probably was a typographical error. It would be inconsistent with the values plotted in Figure 5 of Wells and Salam, and in Figure 3 of Wells [1969WEL]; also the product $\beta_1 k_0$ would then be almost twice that for all the other values for solutions at I = 1 M, regardless of temperature. It is likely that the value of 5.54 M^{-1} (25 °C, 0.3 M Cl^-) corresponds to the point given in Figure 5. In the calculations, the value of β_1 is always derived from the product $\beta_1 k_0$, where k_0 is the bi-molecular rate constant for the reaction of the hexa-aquoiron(II) with hydrogen peroxide. Therefore, the reported values of β_1 are very sensitive to the accuracy of the value of k_0.

The rate constant k_0 was plotted against powers of the anion concentration. In the case of fluoride a straight line was found when plotting k_0 *vs.* $(c_{F^-})^2$, and from this behaviour it was concluded that $FeF_2(aq)$ is the only relevant complex at 25 °C. At 0 °C a straight line was obtained when plotting k_0 *vs.* $(c_{F^-})^3$, and, consequently, it was concluded that FeF_3^- is the only relevant complex at 0 °C. However, the kinetic experiments do not indicate the existence of the monofluorido complex FeF^+. For 1 M $NaClO_4/NaF$ solutions including 4.0×10^{-3} M $HClO_4$ the authors reported $\beta_2(288.15\text{ K}) = 850\ M^{-2}$, $\beta_2(298.15\text{ K}) = 198\ M^{-2}$, $\beta_2(308.15\text{ K}) = 57\ M^{-2}$, $\beta_2(318.15\text{ K}) = 21.4\ M^{-2}$ and $\beta_3(273.15\text{ K}) = 520\ M^{-3}$.

Thermodynamic parameters, $\Delta_f H$ and $\Delta_f S$, were determined[1] from the temperature dependence of the formation constants and were reported for 25 °C at an ionic strength of 1 M:

$FeF_2(aq)$; $-81.6\ kJ\cdot mol^{-1}$ ($-19.5\ kcal\cdot mol^{-1}$), $-224.7\ J\cdot K^{-1}\cdot mol^{-1}$ ($-53.7\ cal\cdot deg^{-1}\cdot mol^{-1}$);

$FeBr^+$; $-72.0\ kJ\cdot mol^{-1}$ ($-17.2\ kcal\cdot mol^{-1}$), $-246.9\ J\cdot K^{-1}\cdot mol^{-1}$ ($-59.0\ cal\cdot deg^{-1}\cdot mol^{-1}$);

$FeCl^+$; $-24.4\ kJ\cdot mol^{-1}$ ($-5.82\ kcal\cdot mol^{-1}$), $-67.4\ J\cdot K^{-1}\cdot mol^{-1}$ ($-16.1\ cal\cdot deg^{-1}\cdot mol^{-1}$).

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[1] In the left-side part of the authors' Figure 5, the results for bromide have been misplotted. The value for 25 °C appears to have been done with A = 0.5, as claimed, but the "log(beta) + A" values for the lower temperatures seem to be out by ~ 1.0 on the y-axis.

The values of $\Delta_r G_m$ as calculated from the authors' Table 3 bromide values of $\Delta_f H$ and $\Delta_f S$ (claimed to be for $I = 1$ M) and from the $I = 4$ M Table 2 bromide β values seem to be in fairly close agreement (perhaps suggesting that these Table 3 values really were from $I = 4$ M results, not results for $I = 1$ M).

Because of the typographical errors and the difficulties in disentangling formation-constant values from the kinetic data [1969WEL], values from this paper are not used further in the present review. The results are discussed further in the Appendix A entries for [1968PO/SUT] and [1969WEL].

[1968ARN/SCH2]

Previous calorimetric data ([1962SCH2]: Schlyter, K., Trans. Roy. Inst. Technol. Stockholm, No. 196 (1962)) on hydrolyzed Fe(III) solutions (5 – 100 mM) in 3 M $NaClO_4$ at 25 °C were recalculated (noting that the original calorimetric data were treated graphically). The $\log_{10} {}^*\beta_{n,m}$ values of -3.046 (1,1), -6.31 (2,1), and -2.91 (2,2) were first taken from [1953HED2]. The authors also adopted the hydrolysis constants reported in [1962SCH2] in an alternative scheme, but as this speciation included the (4,3) species, this second approach is ignored here. The data treatment was performed with the LETAGROPVRID general least-squares regression program and was confined to Fe(III) concentrations ≤ 50 mM which was the range covered in the original work by Hedström. Their recommended enthalpies and entropies of reaction are: $\Delta_r H_M$ ((1,1), 298.15 K) = (46 ± 8) $kJ\cdot mol^{-1}$, $\Delta_r S_M$ ((1,1), 298.15 K) = (96 ± 25) $J\cdot K^{-1}\cdot mol^{-1}$, $\Delta_r H_M$ ((2,2), 298.15 K) = (42 ± 2) $kJ\cdot mol^{-1}$ and $\Delta_r S_M$ ((2,2), 298.15 K) = (84 ± 5) $J\cdot K^{-1}\cdot mol^{-1}$. The (2,2) species dominated the experimental solutions such that the contribution of the (2,1) was neglected.

These thermodynamic quantities are of interest for comparison purposes in this review.

[1968BAR/BAR]

This paper presents the results of a flow study of the formation of FeI_2(g) (1030 to 1353 K), and as part of that study provided a useful review of the previous literature. However, the calculation used to determine a value for $\Delta_f H_m^o$ (FeI_2, cr, 298.15 K) contained an error that was corrected in a later review by two of the same authors [1979BAR/CER]. This changed the reported value from -129.3 $kJ\cdot mol^{-1}$ to -91.2 $kJ\cdot mol^{-1}$. The value was not used directly in deriving any selected values in the present review.

[1968CHA/FLE]

Solid-state cell-potential measurements were performed on 9 different oxide couples, using a "closed system" cell design to avoid mixed potential measurements arising from gas-phase transport between sample and reference couples, which is sometimes a problem with the simpler, stacked-disk configuration. Measured equilibrium potential relationships included the following, which are discussed further in Sections VII.2.2.1 and VII.2.7.2.3.

$Ni(cr) + 3\,Fe_2O_3(cr) \rightleftharpoons NiO(cr) + 2\,Fe_3O_4(cr)$, E/mV = {−69.44 − 0.29425 (T/K)} ± 1.5, 967 to 1373 K.

$NiO(cr) + Fe(cr) \rightleftharpoons Ni(cr) +$ "FeO"(cr), E/mV = {154.13 − 0.10400 (T/K)} ± 0.61, 903 to 1540 K.

$NiO(cr) + 3$ "FeO"(cr) $\rightleftharpoons Ni(cr) + Fe_3O_4(cr)$, E/mV = {405.34 + 0.19644 (T/K)} ± 0.47, 949 to 1272 K.

[1968DOY]

The author shows that the potential of a Pt electrode in O_2-free $FeSO_4$ solutions and in natural fresh waters often corresponds to the Nernst potential for the reaction:

$$Fe^{2+} + 2\,H_2O(l) \rightleftharpoons FeOOH(s) + 3\,H^+ + e^-;\ E^{o} = (0.965 \pm 0.032)\ \text{V}.$$

Spontaneous coating of the electrode with FeOOH appears to be responsible for this potential-determining reaction. The author suggests that the solid phase is probably γ-FeOOH, but it was not definitely identified. Therefore this observed potential can not be applied with any certainty to estimating the Gibbs energy of γ-FeOOH.

[1968FER]

This is a summary of work that was previously published in more detail [1966FER].

[1968KIT/KAT]

Mixtures of silica (form unspecified) and fayalite were heated at 1402, 1417, 1433 and 1447 K. Oxygen partial pressures were set using mixtures of H_2 and CO_2 so that the oxygen partial pressure at which metallic iron began to form from the fayalite/silica mixtures could be determined. The samples were quenched, and the presence of metallic iron was confirmed by microscopy. The oxygen pressures, when combined with consistent auxiliary data for quartz ([1989COX/WAG], [1998CAR/SAL]), and with the values selected in this review for the heat capacity and entropy of α-Fe_2SiO_4 (Section X.2.1.1.1) and Fe(cr) (Section V.2) led to values of $\Delta_f H_m^{o}$(Fe_2SiO_4, α, 298.15 K) between −1471.4 and −1474.0 kJ·mol^{-1}, (average value −(1472.9 ± 2.4) kJ·mol^{-1} (2σ uncertainty)).

[1968LAR]

Enthalpy of solution measurements at 298.15 K were reported for samples of hydrated $FeSO_4$ with H_2O:$FeSO_4$ ratios of 6.92, 6.78, 5.32, 3.98 and 2.46. In each case there was a series of measurements leading to different final solution concentrations of iron(II). Final iron(II) molalities ranged from 0.0034 to 0.020 m. (In the thesis it is reported that the calorimeter was "designed to hold 950 ml of solution", whereas [1968LAR/CER] indicates that the results were "obtained with 950 ml of water in the dewar". Thus, there is probably a small uncertainty in any calculated molal concentrations (< 1%)—only the number of moles dissolved and the molar heats of solution are reported.) The author used the enthalpies of dilution for $NiSO_4$(sln) solutions to calculate the enthalpies of solution to infinite dilution. The enthalpies of dilution for $NiSO_4$ as recalculated from [1956LAN/MIE] in the present review are less negative by 0.03 to 0.04 $kcal{\cdot}mol^{-1}$ than the values used in the original thesis. Comparison with [1959LAN] indicates that the integral enthalpies of dilution for $NiSO_4$ are close to those for $ZnSO_4$, but less positive than those for $CuSO_4$ (by 0.6 $kJ{\cdot}mol^{-1}$ for a 0.01 m solution). Thus, the assumption that the enthalpies of dilution for $NiSO_4$ and $FeSO_4$ are the same could have an inherent uncertainty of about 20%. That said, the constant "corrected" values for $\Delta_{\text{sln}}H_{\text{m}}$ suggest that the author's assumption is reasonable. The reported dilution corrections (or molar quantities) appear to be slightly in error for at least two experiments, dissolution of 0.01241 moles of $FeSO_4{\cdot}2.46H_2O$ and 0.006598 moles of $FeSO_4{\cdot}3.98H_2O$, and the results from these two experiments have been omitted in the present reanalysis. The recalculated enthalpies of solution at infinite dilution for $FeSO_4{\cdot}nH_2O$ are (11.29 ± 0.11) $kJ{\cdot}mol^{-1}$, $n = 6.92$, (10.03 ± 0.16) $kJ{\cdot}mol^{-1}$, $n = 6.78$, $-(2.78 \pm 0.13)$ $kJ{\cdot}mol^{-1}$, $n = 5.32$, $-(13.89 \pm 0.62)$ $kJ{\cdot}mol^{-1}$, $n = 3.98$, $-(29.39 \pm 0.62)$ $kJ{\cdot}mol^{-1}$, $n = 2.46$.

A plot of the solution enthalpy *vs.* the extent of hydration of the salt is almost linear, though there is a slight inflection at a composition near that for the tetrahydrate. The author assumed that the solids were mechanical mixtures of the heptahydrate and the monohydrate, but it is more likely [1964KOH/ZAS2], [2002CHO/SEA] that the mixtures were heptahydrate with tetrahydrate (for $FeSO_4{\cdot}nH_2O$, $n = 6.92, 6.78, 5.30$) and tetrahydrate with monohydrate (for $FeSO_4{\cdot}nH_2O$, $n = 3.98, 2.46$). In either case, the enthalpies of dehydration per mole of water in the hydrate are very similar.

As two compositions were used that are close to $FeSO_4{\cdot}7H_2O$(cr), it is likely that the uncertainty in the extrapolated heat of solution for this compound (11.89 $kJ{\cdot}mol^{-1}$) is fairly small. Uncertainties in the enthalpies of dilution also could be important, and the overall uncertainty in the enthalpy of solution is estimated here as ± 0.5 $kJ{\cdot}mol^{-1}$. For the stoichiometric tetrahydrate, extrapolated heats of solution are – 13.85 $kJ{\cdot}mol^{-1}$ based on results for the four most highly hydrated samples, and – 13.68 $kJ{\cdot}mol^{-1}$ based on results for the two least hydrated samples. The simple average (– 13.77 $kJ{\cdot}mol^{-1}$) is used. The overall uncertainties in the latter measurements are relatively large as fewer samples were dissolved. Consideration is also given to the uncertainties in the enthalpy of dilution, and the uncertainty in the heat of solution of the tetrahydrate is estimated here as ± 1.0 $kJ{\cdot}mol^{-1}$. The extrapolation to the composition to the monohydrate is quite long, and the data are limited. If no tetrahydrate salt were present, the enthalpy of dehydration of the heptahydrate to the monohydrate (and H_2O(l)) is calculated to be 54.1 $kJ{\cdot}mol^{-1}$. However, based on the assumption that a tetrahydrate is present, the extrapolated heat of solution for the monohydrate is $-(44.3 \pm 5.0)$ kJ·mol^{-1}, where the uncertainty is an estimate. The enthalpy at 298.15 K for the reaction

$$FeSO_4 \cdot 7H_2O(cr) \rightleftharpoons FeSO_4 \cdot 4H_2O(cr) + 3\,H_2O(g),$$

is calculated to be (157.67 ± 0.80) kJ·mol^{-1}, where the estimated uncertainty has been slightly reduced to allow for compensating errors in the corrections of the heats of solution to infinite dilution.

The enthalpy at 298.15 K for the reaction

$$FeSO_4 \cdot 4H_2O(cr) \rightleftharpoons FeSO_4 \cdot H_2O(cr) + 3\,H_2O(g),$$

is calculated to be (162.5 ± 5.1) kJ·mol^{-1}.

[1968LAR/CER]

The experimental results for hydrated iron(II) sulfates are described in the discussion of the corresponding thesis [1968LAR]. Some of these results also were published in a conference preprint [1968LAR/HEP]. Heats of solution of $FeSO_4$(cr) hydrates were measured calorimetrically at 25.0 °C as well as those of the corresponding Cu(II), Zn(II) and Cd(II) sulfates. The standard heats of solution for the following hydrates of $FeSO_4.nH_2O$(cr) are given (converted here to kJ·mol^{-1}): n = 6.92, 11.1_3; n = 6.78, 9.92; n = 5.32, -2.9_3; n = 3.98, -14.0; n = 2.46, -29.6 after correction for the heats of dilution reported by [1956LAN/MIE]. These hydrates were considered to be the appropriate mixtures of the integral hepta-, tetra- and mono-hydrates leading to the heats of solution from these integral hydrates of: 11.8, -13.8 and -44.4 kJ·mol^{-1}, respectively. The authors estimated an entropy of solution (iron(II) ion, sulfate ion and liquid water being the products) of -6.7 J·K^{-1}·mol^{-1} from which they derived a S°_{m} (Fe^{2+}, 298.15 K) of -107.1 J·K^{-1}·mol^{-1}.

[1968LUM/JUN]

The authors report thermograms for samples of hydrated iron(II) and iron(III) chlorides (initially $FeCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 6H_2O$) in air (static conditions) and in a flow of nitrogen. The heating rate used was 0.092 K·s^{-1}. The dehydration reactions were followed through to temperatures above 1100 K. The stepwise dehydration scheme reported for $FeCl_2 \cdot 4H_2O$ is inconsistent with studies done with slower heating rates [1960SHE/CHA], [1982ARG] and with an equilibrium study [1949SCH]. FeOCl(cr) was reported as a possible intermediate in the decomposition of the hydrated iron(III) chloride in air and nitrogen above 420 K.

[1968MAI/BOU]

Microcalorimetric measurements are reported for a series of ~300 mg wüstite specimens with compositions from $Fe_{0.889}O$ to $Fe_{0.944}O$. A progressive change in the position and shape of the λ-type anomaly at the Néel transition, at temperatures near 190 K, is documented by a series of measurements at ~140 to ~210 K. Results are presented on a plot normalized to the peak height, and no quantitative $C^{\circ}_{p,\mathrm{m}}$ data are given.

[1968PO/SUT]

The authors discussed the results presented in an earlier paper by Wells and Salam [1967WEL/SAL], and stated that they did not believe the reported value of the $\mathrm{Fe(II)Cl^+}$ stability constant (5.54 $\mathrm{M^{-1}}$; 25 °C; I = 1 M).

The iron(II)–hydrogen peroxide oxidation was re-investigated using spectrophotometric methods. Good constancy of the second-order rate constant k_0 was observed in the absence of chloride. For the purposes of argument, the slightly increased rates in 1.0 M [$\mathrm{HClO_4}$ + HCl] solutions were ascribed to faster oxidation of the monochlorido complex $\mathrm{FeCl^+}$ (as compared to the rate of oxidation of $\mathrm{Fe^{2+}}$). Fitting k_1 (the $\mathrm{Fe(II)Cl^+}$ oxidation rate) and $K_1(\beta_1)$ simultaneously the authors obtained a value of (0.5 ± 0.3) $\mathrm{M^{-1}}$ for $\beta_1(\mathrm{Fe(II)Cl^+}$, 25 °C, 1.0 M). Any effect of the "phenacetin" preservative (0.023% in 3% $\mathrm{H_2O_2}$ aqueous solution) was assumed by the authors to be negligible. Using densities from Söhnel and Novotný [1985SOH/NOV] the $\mathrm{HClO_4}$ molality is calculated to be 1.05 $\mathrm{mol \cdot kg^{-1}}$, and the recalculated value of β_1 (I = 1.05 m $\mathrm{ClO_4^-}$, 25 °C) is (0.48 ± 0.28) $\mathrm{kg \cdot mol^{-1}}$.

Also, from $\mathrm{Fe(III)Cl^{2+}}$ stability measurements by Woods *et al.* [1962WOO/GAL], Po and Sutin concluded that $\beta_1(\mathrm{Fe(II)Cl^+}) << 2.95\ \mathrm{M^{-1}}$, while from the visible-region spectra of $\mathrm{Fe(III)Cl^{2+}}$ in the presence and absence of Fe(II) they concluded that the value of $\beta_1(\mathrm{Fe(II)Cl^+}$, 25 °C; 1.0 M) is less than 0.5 $\mathrm{M^{-1}}$. The authors claimed not to attach much significance to this value, and suggest that other experimental effects may be more important than formation of iron(II) chlorido complexes. Their value is not used further in the present review.

[1968RIZ/SMI]

Solid-state cell-potential measurements on wüstite of variable composition *vs.* the Fe-wüstite couple, using a CaO-stabilized $\mathrm{ZrO_2}$ electrolyte in a closed-tube configuration, yielded linear potential-composition relationships at 1038 K, 1138 K, and 1238 K, contrary to the findings of [1965VAL/RAC] below 1193 K. Limiting compositions are depicted but not tabulated. No evidence was obtained for the three structural variants of wüstite postulated in other studies.

[1968SOU/CHA]

This appears to have been a careful study of oxidation of Fe(II) with $\mathrm{H_2O_2(sln)}$. It was shown that the addition of iron(II) to excess $\mathrm{H_2O_2(sln)}$ gave better reproducibility than when iron(II) was in excess. The average heat of reaction (seven measurements, 1σ uncertainty) for

$$2\,\mathrm{Fe^{2+}(sln)} + \mathrm{H_2O_2(sln)} + 2\,\mathrm{H^+(sln)} \rightleftharpoons 2\,\mathrm{Fe^{3+}(sln)} + 2\,\mathrm{H_2O(sln)}. \qquad \text{(A.71)}$$

was reported as $-(291.2 \pm 2.5)$ kJ·mol^{-1} ($-(69.6 \pm 0.6)$ kcal·mol^{-1}) from addition of solutions of iron(II) perchlorate to aqueous perchloric acid (0.1 M) containing H_2O_2(sln) (~5×10^{-4} M). Similar measurements from addition of an iron(II) ammonium sulfate solution to aqueous sulfuric acid (0.05 M) containing H_2O_2(sln) (~ 4×10^{-4} M) gave $-(293.3 \pm 2.9)$ kJ·mol^{-1} ($-(70.1 \pm 0.7)$ kcal·mol^{-1}). The final iron concentration was 0.0005 M.

The averages of the tabulated values do not lead to exactly the results reported by the authors (also, individual calculations for each experiment only approximately lead to the reported heat). This suggests either omissions in the calculation procedure or minor typographical errors in the paper. No corrections were applied for hydrolysis or complexation, nor were ionic strength corrections applied.

In the 0.05 M H_2SO_4 solution, HSO_4^- would have been partially dissociated. The association/interaction of two different anions with the iron species (*cf.* Section IX.1.2.1.3) complicates any attempt to extrapolate results to $I = 0$. The results for the reaction in sulfate medium are not used further in the present review except for comparison purposes.

In the present review, the authors' calculated average for the reaction in 0.105 mol·kg^{-1} $HClO_4$(sln) is accepted. The limiting law suitable for the ion-interaction treatment suggests that an adjustment of -2.4 kJ·mol^{-1} is appropriate [1996PLY/GRE] and this is applied to obtain -293.6 kJ·mol^{-1}. The 2σ uncertainty for $\Delta_r H_m^\circ$ (A.71) is estimated as 4.0 kJ·mol^{-1}.

[1968WEL/SAL]

The oxidation of Fe(II) by H_2O_2(sln) was studied (photometrically) in the presence of oxoanions. The reaction always obeyed bi-molecular kinetics with different limiting rate constants depending on the nature of the anion. The paper is part of a series of papers dealing with the same subject. Some important observations were made: The rate of reaction did not increase by adding 5.2 mol·dm^{-3} $NaClO_4$ or even 9 mol·dm^{-3} of $HClO_4$ to the reaction solution, indicating that the perchlorate ion itself does not influence the reaction rate. Similarly, no effect on the reaction rate was observed when up to 5.2 mol·dm^{-3} $NaNO_3$ was added. An increase in reaction rate was observed upon addition of SO_4^{2-} ion, which is the basis for deriving a formation constant for the complex $FeSO_4$(aq). Adding $HClO_4$ to a sulfate-containing reaction solution decreased the observed rate constants, indicating that the rate constants depend on the "free" sulfate concentration. Similar conclusions could be drawn for SeO_4^{2-} with respect to $HSeO_4^-$. (The paper also deals with reaction in the presence of trimetaphosphate ($P_3O_9^{3-}$) and triphosphate ($P_3O_{10}^{5-}$) ligands, and in these cases the behaviour seems to be more complicated.)

Evidence for the formation of the 2:1 complex, $Fe(SO_4)_2^{2-}$, was not observed in the restricted concentration range of this study.

Unfortunately, the paper does not provide a full grid of I_c/T-data (μ is the symbol used by the authors for I_c) and the table headings "μ = 1" and "μ = 4" may be misleading because the actual ionic strength is strongly influenced by the presence of Na_2SO_4/$NaHSO_4$.

Densities for electrolytes at the measurement temperature were calculated in the present review from the equations of Söhnel and Novotnỳ [1985SOH/NOV] in an iterative way: First, the density of the $NaClO_4$ electrolyte was calculated at c [$mol\cdot dm^{-3}$]. This density was then fed back to the $\rho(t)$-term of the Söhnel and Novotnỳ approximation (see below) and a further density correction was made for the $NaHSO_4$(sln)/Na_2SO_4(sln) additions. This pragmatic and quick approach produces densities that agree with ± 2% with values obtained by applying the more sophisticated Young's rule [1954YOU/SMI]. Note that the parameterized form of the Novotnỳ and Söhnel equation ($\rho(c,t) = \rho(t) + Ac + Bct + Cct^2 + Dc^{3/2} + Ec^{3/2}t + Fc^{3/2}t^2$) supports this simple approach. The results are listed in Table A-22.

Table A-22: Conversion of molar to molal complexation constants for [1968WEL/SAL].

Electrolytes, temperature and association constant (molar units)	Calculated densities $kg\cdot dm^{-3}$	Conversion factor molarity to molality $dm_{sln}^3\cdot kg_{H_2O}^{-1}$	Association constant and ionic strength (molal units)
(1 M $NaClO_4$ + 0.15 M Na_2SO_4) 25 °C, $\beta_1 = 10$	$\rho = 1.0925$	1.054	$\beta_1 = 9.5$ $I_m = 1.53\ mol\cdot kg^{-1}$
(1 M $NaClO_4$ + 0.2 M Na_2SO_4) 0 °C, $\beta_1 = 55$	$\rho = 1.1016$	1.052	$\beta_1 = 52$ $I_m = 1.68\ mol\cdot kg^{-1}$
(4 M $NaClO_4$ + 0.3 M Na_2SO_4) 35 °C, $\beta_1 = 5.8$	$\rho = 1.3287$	1.256	$\beta_1 = 4.6$ $I_m = 6.2\ mol\cdot kg^{-1}$
(4 M $NaClO_4$ + 1.25 M Na_2SO_4) 45 °C, $\beta_1 = 2.5$	$\rho = 1.4306$	1.3098	$\beta_1 = 1.9$ $I_m = 10.0\ mol\cdot kg^{-1}$
(4 M $NaClO_4$ + 0.7 M $NaHSO_4$) 25 °C, $\beta_{H1} = 1.94$	$\rho = 1.3598$	1.272	$\beta_{H1} = 1.5$ $I_m = 6.0\ mol\cdot kg^{-1}$.
(4 M $NaClO_4$ + 0.22 M $NaHSO_4$) 0 °C, $\beta_{H1} = 4.52$	$\rho = 1.3356$	1.220	$\beta_{H1} = 3.7$ $I_m = 5.1\ mol\cdot kg^{-1}$.
(4 M $NaClO_4$ + 0.3 M $NaHSO_4$) 5 °C, $\beta_{H1} = 3.7$	$\rho = 1.3395$	1.229	$\beta_{H1} = 3.0$ $I_m = 5.3\ mol\cdot kg^{-1}$
(4 M $NaClO_4$ + 0.7 M $NaHSO_4$) 10 °C, $\beta_{H1} = 3.0$	$\rho = 1.3716$	1.253	$\beta_{H1} = 2.4$ $I_m = 5.9\ mol\cdot kg^{-1}$

[1969BER]

Sedimentary rocks, which are stained red with Fe_2O_3, are known as red beds. Berner measured the solubilities of fine-grained, crystalline (confirmed to some extent by XRD), synthetic goethite and hematite in 0.12 $mol\cdot dm^{-3}$ HCl at 358 K (coarse-grained material failed to reach equilibrium) in batch mode with continuous rocking. The goethite had been aged for approximately one year in distilled water at ambient temperature and pH ≈ 7. Previous, similar solubility tests at 298 K failed to reach steady-state iron concentrations after 200 days, even with "very fine grained" samples. In dissolution runs at 358 K, steady-state concentrations were achieved after 20 days— 5.0 mM Fe for hematite and 11.6 mM for goethite. In precipitation runs, steady state was not achieved within 20 days; however, duplicate precipitation curves for hematite cross over the triplicate set of dissolution curves for goethite, confirming that hematite is the more stable phase if it is assumed that the steady-state dissolution plateaux represent equilibrium.

The suspensions were filtered through 0.45 μm frits and analyzed for iron spectrophotometrically (± 2%). In two experiments, equilibrium was studied from oversaturation by the addition of $FeCl_3$, although these solubilities approached, but never attained the solubilities attained from undersaturation after 150 days. The reported solubilities are: 5.054×10^{-4} $mol\cdot dm^{-3}$ (Reaction (A.72)) and 1.164×10^{-3} $mol\cdot dm^{-3}$ (Reaction (A.73)).

$$\tfrac{1}{2}Fe_2O_3(cr) + 3\,H^+ \rightleftharpoons Fe^{3+} + 1\tfrac{1}{2}H_2O(l) \qquad (A.72)$$

$$FeOOH(cr) + 3\,H^+ \rightleftharpoons Fe^{3+} + 2\,H_2O(l) \qquad (A.73)$$

Using the density value of 1000.4 $kg\cdot m^{-3}$ interpolated from [1997SHA/WOO] yields solubilities of 5.074×10^{-4} and 1.169×10^{-3} $mol\cdot kg^{-1}$, respectively, at 0.12 ionic strength (HCl) with the corresponding $\log_{10}{}^{*}\beta_{s,0}$ values of – 0.522 and – 0.138.

Given the excess of HCl in solution, the author makes the reasonable assumption that the activity coefficients are the same in both solutions. Assuming the steady-state dissolution plateaux represent equilibrium solubilities, then $\Delta_r G_m^o$ (358 K) = $RT\cdot\ln(5.0/11.6) = -2.5\ kJ\cdot mol^{-1}$ for the following reaction:

$$\alpha\text{-FeOOH} \rightleftharpoons \tfrac{1}{2}H_2O(l) + \tfrac{1}{2}\alpha\text{-}Fe_2O_3.$$

The author estimated $\Delta_r G_m^o$ (298.15 K) = $-(1.33\pm0.33)$ $kJ\cdot mol^{-1}$; recalculation using $C_{p,m}^o$ expressions from the current review yields only a marginally different value, − 1.29 $kJ\cdot mol^{-1}$, and hence $\Delta_r H_m^o$ = (4.4 ± 0.4) $kJ\cdot mol^{-1}$, uncorrected for surface enthalpies.

This paper also includes a critique of [1949SMI/KID] and some other direct studies of the above reaction that confused equilibria with kinetically controlled steady states and also used misleading phase nomenclature.

Berner discussed the effect of crystallinity on the solubility of both solid phases, noting the enhancement effect for finer and less-crystalline material. Nevertheless, the particle size of his "fine-grained" material was not given and even though it is implied that it is greater than 0.45 μ for both solids, the presence of colloids can not be ruled out. Moreover, although hydrolysis of Fe^{3+} is minimal at the acidity of these experiments, chloride complexation will enhance the solubilities recorded for Reactions (A.72) and (A.73), but would cancel out for the calculations of the difference in Gibbs energies between these phases.

[1969BRY/SME]

An open, inert-gas-filled cell configuration was used to measure the potential difference of the magnetite-hematite couple *vs.* Cu-Cu_2O. The gas composition was slightly oxygenated by decomposition of Cu_2O to "prevent appreciable dissociation of hematite"; 29 potential-difference measurements at 1060 to 1323 K yielded the following relationship, which is discussed further in Section VII.2.2.1.

$$E/\text{mV} = \{-413.7 + 0.363(T/\text{K})\} \pm 3.2$$

[1969FEN/RIL]

Extensive cell-potential measurements are reported for wüstite of variable composition *vs.* the Fe-wüstite and wüstite-Fe_3O_4 couples, spanning the entire wüstite phase field at temperatures up to 1623 K. Non-linearity in potential-difference *vs.* T at fixed composition is interpreted in terms of 3 types of wüstite bounded by order/disorder transitions. There is good agreement with other sources, except [1964BAR2], on external bounding compositions for the wüstite field. The authors pointed out that non-linear behaviour is more difficult to detect with isothermal, variable-composition studies. Giddings and Gordon [1973GID/GOR], however, suggested that the non-linear behaviour can be attributed to drift in wüstite composition, due to oxygen permeation through the solid electrolyte at high temperatures.

[1969FOR]

A formation constant of $FeCl^{2+}$ value of $(4.00 \pm 0.11)\ M^{-1}$ was reported based on spectroscopic measurements (340 nm) at 20 °C for solutions 0.15 M in acid and 0.15 to 0.16 M in ionic strength (maximum chloride concentration 0.127 M). If the total perchlorate molarity also was kept constant (maximum chloride concentration 0.0075 M) a value of $(7.9 \pm 4.4)\ M^{-1}$ was obtained.

[1969IZA/EAT]

Calorimetric measurements of the interaction of about thirty bi- and trivalent cations with sulfate were reported. In general, $(Me_4N)_2SO_4$ solutions were titrated into 0.02 M metal perchlorate solutions at 298.15 K. Activity coefficients were expressed by a modified Debye-Hückel expression

$$\log_{10}\gamma = -Z^2A\sqrt{\mu}/(1 + B\mathring{a}\sqrt{\mu}) + CZ^2\mu$$

($å$ = 0.5 nm, $Bå$ = 1.641 $\mathrm{mol^{-1/2}\cdot dm^{3/2}}$, C = 0.25 $\mathrm{mol^{-1}\cdot dm^3}$), and in which the ionic strength (I_c) was denoted by μ, and the ionic charge by Z.

The final compositions of the solutions are not given, but the authors stated that they used 0.5 to 0.7 M $\mathrm{(Me_4N)_2SO_4}$ solutions to perform the titration. One may thus speculate that titrations ended at a two or threefold excess of $\mathrm{(Me_4N)_2SO_4}$. Hence, the ionic strength of the solution at the end of the titration was most likely in the range $0.12 < I_m < 0.20$ (in the case of bivalent cations, no formation of $\mathrm{Me(SO_4)_2^{2-}}$ complexes was considered).

For the reaction

$$\mathrm{Fe^{2+} + SO_4^{2-} \rightleftharpoons FeSO_4(aq)}$$

$\log_{10}\beta_1^{\circ}$ ($\mathrm{FeSO_4}$, aq) = (2.20 ± 0.06), $\Delta_r H_m^{\circ}$ ($\mathrm{FeSO_4}$, aq) = (0.56 ± 0.02) $\mathrm{kcal\cdot mol^{-1}}$ ((2.34 ± 0.08) $\mathrm{kJ\cdot mol^{-1}}$) and $\Delta_r S_m^{\circ}$ ($\mathrm{FeSO_4}$, aq) = (12.0 ± 0.2) $\mathrm{cal\cdot K^{-1}\cdot mol^{-1}}$ ((50.2 ± 0.8) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$) are given. Correct application of the Gibbs-Helmholtz equation should actually produce $\Delta_r S_m^{\circ}$ ($\mathrm{FeSO_4}$, aq) = (12.9$_4$ ± 0.2) $\mathrm{cal\cdot K^{-1}\cdot mol^{-1}}$ ((50 ± 1) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$).

The value of $\log_{10}\beta_1^{\circ}$ ($\mathrm{FeSO_4}$, aq), as given, was used to back-calculate values for the actual conditions (I_m = 0.12 and 0.20) using the authors' Debye-Hückel expression.

Thus,

$$\log_{10}\beta_1\,(\mathrm{FeSO_4,\ aq})_{[1969IZA/EAT]} = \log_{10}\beta_1^{\circ}\,(\mathrm{FeSO_4,\ aq})_{[1969IZA/EAT]} - 8A\sqrt{I_m}/(1 + Bå\sqrt{I_m}) + 2I_m.$$

Then these values of $\log_{10}\beta_1$ were extrapolated back to zero ionic strength using the SIT:

$$\begin{aligned}\log_{10}\beta_1^{\circ}\,(\mathrm{FeSO_4,\ aq}) = {} & \log_{10}\beta_1\,(\mathrm{FeSO_4,\ aq})_{[1969IZA/EAT]} + 8A\sqrt{I_m}/(1 + 1.5\sqrt{I_m}) \\ & - \varepsilon(\mathrm{Fe^{2+},ClO_4^-})\,m_{\mathrm{ClO_4^-}} - \varepsilon(\mathrm{Fe^{2+},SO_4^{2-}})(m_{\mathrm{SO_4^{2-}}} + m_{\mathrm{Fe^{2+}}}) \\ & - \varepsilon(\mathrm{Me_4N^+,SO_4^{2-}})\,m_{\mathrm{Me_4N^+}}.\end{aligned}$$

Since $\varepsilon(\mathrm{Fe^{2+},ClO_4^-}) \approx 0.37$, $\varepsilon(\mathrm{Fe^{2+},SO_4^{2-}}) \approx 0$, and $-0.12 < \varepsilon(\mathrm{Me_4N^+,SO_4^{2-}}) < 0$ $\mathrm{kg\cdot mol^{-1}}$, the sum of epsilon-terms nearly cancels out under given experimental conditions. It is represented by the estimate (0.00 ± 0.03) $\mathrm{kg\cdot mol^{-1}}$.

For the minimum I_m of 0.12 one obtains $\log_{10}\beta_1^{\circ}$ ($\mathrm{FeSO_4}$, aq) = (2.47 ± 0.07) and for the maximum, I_m = 0.20, $\log_{10}\beta_1^{\circ}$ ($\mathrm{FeSO_4}$, aq) = (2.64 ± 0.07) at 298.15 K.

The average calculated according to the TDB guidelines is $\log_{10}\beta_1^{\circ}$ ($\mathrm{FeSO_4}$, aq) = (2.56 ± 0.15).

Evaluation of osmotic data

A study by Oykova and Balarew [1974OYK/BAL] provided values for the osmotic coefficients for $\mathrm{FeSO_4(sln)}$ solutions from 0.1 m to saturation (1.9641 m) at 25 °C. This study instigated a substantial effort on evaluating formation constants and SIT coefficients from osmotic data.

The osmotic coefficient is a function of the number of dissolved ions/complexes in solution:

$$\log_{10} a_{\mathrm{H_2O}} = \frac{-\phi_1 \sum_k m_k}{\ln(10) \times M_{\mathrm{H_2O}}^{-1}}. \tag{A.74}$$

Even if the iron(II)-sulfate complexes that may form are weak, significant amounts of these species may exist at equilibrium at higher molalities. Thus, strictly speaking, such complexes contribute to the sum Σm_k of molalities in Eq. (A.74), and the molalities of $\mathrm{Fe^{2+}}$ and $\mathrm{SO_4^{2-}}$ are lower than the stoichiometric molality of $\mathrm{FeSO_4}$. Therefore, if evaluating complexation constants from the osmotic data, this needs to be considered.

[1969KOD/KUS]

The decomposition $p_{\mathrm{O_2}}$ of hematite was measured using a McLeod gauge to obtain total p and mass spectrometry to determine the gas composition and thereby correct for CO, $\mathrm{CO_2}$, $\mathrm{CH_4}$, and $\mathrm{H_2O}$ released by outgassing above about 600 °C. Twenty-five measurements from several runs with different powder specimens yielded the following relationship for the approximate T range 1160 to 1480 K.

$$\log_{10}(p_{\mathrm{O_2}}/bar) = 15.63 - \frac{28500}{(T/\mathrm{K})}$$

Because of the relatively low precision of these measurements, especially below 1250 K, as well as the reasons outlined in the synopsis for [1961SAL], this relationship is not discussed further in the current review.

[1969KOS]

The specific-heat results for $\mathrm{FeCl_2(cr)}$ in this paper are those from the earlier publication [1964KOS]. However, in the author's Figure 1, the $C^{\circ}_{p,\mathrm{m}}$ values are plotted against T, and this allows a reviewer to better assess the low-temperature values.

[1969LAN]

This paper presents Gibbs energy values, derived from published sources, for 23 species including 9 aqueous Fe–OH species, 7 Fe–O–H solids (mostly limiting values deduced by the author), and $\mathrm{FeCO_3(s)}$. It is perhaps the first systematic evaluation of the solubility and stability of Fe(III) oxides and oxyhydroxides (hematite, maghemite, goethite, lepidocrocite, and amorphous "$\mathrm{Fe(OH)_3}$"). The author's calculated activity products, $K^{\circ}_{\mathrm{s}} = a_{\mathrm{Fe^{3+}}} a^3_{\mathrm{OH^-}}$, range from an upper limit of $10^{-(37.1\pm0.5)}$ for freshly precipitated "$\mathrm{Fe(OH)_3}$" to a lower limit of $10^{-(41.9\pm0.4)}$ for well-crystallized hematite.

Langmuir also reported $\log_{10} K_s = 10^{-(10.55\pm0.03)}$ for $FeCO_3(cr) \rightleftharpoons Fe^{2+} + CO_3^{2-}$ based on three of his own unpublished measurements at 25 °C. No experimental details were provided, and it is not clear from the paper whether the reported uncertainty is an average deviation, a standard deviation, or a 95% confidence limit. Langmuir also reported $\log_{10} K = 10^{-(10.65\pm0.03)}$ at 30 °C from a recalculation of the data in [1918SMI]. This is consistent with the later recalculation of Preis and Gamsjäger [2002PRE/GAM] and with the recalculation in the present review (see the Appendix A entry for [1918SMI]). Thus, it would appear that reasonable activity corrections and auxiliary data were used in Langmuir's treatment of his own data.

It is unfortunate that the lack of experimental details precludes recalculation of Langmuir's results for $FeCO_3(cr)$. The value from this study is not used directly in the final assessment, but does provide confirmatory evidence for values from other studies [1918SMI], [1981REI/JOH], [1992GRE/TOM].

[1969MOR/SAT]

A large number of cell-potential measurements were made on six different solid-state electrochmical cells involving oxides of Fe, Co, Ni, and Cu, using CaO-stabilized ZrO_2 and Y_2O_3-doped ThO_2 electrolytes and stacked-pellet cell designs. The authors noted good performance of these electrolytes in the temperature range ~970 to 1370 K and at oxygen chemical potentials corresponding to effective p_{O_2} values from 10^{-20} to 1 bar, with overall reproducibility within ±3 mV, and stable potentials were maintained for up to 20 hours. The experimental potential relationships included the following three, which are discussed further in Sections VII.2.2.1 and VII.2.7.2.3 of this review.

(Fe-wüstite *vs.* Ni-NiO) $E/\text{mV} = 141 + 0.112(T/\text{K})$, $1050\ \text{K} < T < 1350\ \text{K}$

(Fe-wüstite *vs.* wüstite-magnetite) $E/\text{mV} = -264 + 0.311\ (T/\text{K})$, $1075\ \text{K} < T < 1250\ \text{K}$

(Ni-NiO *vs.* magnetite-hematite) $E/\text{mV} = -108.7 + 0.319\ (T/\text{K})$, $1070\ \text{K} < T < 1250\ \text{K}$

[1969MOR/WIL]

In this study, extraction of metal ions by the liquid cation-exchanger dinonylnaphthalene sulfonic acid (HDNNS) dissolved in heptane was used for speciation and determination of the stability constant of aqueous Fe(III) complexes. The chlorido and bromido complexes of iron(III) in a solution 1 M in ionic strength H(ClO_4^-, Cl^- or Br^-) were investigated. The radioactivity of ^{59}Fe was used to analyse for iron in the organic and aqueous phases. The decrease in the Fe distribution ratios in the presence of chloride or bromide was interpreted as resulting from formation of two complexes FeX^{2+} and FeX_2^+ ($X^- = Cl^-$ or Br^-) in the aqueous phase. The relation used for the distribution ratio as a function of the chloride or bromide concentrations was:

$$D = (D_0 + D_1\beta_1 c_{X^-} + D_2\beta_2 c_{X^-}^2) / (1 + \beta_1 c_{X^-} + \beta_2 c_{X^-}^2)$$

where

- D is the experimental distribution ratio for an aqueous phase containing a concentration c_{X^-} of chloride or bromide;
- D_0, D_1 and D_2 are the Fe distribution ratios if only a single Fe(III) species, Fe^{3+}, FeX^{2+} or FeX_2^+, were present in the aqueous phase.
- β_1 and β_2 are the formation constants of the 1:1 and 2:1 halide complexes.

This relation took into account the formation of two complexes and the possibility that these two cationic complexes could be extracted. It was found for the chlorido complexes at $I_c = 1$ and 25 °C:

$$\beta_1 = (4.3 \pm 0.5)\ \mathrm{kg{\cdot}mol^{-1}} \text{ and } \beta_2 = (5.5 \pm 2.5)\ \mathrm{kg^2{\cdot}mol^{-2}}.$$

These values are in line with the other literature values, and have been used in our SIT treatment for the calculation of values for K_1° and $\varepsilon(\mathrm{FeCl}^{2+}, \mathrm{ClO}_4^-)$. The measurements were done in a mixed medium, $\mathrm{HClO_4}$-HCl, and in principle this presents a complication in determining the "best" value for K_1°. However it has been found that the values of $\varepsilon(\mathrm{Fe}^{3+}, \mathrm{ClO}_4^-)$ and $\varepsilon(\mathrm{Fe}^{3+},\mathrm{Cl}^-)$ are not very different, and as $\varepsilon(\mathrm{H}^+, \mathrm{ClO}_4^-)$ and $\varepsilon(\mathrm{H}^+,\mathrm{Cl}^-)$ also have similar values (0.14 and 0.12 $\mathrm{kg{\cdot}mol^{-1}}$), it was concluded that HCl can replace $\mathrm{HClO_4}$ without changing the ionic strength effects too much.

K_2 values are scarcer in the literature, and the value from these measurements is (1.23 ± 0.58) $\mathrm{kg{\cdot}mol^{-1}}$ after conversion to a molal constant, in accord with other data of the literature (but with no better precision).

Formation constant values for the bromido complexes, $\beta_1 = (0.75 \pm 0.05)$ $\mathrm{kg{\cdot}mol^{-1}}$ and $\beta_2 = (0.42 \pm 0.10)$ $\mathrm{kg^2{\cdot}mol^{-2}}$, are also in accord with other literature results, showing that bromide forms weaker complexes than chloride, and confirming the rather hard character of Fe^{3+} in the classification of hard and soft bases and acids.

The investigation technique used in this study is very similar to that described by White *et al.* [1961WHI/KEL]. Even the chloride ligand concentration ranges investigated were the same. However the number of experimental points was greater in the present study, and the plot of D = f(ligand), which looked like a straight line in the paper of White *et al.*, clearly showed curvature due to the formation of the 2:1 complex.

[1969NIK/PAL]

Measurements were made of the potential of the Fe(III)/Fe(II) couple in $\mathrm{HCl/HClO_4}$ aqueous solutions (Pt and Ag/AgCl electrodes) at 25 °C at 1.0 and 4.0 M total acid. The iron concentrations were ~ 10^{-4} M. The reported chlorido-complex formation constant[1]

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[1] In the original nomenclature of the authors, K_1 and K_2 were the dissociation constants of the complex. Here, we use K_1 and K_2 as the nomenclature for the stepwise complexation (formation) constants, as is done elsewhere in the present review.

values were (10.5 ± 0.2) M^{-1} and (0.95 ± 0.19) M^{-1} for K_1 and K_2 in the 4.0 M acid and (3.7 ± 0.2) M^{-1} for K_1 in the 1.0 M acid. After corrections for the influence of the Fe(II)-Cl^- interaction these values were used as part of the determination of values of K_1° and $\varepsilon(\mathrm{FeCl}^{2+}, \mathrm{ClO}_4^-)$ by the SIT method. These corrections were done by applying the following procedure:

a) A table of the variation of the potential, E, of a platinum electrode as a function of chloride molal concentrations was established using the revised formation constants of the original paper (Eq. (A.75), not from the raw data from the authors' Figures 2 and 3)

$$E = E^{\circ} + ((RT\ln(10))/F)\log_{10}\{c_{\mathrm{Fe(III)_{total}}}/(c_{\mathrm{Fe(II)_{total}}}(1 + K_1 c_{\mathrm{Cl^-}} + K_1K_2 c^2_{\mathrm{Cl^-}})\}. \quad \text{(A.75)}$$

Here $c_{\mathrm{Fe(III)_{total}}}$ and $c_{\mathrm{Fe(II)_{total}}}$ stand for the concentrations of the total iron(III) and (II) present, and K_1 and K_2 are the stability constants of Fe^{3+} 1:1 and 2:1 chlorido complexes.

b) Fitting of these values to the Nernst equation in which the formation of the iron(II) complexes has been introduced (Eq. (A.76)). That fitting by a non-linear process yields the corrected cumulative formation constant values, β'_{1m} and β'_{2m}, for the Fe^{3+} complexes.

$$E = E^{\circ} + ((RT\ln(10))/F)\log_{10}\{(c_{\mathrm{Fe(III)_{total}}}(1 + \beta_{1m}(\mathrm{VIII.2})\, m_{\mathrm{Cl^-}}))/ \\ (c_{\mathrm{Fe(II)_{total}}}(1 + \beta'_{1m}\, m_{\mathrm{Cl^-}} + \beta'_{2m}\, m_{\mathrm{Cl^-}}{}^2))\} \quad \text{(A.76)}$$

where β_{1m}(VIII.2) is the formation constant of $\mathrm{Fe^{II}Cl^+}$.

When applied to the data of Nikol'ski *et al.* from experiments in 1 M ($HClO_4$, HCl) by using β_{1m}(VIII.2) = 0.022 kg·mol^{-1} derived from the values of β°_{1m}(VIII.2) and $\Delta\varepsilon$ in perchlorate medium given in this book (0.1 kg·mol^{-1} and − 0.12 kg·mol^{-1}, respectively) this yielded for the values of the formation constant of the first iron(III) chlorido complex: β'_{1m} = (3.59 ± 0.20) kg·mol^{-1} (corrected constant), instead of β_{1m} = (3.52 ± 0.20) kg·mol^{-1}, the initial constant after conversion to mass units. This correction is negligible and much smaller than the uncertainties.

In 4 M ($HClO_4$, HCl) the stability of the $FeCl^+$ complex increases, β_{1m}(VIII.2) = 0.033 kg·mol^{-1}, and for the iron(III) cumulative complexation constants the non-linear fit yields β'_{1m} = 8.8 kg·mol^{-1} (instead of β_{1m} = 9.1 kg·mol^{-1}) and β'_{2m} = 10 kg^2·mol^{-2} (instead of β_{2m} = 7.6 kg^2·mol^{-2}). This leads to a value of the corrected second stepwise complexation constant K'_{2m} of 1.14 kg·mol^{-1} instead of K_{2m} = 0.83 kg·mol^{-1}.

In the present review the corrected values from this paper, obtained in mixed $HClO_4$, HCl solutions, have been included in the overall optimization of K_1°, $\varepsilon(\mathrm{FeCl}^{2+}, \mathrm{ClO}_4^-)$, K_2° and $\varepsilon(\mathrm{FeCl_2}^{+}, \mathrm{ClO}_4^-)$ values determined with the SIT formalism. As explained in the main text and in other Appendix A entries for similar cases (*e.g.*, [1969MOR/WIL]), this was motivated by the similarity of the values of $\varepsilon(\mathrm{Fe}^{3+}, \mathrm{ClO}_4^-)$ and $\varepsilon(\mathrm{Fe}^{3+},\mathrm{Cl}^-)$ and also of $\varepsilon(\mathrm{H}^+, \mathrm{ClO}_4^-)$ and $\varepsilon(\mathrm{H}^+,\mathrm{Cl}^-)$.

In mixed electrolyte solutions ($HClO_4$,HCl) such as those used by the authors there is a variation of the density of the solutions and of the coefficient ρ for conversion molar to molal concentrations. For constant molar ionic strengths the molal ionic strength is variable. For this paper and for similar cases [1969MOR/WIL], [1972SEK/TET] we used ξ values approximated for solutions (x M HCl + y M $HClO_4$) of total ionic strength $I_c = (x + y)$ using the expression

$$\xi_{\text{mixture}} = \{x(\xi_{\text{HCl}}\ (\text{at } I_c)) + y(\zeta_{\text{HClO}_4}\ (\text{at } I_c))\}/(x + y).$$

Thus, for a solution (0.5 M $HClO_4$ + 0.5 M HCl), with $\xi_{\text{HCl}} = 1.0222$ and $\zeta_{\text{HClO}_4} = 1.0508$ dm^3 of solution per kg of H_2O for solutions, both at $I_c = 1$ M (Table II-5), ξ_{mixture} is calculated to be $\{(0.5)1.0508 + (0.5)1.0222\} = 1.0365$ dm^3 of solution per kg of H_2O (and similarly 1.1532 dm^3 of solution per kg of H_2O is calculated for the corresponding $I_c = 4$ M solutions (2.0 M HCl + 2.0 M $HClO_4$)).

[1969PAL/STR]

Measurements were made of the potential of the Fe(III)/Fe(II) couple in HCl/$HClO_4$ aqueous solutions (Pt and H_2(Pt) electrodes) at 25 °C at 6.0 M total acid. The iron concentrations were ~ 10^{-5} M. The ratio of chloride to perchlorate spanned the entire concentration range. The reported chlorido-complex formation constant values were 80, 2.85 and 0.10 M^{-1} for K_1, K_2 and K_3, respectively, in the 6.0 M acid. Tagirov *et al.* [2000TAG/DIA] provided an estimated uncertainty of ± 0.5 M^{-1} for the value of K_2. The ionic strength used in this study was ~ 7.2 m, beyond the range of validity of the SIT model. So, these results are not used in the present review for determination of the K_n° values for iron(III) chlorido complexes.

[1969PAN/WEL]

Pankratz and Weller [1969PAN/WEL] carried out heat-capacity (adiabatic calorimetry) measurements from 53.3 to 296.4 K, and drop-calorimetry measurements (reference temperature 298.15 K) from 406.5 to 899.8 K for $Fe_2(SO_4)_3$(cr). As noted by Majzlan *et al.* [2005MAJ/NAV], the report does not indicate whether the solid was the trigonal or monoclinic form (or a mixture). The material was noted as having an X-ray diffraction pattern consistent with ASTM pattern 14-253 [1965BAR/ADA], but this pattern has been deleted from ASTM records when later patterns became available. Posnjak and Merwin [1922POS/MER] found both forms in their syntheses.

The adiabatic-calorimetry results for temperatures above 100 K are similar to those found by Majzlan *et al.* [2005MAJ/NAV] for the monoclinic form (agreement is better than 1%). For temperatures below 80 K the Pankratz and Weller values are greater than those of Majzlan *et al.*, and the difference increases with decreasing temperature. It seems unlikely that this behaviour is related to a trigonal-monoclinic transformation, and more likely reflects a systematic experimental problem. For temperatures above 100 K, the uncertainty in the reported heat-capacity values is estimated in this review as ± 0.21 $J\cdot K^{-1}\cdot mol^{-1}$.

The drop-calorimetry results indicate a sharp endothermic transformation between 795 and 807 K. This may (or may not) be related to a transformation between the two polymorphs, or may be associated with impurities in the sample.

A function

$$(H(T) - H(298.15\ \text{K}))/\text{kJ}\cdot\text{mol}^{-1} = 263.77(T/\text{K}) + 0.10882(T/\text{K})^2 + 5108743(T/\text{K})^{-1} - 105450$$

was fit to the combined drop-calorimetry results from experiments using samples with initial temperatures between 406 and 800 K (weighted assuming an uncertainty of 0.3%) and the heat-capacity results above 350 K from the study of Majzlan *et al.* [2005MAJ/NAV] (which meshed smoothly with the drop-calorimetry measurements, and which were weighted with an assumed uncertainty of 0.1 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$).

A polynomial function

$$(H(T) - H(298.15\ \text{K}))/\text{kJ}\cdot\text{mol}^{-1} = 251.93(T/\text{K}) + 0.10426(T/\text{K})^2 - 84383$$

was fit to the drop-calorimetry results from experiments using samples with initial temperatures above 800 K. Using values from these equations, the enthalpy of the "transformation" (assumed to be at 800 K) was calculated to be 2.3 $\text{kJ}\cdot\text{mol}^{-1}$. However, even the uncertainty in the transition temperature introduces an uncertainty of 0.8 $\text{kJ}\cdot\text{mol}^{-1}$. Furthermore, if heat-capacity results for temperatures below 350 K are also used, it is necessary to introduce extra terms in the enthalpy equation. Thus, the uncertainty in the "transformation" enthalpy is estimated here as ± 1.0 $\text{kJ}\cdot\text{mol}^{-1}$. If the endothermic "transformation" is the result of a phase change in the $Fe_2(SO_4)_3$(cr) (rather than the effect of an impurity), the value found still may be a lower limit, as the initial solid might have been a mixture of monoclinic and trigonal forms.

[1969PRI]

Pribylov reported thermograms for dehydration of $FeSO_4\cdot7H_2O$(cr). Dehydration was carried out at a series of different pressures from 27 to 286 °C, and the tetrahydrate, monohydrate and the anhydrous salt were identified during the process. The reported enthalpies of dehydration are somewhat greater than were found from equilibrium measurements (see Section IX.1.2.2.4), and can be no more than a rough guideline to the equilibrium values. The information in this paper is not used further in the present review.

[1969RIZ/GOR]

Extensive cell-potential measurements are reported for Fe-wüstite *vs.* air, wüstite-Fe_3O_4 *vs.* air, wüstite (variable composition) *vs.* air, Fe-wüstite *vs.* wüstite-Fe_3O_4, and Fe-wüstite *vs.* wüstite (variable composition). A number of fitted expressions relating $\log_{10} p_{O_2}$ to $1/T$ are given for various, apparently arbitrary ranges of T. The results show large deviations from [1988NEI] in oxygen chemical potential for the wüstite-Fe_3O_4 couple (>6 $\text{kJ}\cdot\text{mol}^{-1}$ below 1000 K, increasing with decreasing temperature).

There are unusual results indicating multiple 2-phase regions near the wüstite-Fe_3O_4 boundary, which were not confirmed in later studies from the same laboratory that took account of oxygen permeation effects [1974GID/GOR]. The data from this study are therefore not used in the current review. There is a useful compilation of wüstite phase-boundary compositions from six previous studies (their Table IV).

[1969SID/GOR]

This paper is a report on an amperometric study of complexation of sulfate with iron(III). A solution of iron(III), 9.15×10^{-4} M, was titrated with 0.05 M H_2SO_4 in aqueous perchloric acid solution at 25 °C. The ionic strength was kept constant at 0.058 M. In their calculations the value used by the authors for $K^{-1}_{c1,1(HSO_4^-)}$, the deprotonation constant of HSO_4^-, was 0.012 M (the notation in the original paper was $K_{HSO_4^-}$). The experimentally determined value of the complexation constant was (870 ± 17) M^{-1} (2σ statistical uncertainty). Despite the low acid concentration, no correction for hydrolysis seems to have been attempted, and the result is not used further in the present review.

[1969WEL]

The difficulty in evaluating $\beta_1(Fe(II)Cl^+)$ from kinetic data was discussed. Problems arise because β_1 is determined by regression using differences of rate constants as parameters. The formation constant value is very sensitive to even small errors in these differences. The author provided the value (6.0 ± 0.3) $dm^3 \cdot mol^{-1}$ for $\beta_1(Fe(II)Cl^+$; $I = 1$ M ClO_4^-, 25 °C). This paper has the same calculation problems as an earlier study from the same group [1967WEL/SAL], and appears to have been based on at least some of the same data. The final β_1 value is always calculated from the product of a rate constant k_0 multiplied by β_1 (the author uses $k_0 = 48.1$ $dm^3 \cdot mol^{-1} \cdot s^{-1}$). Hence, the quality of the constant depends not only on the actual fit but also on the quality of the underlying rate constant values. Those in turn seemed to be sensitive to the presence of trace amounts of organic impurities in the reagents. The author used peroxide without any inhibitor to preclude decomposition of the reactant, and rejected the results of Po and Sutin [1968PO/SUT], as those authors used hydrogen peroxide solutions that did contain an organic inhibitor.

Using densities from Söhnel and Novotný [1985SOH/NOV] the $NaClO_4$ molality is calculated to be 1.05 $mol \cdot kg^{-1}$, and the recalculated value of β_1 ($I = 1.05$ m ClO_4^-, 25 °C) is (5.7 ± 0.3) $kg \cdot mol^{-1}$. However, because of the unresolved discrepancies between the results of this study and that of Po and Sutin [1968PO/SUT], this value is not used further in the present review.

[1969WES/GRO]

This paper presents detailed heat-capacity measurements for magnetite at temperatures below 350 K. Magnetite was prepared from mixed Fe and Fe_2O_3 powders, heated for 2 days at 1273 K. The resulting analyses were very close to theoretical values for stoichiometric Fe_3O_4 (found 72.40% Fe, 24.055% Fe(II); theoretical 72.36% Fe, 24.12% Fe(II); Ni + Si + Cu + Mn < 0.01%). X-ray diffraction indicated single-phase magnetite, though the lattice parameter, a_0 = (8.3938 ± 0.0005) Å, is slightly lower than current values for stoichiometric Fe_3O_4 (see Section VII.2.7).

Heat-capacity measurements were made on a 134.584 g specimen; 127 $C^{\circ}_{p,\mathrm{m}}$ values between 6.49 and 347.94 K are presented, including 65 in the Verwey transition region between 106.64 and 128.50 K. The latter revealed a major peak at 118.9 K and a minor peak at 113.3 K, which later studies suggest would indicate some chemical heterogeneity and/or residual stress (see, *e.g.*, [1991SHE/KOE], [1994TAK/AKI]). The purity of a similar material has also been questioned by Hemingway [1990HEM], whose comments were refuted by Grønvold *et al.* [1993GRO/STO]. The data are used in the current evaluation (Section VII.2.7.1) without any correction for possible impurities.

The authors obtained $C^{\circ}_{p,\mathrm{m}}$ (Fe_3O_4, cr, 298.15 K) = 150.79 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ and S°_{m} (Fe_3O_4, cr, 298.15 K) = 146.15 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$.

The discussion focuses on the Verwey transition, including structural, electrical and magnetic as well as thermodynamic aspects. Spin-wave contributions to the heat capacity below 10 K are also discussed.

[1969ZVY/LYA]

This paper reports a potentiometric investigation of iron(III) sulfato complexation in the pH range between 2 and 2.5. Potential and pH measurements were carried out at 25, 35 and 45 °C, and the ionic strength was kept constant (3 M) using $NaClO_4$ (with $HClO_4$). In their calculations the values used by the authors for $K^{-1}_{\mathrm{c1,1(HSO_4^-)}}$, the deprotonation constant of HSO_4^-, were 0.128, 0.091 and 0.071 at 25, 35 and 45 °C, respectively (the notation in the original paper was $K_{\mathrm{HSO_4^-}}$), and values for the hydrolysis constants of Fe(III) (I = 3.0 M) were also reported. The results were interpreted in terms of four species, $FeSO_4^+$, $Fe(SO_4)_2^-$, $Fe_2(OH)_2SO_4^{2+}$ and $Fe_2(OH)_2(SO_4)_2(aq)$. The reported value at 25 °C for K_1, 170 $\mathrm{M^{-1}}$, is marginally consistent with those from other studies, *e.g.,* [1959MAT], [1977ASH/HAN2], as is the variation of the value with temperature [1977ASH/HAN2]. No experimental data suitable for recalculation were provided, and no strong case was made as to why the specific hydrolytic sulfate species were chosen. The values have not been used further in the present review except for Δ_rH_2 = – 15.8 $\mathrm{kJ\cdot mol^{-1}}$, the sole value available in the literature, which has been used for minor temperature-effect corrections. It has been calculated by applying the van't Hoff formula to the three formation constants given in the original paper at 25, 35 and 45 °C after conversion into $K_{2m\mathrm{Fe(SO_4)_2^-}}$ constants.

However this paper was one of the first to try to take into account the possible existence of stable mixed OH^-/SO_4^{2-} monomeric and polymeric species. The pH range and sulfate concentrations chosen for this study were more favorable for the formation of such species than the conditions used by the earlier authors *e.g.*, Mattoo [1959MAT] who worked at lower pH. The concentration of iron(III) was varied between 0.01 and 0.1 M, and the sulfate between 0.01 and 0.5 M. That made it reasonable to postulate the presence of the species listed above. It must be stressed out that it is difficult to assign the formula of so many species on the basis of only limited types of data; here the Fe^{3+} concentration from the potentiometry and the pH change due to neutralisation of the acidity. Very precise measurements and sophisticated calculation programs are necessary to interpret the data qualitatively and quantitatively. Later, other investigators [1988KHO/ROB], using the same principles of speciation but with more modern equipment and computer programs (and a considerably greater number of data points) rejected the formulation of the mixed species given by the authors of the present paper.

[1970ASH]

The heat of solution of $FeCl_2(cr)$ in aqueous hydrochloric acid ($87HCl\cdot4640H_2O$, per mole $FeCl_2$) at 298 K was reported to be $-(78.99 \pm 0.96)\ kJ\cdot mol^{-1}$. This value is consistent with other measurements, but in the absence of appropriate values for the enthalpy of dilution in the mixed electrolyte solution, the heat of solution is not used in the calculation of $\Delta_f H_m^o(Fe^{2+})$.

[1970BER/TUM]

The heat of reaction of Fe^{2+} (as the sulfate) with $H_2O_2(sln)$ was measured in sulfate medium ($\sim0.01\ mol\cdot kg^{-1}\ H_2SO_4(sln)$). The final iron(II) molality was ~0.003 to 0.009 $mol\cdot kg^{-1}$ (the actual iron molalities are specified only to two significant figures, but they can be back-calculated more precisely from the final molar enthalpies of solution)[1]. A value of $-(297.52 \pm 0.08)\ kJ\cdot mol^{-1}$ was reported for the reaction:

$$2\,Fe^{2+}(sln) + H_2O_2(sln) + 2\,H^+(sln) \rightleftharpoons 2\,Fe^{3+}(sln) + 2\,H_2O(sln).$$

Recalculations show that the reported uncertainty was underestimated (σ = $0.67\ kJ\cdot mol^{-1}$). No ionic strength corrections or allowance for heats of complexation (or interaction) of the iron species with sulfate was reported.

In the 0.01 m H_2SO_4 solution, HSO_4^- would have been partially dissociated. The association/interaction of two different anions with the iron species (*cf.* Section IX.1.2.1.3) complicates any attempt to extrapolate results to $I = 0$. The results for the reaction in sulfate medium are not used further in the present review except for comparison purposes.

[1970CAM/BOU]

A thermogravimetric method in $CO\text{-}CO_2$ gas mixtures was used to determine the wüstite phase boundary. Eight measurements (FeO_x composition) are given for the Fe-

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[1] There appears to be a typographical error in column 4, line 1 of Table 2 (the moles of $FeSO_4$ probably should be 0.026, not 0.052).

wüstite boundary at 973 to 1348 K, together with 14 measurements for the wüstite-magnetite boundary at 1073 to 1579 K. Equilibrium gas compositions are not given.

[1970CIR/BUR]

This paper is mainly concerned with CaO-wüstite and MgO-wüstite solid solutions, but it includes some data (equilibrium solid and CO-CO_2 gas compositions) on the pure Fe-wüstite couple at 1073 to 1373 K.

[1970EHR/LEI2]

This spectrophotometric study of the first hydrolysis constant of Fe^{2+} was performed in 2 M $(NH_4)_2SO_4$ ([Fe] = $5 \times 10^{-5} - 10^{-3}$ M) and $NaClO_4$ ([Fe] = 4×10^{-5} and 10^{-4} M), presumably at 25 °C, and an additional series of measurements was made of the formation of $Fe(OH)_3^-$ in the latter medium. The determination of pH was not described. It is quite reasonable to ignore contributions from the second hydrolysis step, but there is a strong possibility that the results in 2 M $(NH_4)_2SO_4$ may be adversely affected by complexation of Fe^{2+} with ammonia and sulfate, such that their reported value for $\log_{10} {}^*K_{1,1}$ of $-(8.51 \pm 0.01)$ is rather suspect. The corresponding value in 2 M $NaClO_4$ of $-(8.07 \pm 0.01)$ may be more meaningful although the reported uncertainty is far too low. Their value for the quasi-stepwise hydrolysis equilibrium,

$$FeOH^+ + 2H_2O(l) \rightleftharpoons Fe(OH)_3^- + 2H^+$$

of $\log_{10}({}^*K_{2,1}{}^*K_{3,1}) = -(25.67 \pm 0.03)$ is difficult to evaluate in view of the pH being reported as high as 13.70 (ionic strength was maintained at 2 M with addition of $NaClO_4$ although hydroxide ions would provide a significant contribution) to establish the $Fe(OH)_3^-$ spectrum, also assuming no higher-order species were formed. The authors discussed measurements of the solubility of $Fe(OH)_2(s)$ but no reliable data can be gleaned from this work and no solid phase characterization was forthcoming.

This work provides a rare value of $\log_{10}({}^*K_{2,1}{}^*K_{3,1})$ (I = 2 M, 25 °C), but in the absence of raw experimental data to allow re-evaluation and in view of the shortcomings described above, the values provided are useful for comparison purposes only.

[1970KAL]

This paper refers to the thesis [1970KAL2] by the author that contains the same calculated and rounded isopiestic data for $NaClO_4$(sln) and $Al(ClO_4)_3$(sln) amongst similar data for other salts and lists only evenly spaced molalities and the corresponding water activities and activity coefficients. Subsequently it was discovered that the original raw isopiestic data were taken from two diploma theses (R. Rothenbach, Diplomarbeit, TU Dresden, 1967; G. Horn, Diplomarbeit, TU Dresden, 1968) which were not in hand at the time this review was completed. No experimental details are provided in this paper, although the companion paper [1970KAL/HOR] indicates that the reference solution was $CaCl_2$ whose osmotic coefficients were taken from

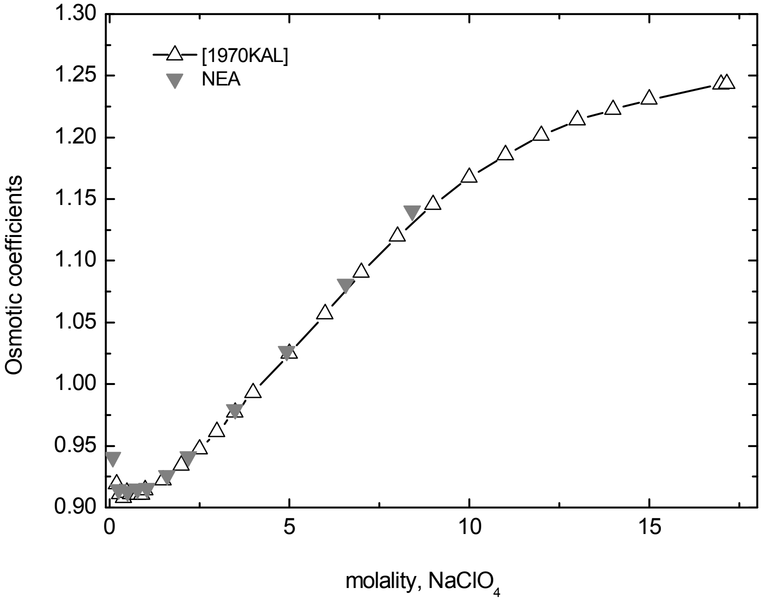
[1959ROB/STO]. Below are tabulated the apparently smoothed results for $NaClO_4$ and $Al(ClO_4)_3$, where the former are treated to gauge the accuracy of the data presented here.

Table A-23: Reported water activities at 25 °C and calculated osmotic coefficients for sodium perchlorate and aluminium chloride

m $NaClO_4$	a_w $NaClO_4$	ϕ $NaClO_4$	m $Al(ClO_4)_3$	a_w $Al(ClO_4)_3$	ϕ $Al(ClO_4)_3$
0.20	0.9934	0.9189	0.30	0.9775	1.0517
0.30	0.9902	0.9111	0.40	0.9687	1.1047
0.40	0.9870	0.9079	0.50	0.9587	1.1694
0.50	0.9837	0.9123	0.60	0.9474	1.2510
0.60	0.9805	0.9109	0.70	0.9340	1.3545
0.70	0.9773	0.9104	0.80	0.9191	1.4630
0.80	0.9741	0.9104	0.90	0.9027	1.5792
0.90	0.9709	0.9107	1.00	0.8848	1.6985
1.00	0.9676	0.9141	1.20	0.8435	1.9689
1.50	0.9514	0.9218	1.40	0.7977	2.2407
2.00	0.9349	0.9342	1.60	0.7461	2.5401
2.50	0.9182	0.9474	1.80	0.6891	2.8711
3.00	0.9013	0.9614	2.00	0.6311	3.1938
3.50	0.8841	0.9768	2.50	0.4822	4.0485
4.00	0.8667	0.9927	3.00	0.3478	4.8856
5.00	0.8314	1.0249	3.143 (sat)	0.3127	5.1331
6.00	0.7958	1.0566			
7.00	0.7596	1.0902			
8.00	0.7242	1.1195			
9.00	0.6898	1.1452			
10.00	0.6566	1.1676			
11.00	0.6250	1.1859			
12.00	0.5948	1.2016			
13.00	0.5663	1.2140			
14.00	0.5397	1.2227			
15.00	0.5142	1.2307			
17.00	0.4671	1.2428			
17.16 (sat)	0.4636	1.2433			

Treatment of the above data for both solutes to derive their interaction coefficients yields the plots shown in Figure A-16.

Figure A-15: Plots of osmotic coefficients for $NaClO_4$ and $AlCl_3$ where the former shows reasonable agreement with the tabulated results of the NEA giving support for the reliability of the corresponding aluminium perchlorate data.



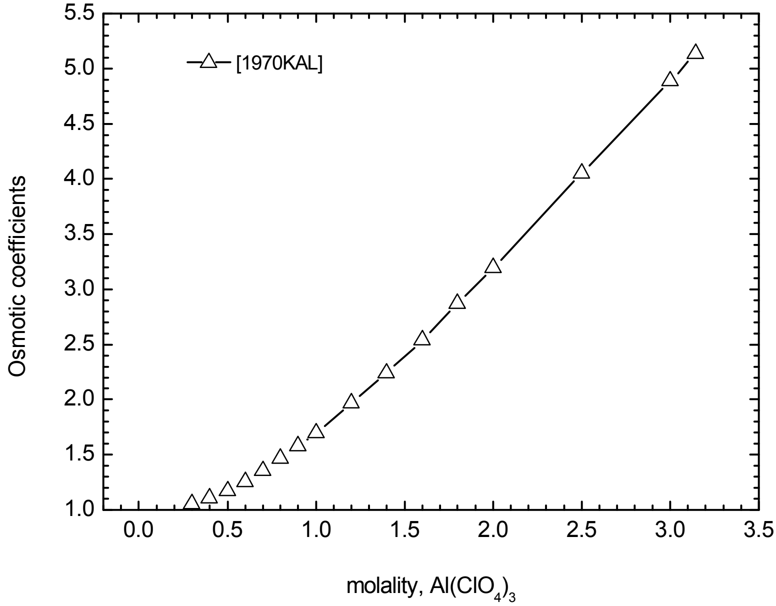
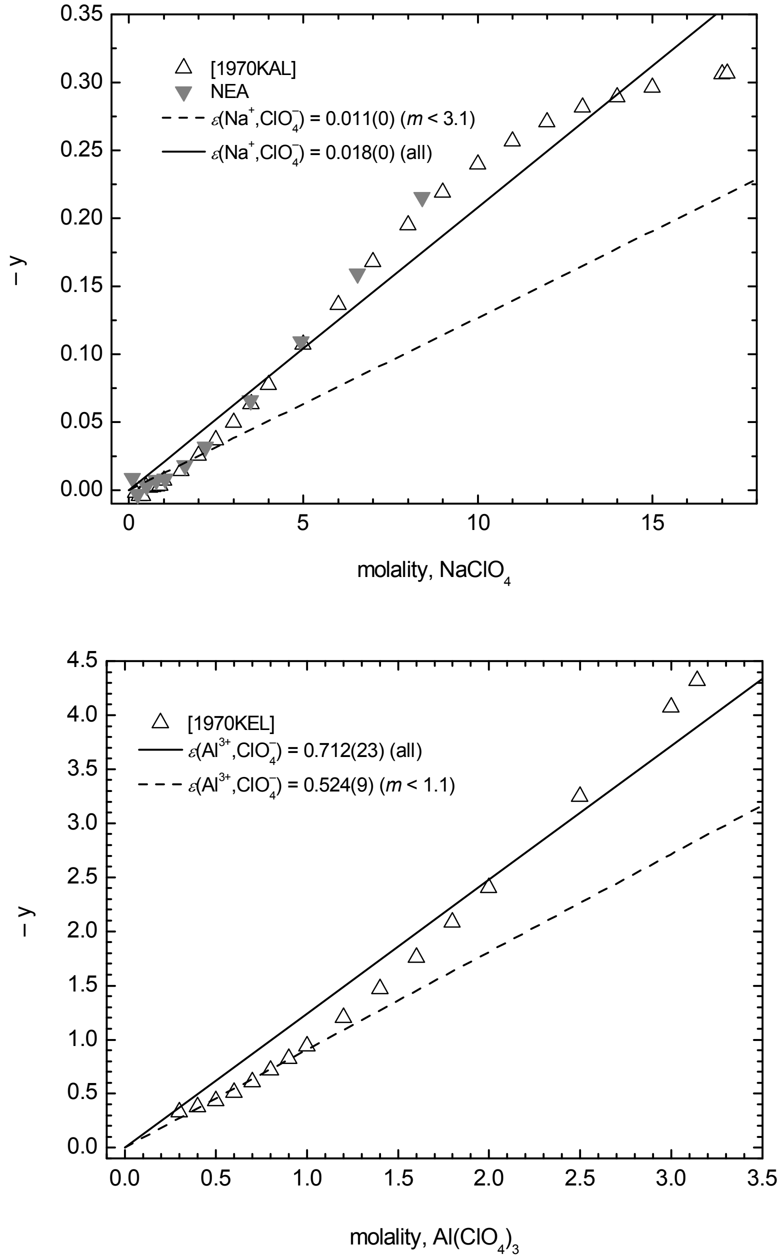


Figure A-16: Plot of Eq. (A.77) for $Al(ClO_4)_3$ at 25 °C, where the first plot for $NaClO_4$ is given to show that not only do the results of Kalman appear compatible with those recommended by the NEA but the resulting $\varepsilon(Na^+, ClO_4^-)$ value determined for data at $I_m \le 3$ is compatible with (0.01 ± 0.01) kg·mol^{-1} tabulated in the Appendix.



$$y = 1 - \phi - \frac{3.516}{I_m(3.375)}\left[1 + 1.5\sqrt{I_m} - 2\ln(1 + 1.5\sqrt{I_m}) - \frac{1}{1 + 1.5\sqrt{I_m}}\right] = -1.727\varepsilon(\mathrm{Al}^{3+}, \mathrm{ClO}_4^-)m_{\mathrm{Al}} \quad \text{(A.77)}$$

The choice of limiting the linear regression to $I_m \leq 1$ mol·kg^{-1} is admittedly random, but the resulting $\varepsilon(\mathrm{Al}^{3+}, \mathrm{ClO}_4^-)$ value of (0.52 ± 0.01) kg·mol^{-1} consequently provides a conservative estimate of $\varepsilon(\mathrm{Al}^{3+}, \mathrm{ClO}_4^-)$ by remaining well within the applicability region of the SIT treatment.

The value of $\varepsilon(\mathrm{Al}^{3+}, \mathrm{ClO}_4^-)$ of 0.52 kg·mol^{-1} was chosen by this review to compare with those of the lanthanide analogues. Note that the uncertainty should be raised to ±0.03 kg·mol^{-1} to take into account that fact that the $CaCl_2$ reference data came from the Appendix of the book by Robinson and Stokes [1959ROB/STO] who presented only smoothed data from previous uncited literature data that have long been superseded.

[1970KAL2]

This thesis was referred to in [1970KAL] by the author, but in fact does not contain the raw isopiestic data for $NaClO_4$(sln) and $Al(ClO_4)_3$(sln) as suggested in the synopsis of the paper. Rather it contains calculated and rounded data in Table 20, page 117 (see Table A-23 in synopsis [1970KAL]) which were derived from earlier diploma theses (*viz.* R. Rothenbach, Diplomarbeit, TU Dresden, 1967; G. Horn, Diplomarbeit, TU Dresden, 1968) that were not available at the time the review of [1970KAL] was carried out.

[1970KAL/HOR]

Isopiestic measurements were made in a chamber evacuated to 18 Torr fitted with six silver-plated cups. The chamber was shaken in a thermostat at (25.00 ± 0.05) °C with equilibration times varying from 10 to 70 hours depending on the concentration. The reference solution was $CaCl_2$ whose osmotic coefficients were taken from the classic book [1959ROB/STO], noting that their tabulated values are smoothed. The activity coefficients of the aqueous solutions of $Cd(ClO_4)_2$, $Al(ClO_4)_3$ and NH_4SCN are reported here and are apparently also smoothed values as they are reported at fixed concentration intervals. Moreover, the corresponding concentrations of the standard $CaCl_2$ solutions are not given.

The same results for aqueous $Cd(ClO_4)_2$ and $Al(ClO_4)_3$ are given in a companion paper [1970KAL] and the SIT treatment of the resulting osmotic coefficients is given in that synopsis.

[1970KIN/WEL]

Twenty-nine $C^{\circ}_{p,\mathrm{m}}$ measurements are reported for a 253.51 g sample of natural goethite at 53.07 to 295.98 K. Unspecified corrections were made for impurities (in weight-%, SiO_2 1.73, Al_2O_3 0.54, Mn_2O_3 0.81, MgO 0.18) and 1.3 weight-% excess H_2O was treated as ice. Only the corrected $C^{\circ}_{p,\mathrm{m}}$ values were tabulated. The following standard quantities were derived:

$$C^{\circ}_{p,\mathrm{m}}\,(\mathrm{FeOOH},\,\alpha,\,298.15\ \mathrm{K}) = 74.48\ \mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$$

$$S^{\circ}_{\mathrm{m}}\,(\mathrm{FeOOH},\,\alpha,\,298.15\ \mathrm{K}) = (60.38 \pm 0.63)\ \mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$$

The latter value includes a contribution of 1.88 $\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$ for the temperature interval from 0 to 51 K, based on extrapolation of a fitted Debye function.

[1970LEV/RAT]

The authors carried out careful measurements of potentials of the solid-state galvanic cell

$$\mathrm{Pt|Fe,\ Fe_2SiO_4,\ SiO_2(quartz)|(La_2O_3)ThO_2|``FeO",Fe|Pt}$$

between 1100 to 1300 K to determine the oxygen chemical potentials corresponding to equilibrium.

The measured potentials for the cell are in excellent agreement with later measurements of O'Neill [1987NEI2] and Jacob *et al.* [1989JAC/KAL] for similar cells. Levitskiy and Ratiani used then current thermodynamic values to convert their measured potentials to values of Gibbs energies of reaction, and reported −1476.5 $\mathrm{kJ{\cdot}mol^{-1}}$ (−352.9 $\mathrm{kcal{\cdot}mol^{-1}}$) for $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}\,(\mathrm{Fe_2SiO_4},\,\alpha,\,298.15\ \mathrm{K})$. When, instead, the corresponding reference electrode values from O'Neill are used, along with consistent auxiliary data for quartz ([1989COX/WAG], [1998CAR/SAL]) and oxygen [1989GUR/VEY]), and with the values selected in this review for the heat capacity and entropy of α-$\mathrm{Fe_2SiO_4}$ (Section X.2.1.1.1) and Fe(cr) (Section V.2), an average value of $-(1476.7 \pm 0.7)\ \mathrm{kJ{\cdot}mol^{-1}}$ (2σ uncertainty) is obtained for $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}\,(\mathrm{Fe_2SiO_4},\,\alpha,\,298.15\ \mathrm{K})$[1]. The recalculated values are essentially independent of the temperature of the original measurements.

The English translation (Russian Metallurgy, (6), (1970), 45-54) was "abridged" and does not include the primary data.

[1970PIC/DOD]

The oxygen chemical potential of wüstite as a function of composition at 1173 K was determined thermogravimetrically in CO-$\mathrm{CO_2}$ atmospheres. Higher precision was achieved than in the more extensive study of [1965VAL/RAC]. Slight non-linearity was observed in the relationship between $\log_{10} p_{\mathrm{O_2}}$ and O/Fe, with a change in slope near the composition $\mathrm{FeO_{1.0947}}$. Limiting compositions for the wüstite field are not given.

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[1] The authors' result for experiment number "14" is omitted in the recalculation, as there seems to be a typographical error in the original table.

[1970ROW/SUT]

In this study, results are reported from investigations to determine the equilibrium constant for the formation of the inner-sphere complex $FeCl^{2+}$ as a function of ionic strength (molar scale) between $I_c = 1$ and $I_c = 6$ at 25 °C, and the rate of approach to equilibrium at $I_c = 6$ was measured by the stopped-flow technique. Spectrophotometric detection of iron(III) chlorido complexes was used in the two studies. To avoid the interference of the $FeCl_2^+$ complex, the ratio Fe^{3+}/Cl^- was always kept greater than 5.

The observed rate constant for the formation of $FeCl^{2+}$ can be described by: $k_{obs} = k_d + k_f\,[\,c_{Fe(III)_{total}} + c_{Cl^-_{total}}\,]$.

The rate constants for dissociation, k_d, and formation, k_f, were determined at 2.5, 25.1 and 44.6 °C in 6 M $HClO_4$ ($I = 6$) and the enthalpies of activation deduced, $\Delta H_d^{\ddagger}$ (dissociation enthalpy of activation) = (63.57 ± 2.51) $kJ\cdot mol^{-1}$, and $\Delta H_f^{\ddagger}$ (formation enthalpy of activation) = (63.57 ± 2.51) $kJ\cdot mol^{-1}$, leading to $\Delta_r H$ ((VIII.3), 6 M, 298 K) = (0.0 ± 3.3) kJ mol^{-1} for the reaction to form the inner-sphere $FeCl^{2+}$ complex.

At constant ionic strength the rate constants decrease with increasing acidity. The rate constant for the forward reaction (formation of $FeCl^{2+}$) increases much more with increasing ionic strength than the rate constant for dissociation of the complex, and is responsible of the strong increase of the stability constant. As the formation of $FeCl^{2+}$ requires removal of a water molecule from the inner sphere of the iron(III) ion, the strong variation of the reaction rate can be attributed to changes in water activity.

This spectrophotometric investigation yielded values for the formation constant of $FeCl^{2+}$ varying from (5.2 ± 0.4) to (110 ± 3) M^{-1} for solutions 1 to 6 M in $HClO_4$.

In this paper there is a detailed discussion that shows that the amounts of $FeCl_2^+$ within the conditions of the study were negligible. There is also a discussion dealing with the possibility of detecting an outer-sphere chlorido complex. Correlated with this problem was the question of whether the molar decadic absorption coefficients of $FeCl^{2+}$ vary as a function of $HClO_4$ concentration. Contrary to Coll *et al.* [1959COL/NAU], the authors concluded that there is variation of the maximum molar decadic absorption coefficient from 140 $m^2\cdot mol^{-1}$ in 1 M $HClO_4$ to 290 $m^2\cdot mol^{-1}$ at 9 M $HClO_4$. This assumption led to the conclusion that it is difficult to investigate outer sphere $FeCl^{2+}$ by spectrophotometry, for there are two possible reasons for changes in UV-visible light absorption change, the molar decadic absorption coefficient decreases at low ionic strength, or the presence of an outer-sphere complex that is transparent at the wavelengths used in the experiment. The stopped–flow technique is not sufficiently rapid to follow the formation or dissociation of the outer-sphere species, which forms in times close to 10^{-5} s.

In the present review the molar concentrations and formation constants were converted to molal values by using Table II-5 values. A polynomial fit to the values was carried out and the coefficients were used to calculate the conversion factors to any concentration of $HClO_4$. An SIT extrapolation ($m \le 8.5$ m) was used to obtain a value of (1.67 ± 0.05) for $\log_{10} K_1^\circ$. However this result, obtained in a separate treatment of the data, was not taken into account in the SIT overall optimization because of the errors caused by the assumption that the molar absorption coefficients of $FeCl^{2+}$ vary with the ionic strength. This problem was addressed later by Schwartz and Dobson [1976SCH/DOD].

[1970SIN/STU]

This paper reports experiments to determine the equilibrium concentration of iron(II) in the presence of carbonate. The experiments were carried out in weakly acidic and neutral aqueous solutions at 17, 22, 22.5 and 30 °C. The authors examined the precipitated product by X-ray diffraction. They concluded that the material was crystalline siderite, and that the key equilibrium was

$$FeCO_3(s) + H^+ \rightleftharpoons Fe^{2+} + HCO_3^- .$$

This seems reasonable; however, this siderite was precipitated at ambient temperature. Although aged for several months, solubility of this solid may well have differed from material synthesized at higher temperature and used by other investigators.

In their Figure 4, the authors provided the experimental points, unbiased by model assumptions, for 22.5 °C, I = 0.10 M ($NaHCO_3$ + $NaClO_4$). Although, unfortunately, individual values for $c_{Fe^{2+}}$ and $c_{HCO_3^-}$ are not listed, the values of the product of the two concentrations are shown. The calibration curves for the Fe^{2+} ion-selective electrode also are given. No detailed results are provided for the experiments at other temperatures.

The hydrogen ion concentrations were measured using a combination "pH" electrode calibrated with HCl solutions of the same ionic strength. In principle, this allows the "model-free" determination of the difference $(pK_{2c} - pK_{s,0,c})$ (where K_{2c} is the well-known dissociation constant of HCO_3^-, $\log_{10} K_2^\circ = -(10.329 \pm 0.020)$ [1992GRE/FUG]). The solubility product $K_{s,0,c}$ is the concentration solubility product for the reaction

$$FeCO_3(cr) \rightleftharpoons Fe^{2+} + CO_3^{2-} .$$

The authors fitted a linear equation

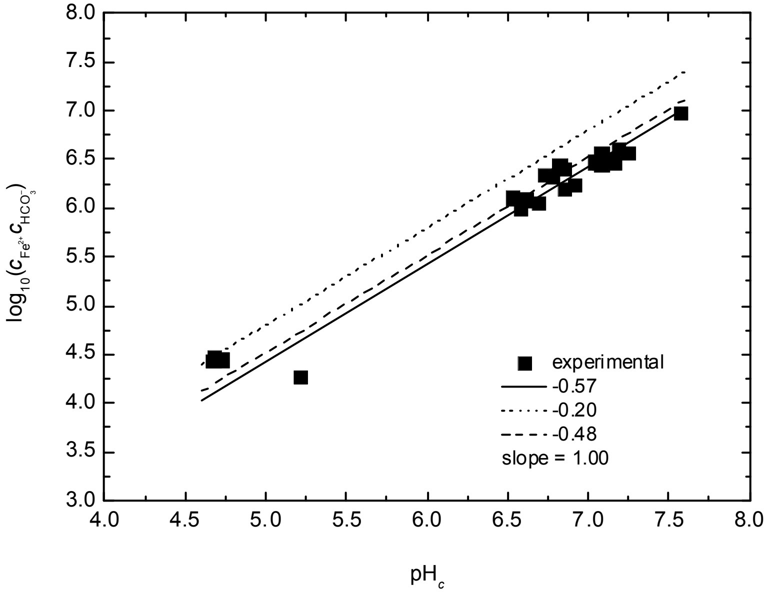
$$-\log_{10}(c_{Fe^{2+}} c_{HCO_3^-}) = -\log_{10} c_{H^+} + (pK_{2c} - pK_{s,0,c})$$

to the values using a fixed slope of 1.0 to obtain an intercept of −(0.57 ± 0.17) for the value of $(pK_{2c} - pK_{s,0,c})$. The implicit assumption that $c_{HCO_3^-} >> c_{CO_3^{2-}}$ is fulfilled to within 0.1% in the narrow experimental pH_c-range 5 to 7.5. Thus, the model used to derive the line in the authors' Figure 4 is thought to be reliable.

Calculation of $\log_{10} K_{2c}$ at I = 0.10069 m $NaClO_4$ (density correction factor of 1.0069) from $\log_{10} K_2^\circ$ using the SIT produces $\log_{10} K_{2c}$ = – (9.902 ± 0.020), and from this one obtains $\log_{10} K_{s,0}^\circ$ = – (9.33 ± 0.17). With $\varepsilon(Fe^{2+}, ClO_4^-)$ = (0.37 ± 0.04) $kg \cdot mol^{-1}$, as derived in this review, the extrapolation from I = 0.10069 m $NaClO_4$ to I = 0 gives $\log_{10} K_{s,0}^\circ$ = – (10.18 ± 0.17). The final value as given by the authors, corrected with the Davies approximation and then adjusted to 25 °C, was $\log_{10} K_{s,0}^\circ$ = – (10.24 ± 0.17).

Re-evaluation of the data from Figure 4 using a weighted (2 parameter) linear regression as outlined in TDB-3 produces a slope of (0.85 ± 0.03) (and an intercept of (0.45 ± 0.18) which leads to rather large value of $\log_{10} K_{s,0}^\circ$ = – (11.2 ± 0.2)). Weights were estimated from the scatter of the data. If the only important iron(II) species is Fe^{2+} and the same Fe(II) solid is at equilibrium over the entire pH range of the experiments, the slope must be 1.00 (Figure A-17), so the smaller slope indicates that there is a problem with these data. The result is sensitive to the weights assigned to individual experimental points, and particularly to the potential outlier at pH_c = 5.2.

Figure A-17: Refitting of the data of [1970SIN/STU]. The lines represent values for a slope of 1.00 with intercepts of – 0.57 ([1970SIN/STU] least-squares fit, $\log_{10} K_{s,0}^\circ$ = – 10.2), – 0.48 ([1970SIN/STU], fit only to points with pH_c < 7.0), – 0.20 (using $\log_{10} K_{s,0}^\circ$ = – 10.6).



The experimental solubilities are higher than those reported from most other studies at similar temperatures (except for the two lowest ionic strength results of Silva *et al.* [2002SIL/LIU]). Bruno *et al.* [1992BRU/WER] suggested that this was because Singer and Strum approached equilibrium from oversaturated solutions (also see Jensen *et al.* [2002JEN/BOD]). However, the measurements of Geeenberg and Tomson [1992GRE/TOM] also were made using solutions in which equilibrium was approached from oversaturation.

Using an ion-sensitive electrode the authors found no electrode potential differences between a calibration curve in $Fe(ClO_4)_2$-solutions and the experimental $c_{Fe^{2+}}$ solutions containing HCO_3^- / CO_3^{2-} (such that $(c_{HCO_3^-} + 2c_{CO_3^{2-}}) \le 0.011$ M). It was concluded that the formation constant for $FeHCO_3^+$ is < 10 $dm^3 \cdot mol^{-1}$ and for $FeCO_3(aq)$ should be less than 1×10^5 $dm^3 \cdot mol^{-1}$.

The latter conclusion is marginally discrepant with the results of Bruno *et al.* [1992BRU/WER] who reported a value greater than 3×10^5 for this constant. Hence, it could be that the experimental points at $pH_c > 7$ were affected by barely detectable, but still significant, amounts of $FeCO_3(aq)$. If this was the case, the data points at $pH_c > 7$ would be moved up in the authors' Figure 4, thereby slightly increasing the value of the intercept.

The results from this study indicate that iron(II) carbonato complexes are unlikely to be substantially stronger than suggested by Bruno *et al.* [1992BRU/WER]. The solubility results *are* consistent with those from the study of Bardy and Péré [1976BAR/PER] who also used unheated precipitate. However, the results of Singer and Stumm are inconsistent with those found in other studies that used heat-treated material, and are not used further in the present review.

[1970SWE/BAE]

A plug-flow reactor was used to study the solubility of Fe_3O_4 from 50 to 300 °C using feed solutions (1×10^{-4} m HCl to 4×10^{-4} m KOH) presaturated at 25 °C with 1 atm H_2. The magnetite charge was characterized before and after the experimental series and although the authors claim that γ-Fe_2O_3 was not present, subsequent work [1980TRE/LEB] indicates that in basic solutions oxidation had indeed occurred such that the data for the stability of $Fe(OH)_3^-$ are probably not valid. The equilibria are represented by:

$$\tfrac{1}{3}\,Fe_3O_4(cr) + (2-b)H^+ + \tfrac{1}{3}\,H_2(g) \rightleftharpoons Fe(OH)_b^{(2-b)+} + (\tfrac{4}{3}-b)H_2O.$$

Due to the use of only weak acidic and basic solutions to change the pH of the feed stock, calculation of the actual H^+ molality required iteration with the projected iron(II) speciation in solution, as well as the partial pressure of H_2, the appropriate value of K_w and the initial H^+ or OH^- molality, constrained by a charge-balance equation. There appears to be no consideration of activity coefficients, presumably due to the low ionic strengths employed and to the large uncertainty introduced in the estimation of pH. The one constraint placed on their fit of the data was to fix $\Delta S^{\mathrm{o}}_{\mathrm{s},0}$ (298.15 K) = – 105.9 J·K^{-1}·mol^{-1} for the equilibrium corresponding to b = 0. The authors stated that this assumption had minimal effect on the values of $^{*}\beta_{1,1}$ but did affect the enthalpy of reaction. They report the following values at 25 °C: $\log_{10}{}^{*}\beta^{\mathrm{o}}_{\mathrm{s},0} = 12.02$, $\log_{10}{}^{*}\beta^{\mathrm{o}}_{\mathrm{s},1} = 2.70$, $\log_{10}\beta^{\mathrm{o}}_{\mathrm{s},2} = -8.54$ and $\log_{10}{}^{*}\beta^{\mathrm{o}}_{\mathrm{s},3} = -17.42$, although the latter is now believed to be an artifact of the presence of Fe(III) in solution at high pH. These solubility constants lead to estimates of $\log_{10}{}^{*}K^{\mathrm{o}}_{1,1} = -(9.3 \pm 0.5)$ and $\log_{10}{}^{*}K^{\mathrm{o}}_{2,1} = -11.24$.

The authors provided the following table of parameters for the general fitting equation corresponding to the solubility equilibrium given above:

$$\ln\beta_{\mathrm{s}b} = [-A/T\ B\{\ln(T/K) - 1\} + D]/R \qquad \text{(A.78)}$$

where the results for b = 3 have been discarded. These functions are plotted in Figure A-18.

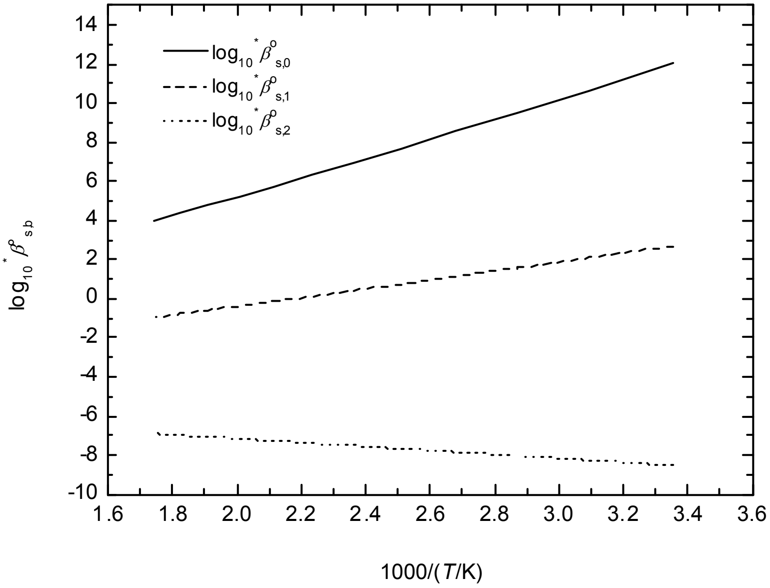
This review accepted the values of $\log_{10}{}^{*}\beta^{\mathrm{o}}_{\mathrm{s},b}$ for b = 0, 1 and 2 (no asterisk), and combined them with those of [1980TRE/LEB] in new fits *vs*. temperature to obtain the thermodynamic parameters of the hydrolysis products at 25 °C. These fits are shown and discussed in the synopsis to [1980TRE/LEB], noting that solubility measurements provide the only means of estimating the hydrolysis constants, $^{*}\beta^{\mathrm{o}}_{2,1}$ and $^{*}\beta^{\mathrm{o}}_{3,1}$, of Fe^{2+}, albeit with large uncertainties, at the present time due to the insolubility of iron(II) hydroxides and oxides.

Table A-24: Parameters for Eq. (A.78) given in [1970SWE/BAE] (units converted from cal to J).

b	A/J·mol^{-1}	B/J·mol^{-1}·K^{-1}	D/J·mol^{-1}·K^{-1}
0	– 112449	41.05	– 339.78
1	– 49091	14.02	– 178.74
2	19309	0 *	– 98.62

* Fixed at zero.

Figure A-18: Plot of the solubility constants derived from the fitting function given in Eq. (A.78).



[1970VEC/ROG]

Vecher and Rogach reported measurements for the cell Pt, Mo | Ni, NiF_2 | CaF_2 | FeF_2, Fe | Mo, Pt at temperatures from 885 to 1000 K. The results were not tabulated, but were summarised using a linear equation:

$$E(\text{A.79})/\text{mV} = 84.3 + 0.001\ (T/\text{K})$$

$$NiF_2(cr) + Fe(cr) \rightleftharpoons FeF_2(cr) + Ni(cr). \qquad (A.79)$$

Potentials calculated using this equation differ from those found in similar studies [1966LOF/MCI], [1973SKE/PAT], [1975CHA/KAR], [1981SCH/GOK], [1988AZA/SRE] by approximately 200 mV, and were questioned by Bagshaw [1972BAG]. The authors acknowledged that their results were in error [1972VEC/ROG], [1978PET/VEC], and indicated that the results had been adversely affected by the volatility of NiF_2 in the cells. The results for the reaction

$$Fe(s) + CoF_2(s) \rightleftharpoons FeF_2(s) + Co(s)$$

in the later paper [1978PET/VEC] agree reasonably with those obtained by other groups (*e.g.*, [1975CHA/KAR]).

[1971BOG/GOR]

The authors reported a differential thermogram for a sample of hydrated iron(II) chloride (initially $FeCl_2 \cdot 4H_2O$) with endotherms at 349, 393, 441 and 505 K (76, 120, 168 and 232 °C). The latter three temperatures correspond reasonably well with values from earlier work [1949SCH], while the lowest transition temperature may correspond to dehydration of the tetrahydrate to the dihydrate and $H_2O(l)$. The heating rate used was $0.056\ K \cdot s^{-1}$.

[1971CHI/TSV]

Mass spectrometric measurement of hematite decomposition yielded the following relationship for the equilibrium p_{O_2} over Fe_3O_{4+x} + Fe_2O_{3-y} at 1030 to 1200 K.

$$\log_{10}(p_{O_2}/bar) = 14.10 - \frac{25200}{(T/K)}$$

This result is compared with solid-state cell-potential measurements in Section VII.2.2.1. Much higher dissociation pressures were observed over single-phase, stoichiometric hematite at 903 to 982 K.

$$\log_{10}(p_{O_2}/bar) = 6.13 - \frac{13750}{(T/K)}$$

This emphasizes the importance of the small composition range of hematite in determining the dissociation p_{O_2}, even at such relatively low temperatures.

A series of measurements on the magnetite-wüstite equilibrium at 1490 to 1600 K is beyond the scope of the current review.

[1971FRE]

This paper is a report of a study of equilibrium between $FeCO_3$ and hematite-magnetite or graphite buffers at 0.5, 1.0 and 2.0 kbar. $FeCO_3$ (synthesized by thermal decomposition of $FeC_2O_4 \cdot 2H_2O$ at 350 to 380 °C, 2 kbar $H_2O(g)$) was used. The reaction was

$$3\,FeCO_3(s) + \tfrac{1}{2}O_2(g) \rightleftharpoons Fe_3O_4(s) + 3\,CO_2(g).$$

For the first buffer, the experimental equilibrium temperatures were ~ 362 - 364 °C (0.5 kbar and 1.0 kbar only). For the second buffer, the experimental equilibrium temperatures were ~ 455 to 465 °C (also see [1965FRE/ROS]). These temperatures are 150 to 200 K greater than estimated from then-current thermodynamic data. As discussed by the authors, the uncertainties in the equilibrium constants were not sufficiently small to allow a good assessment of the enthalpies of reaction at 0.5 and 1.0 kbar (though the values appear to differ substantially from the then-current thermodynamic data, and the sign of $d(\Delta_r G/dT)$ is reversed).

[1971HEM/RIC]

The kinetics of the reaction, $FeOH^{2+} + H_2O(l) \rightleftharpoons Fe(OH)_2^+ + H^+$, were studied at $I \leq 3 \times 10^{-4}$ M (total iron(III) perchlorate concentrations of 0.781 - 6.83 × 10^{-5} M) at 25 °C by the electric field jump relaxation kinetic method. The rate of the first hydrolysis step was too fast to be measured (accessible relaxation times of 0.3 to 10 μs). The authors used $\log_{10}{}^*K^o_{1,1}$ and $\log_{10}{}^*K^o_{2,1}$ values of − 2.46 and − 4.7, respectively, from [1938LAM/JAC], and $\log_{10}{}^*K^o_{2,2}$ of 1.48 from [1955MIL/VOS] to speciate their solutions. The measurement of solution pH was not described. They measured the rate constants: (forward reaction) $k_2 = (6.1 \pm 0.4) \times 10^4\ s^{-1}$ and (reverse reaction) $k_{-2} = (8.0 \pm 1.0) \times 10^9\ M^{-1}{\cdot}s^{-1}$, corresponding to a $\log_{10}{}^*K^o_{2,1}$ value of − 5.1. They estimate k_1 at *ca*. $3 \times 10^7\ s^{-1}$, which is much faster than for Cr^{3+} and Al^{3+}, for example.

This is an interesting study but it does not contain results relevant to this review apart from the approximate value of $\log_{10}{}^*K^o_{2,1}$.

[1971LAN]

The relative stabilities of goethite and hematite were calculated as a function of particle size, based in part on the heat-of-dissolution study of these two phases by [1966FER] and ignoring surface entropy. The following expression (as corrected by Langmuir in 1972) was obtained for the Gibbs energy at 298 K of the reaction:

$$2\,\alpha\text{-FeOOH} \rightleftharpoons \alpha\text{-Fe}_2\text{O}_3 + \text{H}_2\text{O(l)}$$

$$\Delta_r G^o_m/\text{kJ}\cdot\text{mol}^{-1} = (2200 \pm 2500) - \frac{303}{x} + \frac{143}{y}$$

where x and y are the average particle dimensions of goethite and hematite, respectively (assuming cubic geometry, a poor assumption in the case of goethite). This expression suggests that well-crystallized goethite is stable with respect to well-crystallized hematite in liquid water at 298 K.

The surface-energy data for goethite have been superseded by [2005MAJ/NAV], and those for hematite are questionable because of the relatively low-temperature, dry conversion of goethite used by Ferrier [1966FER] to obtain finely divided hematite (see further discussion in Section VII.2.9). An alternative treatment of data from [1966FER] and other sourecs is given by [1994DIA/KHO].

[1971LAN/WHI]

The activity product, defined by the authors as a logarithmic quantity, $pQ = -\log_{10}\{Fe^{3+}\}\{OH^-\}^3$ (*i.e.*, $-\log_{10} a_{Fe^{3+}} a^3_{OH^-}$ in the nomenclature of the present review), was determined for aqueous solutions in contact with synthetic Fe oxyhydroxide precipitates at 25 °C as a function of pH titration and subsequent aging, based on measured pH, Eh, and dissolved Fe(II) and/or Fe(total) analysis, taking into account cation hydrolysis and sulfate complexation. Similar measurements were reported for 24 different iron-containing well waters at temperatures near 15 °C.

Several of the values of pQ for aged, synthetic precipitates, and many of those for the well waters, represent solubilities up to two orders of magnitude too low (pQ = 42 to 44) to be consistent with current thermodynamic values for goethite and Fe^{3+}, *i.e.*, they represent $\Delta_{\mathrm{diss}}G^{\mathrm{o}}_{\mathrm{m}}$ up to ~ 10 kJ·mol^{-1} too positive. It is possible that there were difficulties measuring the Nernst potential of the Fe^{2+}/FeOOH(s) couple, as discussed by Doyle [1968DOY], who observed a negative bias of about 100 mV in some attempted potential measurements on this couple, which corresponds to a negative bias of two orders of magnitude in the Fe^{3+} activity.

[1971MES]

Potentiometric titrations were performed at 25 °C in a Harned-type cell with liquid junction (0.0069 mol·kg^{-1} KCl) *vs.* initial concentrations of 3.1×10^{-3} mol·kg^{-1} $FeCl_2$ and 4.7×10^{-4} mol·kg^{-1} HCl. A more concentrated NaOH titrant was used and the E_{lj} was considered to remain constant during the titration. It appears that the results of two titrations are listed with $\bar{n} = (h - H)/c_{\mathrm{Fe_{total}}}$ values reaching 0.00400 and 0.00566, presumably before precipitation of iron(II) hydroxide phases occurred. A $\log_{10}{}^{*}K_{1,1}$ value of – (9.58 ± 0.08) was reported based on an undisclosed number of titrations. The average ionic strength can be estimated as 0.0097 consisting mainly of unhydrolyzed dissociated $FeCl_2$(sln).

The assumption that E_{lj} was constant during these titrations with no supporting electrolyte is dubious and the uncertainty in $\log_{10}{}^{*}K_{1,1}$ was doubled accordingly to allow for a 5 mV junction potential. This value of $\log_{10}{}^{*}K_{1,1}$ may be judged as a fairly reliable measurement and should be included in the data assessment:

Consider:

$$Fe^{2+} + H_2O(l) \rightleftharpoons FeOH^{+} + H^{+}$$

$$\log_{10}{}^{*}\beta_{1,1} + 2D = \log_{10}{}^{*}\beta^{\mathrm{o}}_{1,1}$$

Assuming I_m = 0.0097, D = 0.044, $\log_{10}{}^{*}\beta^{\mathrm{o}}_{1,1} = -9.49$, as also reported by Mesmer.

Therefore, the review accepts this value of $\log_{10}{}^{*}\beta^{\mathrm{o}}_{1,1} = -(9.49 \pm 0.16)$.

[1971WIL]

As part of a broader study, Williams used an electrode of the form

$$Pt|O_2(1\ \mathrm{atm.})|(CaO)_{0.15}(ZrO_2)_{0.85}|O_2(f_i)|Pt$$

to measure the fugacity of oxygen in a CO_2/H_2 mixture which was equilibrated with mixtures of iron and SiO_2(α-cristobalite) at 1198 and 1451 K. The samples were quenched, and the oxygen fugacities for the conditions resulting in formation of fayalite were bracketed. At 1198 K f_{O_2} was $10^{-16.59}$ bar; at 1451 K f_{O_2} was $10^{-12.79}$ bar. Based on consistent auxiliary data for α-cristobalite ([1982RIC/BOT], [1989COX/WAG]) and oxygen [1989GUR/VEY], and with the values selected in this review for the heat capacity and entropy of α-Fe_2SiO_4 (Section X.2.1.1.1) and Fe(cr) (Section V.2), values of -1465.3 kJ·mol^{-1} and -1477.0 kJ·mol^{-1} are calculated for $\Delta_f H_m^\circ$ (Fe_2SiO_4, α, 298.15 K). The reason for the large difference in the values based on the experiments at the two different temperatures is not clear, though the result from the measurement at 1451 K is consistent with results from calorimetric [1952KIN] and galvanic-cell [1987NEI2] measurements. The results from this study are not used further in the present review except for comparison purposes.

[1972BAG]

In this note, Bagshaw questioned the results of Vecher and Rogach [1970VEC/ROG] concerning the potential of the cell Pt, Mo | Ni, NiF_2 | CaF_2 | FeF_2, Fe | Mo, Pt. He also reported a linear equation:

$$E(\text{A.80})/\text{mV} = 287.9_6 + 0.1_1\,(T/\text{K})$$

for

$$NiF_2(cr) + Fe(cr) \rightleftharpoons FeF_2(cr) + Ni(cr) \qquad (\text{A.80})$$

based on his own studies from 866 to 1054 K. These results do not appear to have ever been published elsewhere. A third-law analysis has been done using auxiliary values from the present review, and thermodynamic quantities for Ni(cr) and NiF_2(cr) from Gamsjäger *et al.* [2005GAM/BUG]. This leads to values of -710.5 and -711.8 kJ·mol^{-1} for $\Delta_f H_m^\circ$ (FeF_2, cr, 298.15 K) based on the potentials at 866 and 1051 K.

As discussed in the Appendix A entry for Lofgren and McIver [1966LOF/MCI], Bagshaw also reported an equation that had been fitted to their results.

[1972BON/HEF]

The fluorido complexes of divalent transition metals were investigated potentiometrically with a fluoride ion-sensitive electrode in 1 M $NaClO_4$ at 25 °C. Specific precautions were taken in the case of Fe(II) because of its sensitivity to oxidation in the presence of traces of oxygen. Since iron(II) was supplied in the form of $FeSO_4\cdot 7H_2O$, barium perchlorate solution was added to precipitate the excess sulfate. The presence of precipitated $BaSO_4$ was found not to affect the performance of the fluoride electrode. Titrations were performed under argon gas. Due to its sensitivity to oxidation the Fe(II) system was investigated under a variety of conditions. In several experiments NaI was added (0.1 M) to reduce possible traces of iron(III) that might have been present. A series of experiments was performed in solutions that had previously been degassed with hydrogen to produce a reducing environment. In all cases no appreciable deviation was observed compared to the other measurements on iron(II)-fluoride complexation. At 298.15 K the authors calculated a value of (6.7 ± 0.30) dm^3·mol^{-1} for β_1(298.15 K, 1 M $NaClO_4$), which gives a value of (6.4 ± 0.3) kg·mol^{-1} for β_1(298.15 K, 1.0515 m $NaClO_4$) in the molal scale when converted according to the density tables of Söhnel and Novotny [1985SOH/NOV].

[1972DAV/SME]

This paper is primarily concerned with solid-state cell-potential measurements on (Ni,Fe)O_x oxides coexisting with Fe-Ni alloys. It includes the following relationship obtained for the Fe-wüstite couple *vs*. Ni-NiO at 873 to 1323 K.

$$E/\text{mV} = 157.1 + 0.101(T/\text{K}) \pm 0.9$$

[1972EVA/WES]

The authors make the case for a "multiple-ordering" theory of the low-temperature [Verwey] transition in Fe_3O_4, based on bifurcated C_p peaks obtained with two samples from very different preparative routes: dry synthesis per [1969WES/GRO] and hydrothermal synthesis as later described in [1976BAR/WES]. The C_p curves for these specimens at 105 to 130 K are plotted, but no data are tabulated; the plots presumably correspond to data published in [1969WES/GRO] and [1976BAR/WES]. Peaks occur about 4 K higher for the hydrothermal material, which contained traces of Mn^{2+}, than for the dry synthetic product. There are differences in the peak profiles, but "areas under the peaks are not appreciably different", *i.e.*, the transformation enthalpies are similar.

[1972KOR/PER]

Temperature-jump relaxation kinetics of the aquation (chloride ligand substitution by water) reaction of $Fe(H_2O)_5Cl^{2+}$ was followed spectrophotometrically over the temperature range 10 to 33.6 °C in Li, K and Cs nitrate solutions. At I = 1 M, 28 °C and with [Fe(III)] = 2×10^{-4} M, they report that $K_{1\text{FeOH}^{2+}} = (c_{\text{H}^+} c_{\text{FeOH}^{2+}}) / c_{\text{Fe}^{3+}}$ = $(2.6 \pm 0.2) \times 10^{-3}$ in $LiNO_3$, $(1.8 \pm 0.3) \times 10^{-3}$ in KNO_3 and $(1.2 \pm 0.1) \times 10^{-3}$ kg·mol^{-1} in $NaClO_4$.

The small formation constant for $Fe(H_2O)_5Cl^{2+}$ was interpolated from the results by [1942RAB/STO] in $NaClO_4$ solutions. Most of the experiments were carried out at [H+] ≥ 0.1 M, where the reaction paths are believed to be:

Path 1: $Fe(H_2O)_5Cl^{2+} + H_2O(l) \rightleftharpoons Fe(H_2O)_6^{3+} + Cl^-$

Path 2: $Fe(H_2O)_5Cl^{2+} \rightleftharpoons Fe(H_2O)_4Cl(OH)^+ + H^+$ (very fast)

$Fe(H_2O)_4Cl(OH)^+ + H_2O(l) \rightleftharpoons Fe(H_2O)_5(OH)^{2+} + Cl^-$

such that $Fe(H_2O)_4Cl(OH)^+$ is an intermediate in Path 2 of the aquation process.

Values of k_1 for the acid-independent path (1) are quoted at 25 °C and 0.89 M ionic strength as being: (3.9 ± 0.4) (KNO_3) and (10 ± 1) ($LiNO_3$); presumably the units are s^{-1}, although this is not stated anywhere in the paper. Path 2 involves an apparent second-order rate constant with values of (4.0 ± 0.4) M^{-1}·s^{-1} (KNO_3) and (2.0 ± 0.2) M^{-1}·s^{-1} ($LiNO_3$) that is a product of the acid dissociation constant for the hydrolysis step and the subsequent second aquation step. Tentative values of these two contributions are $^*K_1 = (c_{\text{FeClOH}^+} c_{\text{H}^+}) / c_{\text{FeCl}^{2+}}$ = (0.012 ± 0.002) and k_2' = (810 ± 100) s^{-1} (though the authors note that the reported uncertainty does not include possible systematic errors) at

0.4 M (identity of the salt was not given) ionic strength at presumably 25 °C. The result for ${}^{*}K_1$ was later rejected by Byrne and Kester [1981BYR/KES] who found by spectrophotometry that the formation constant of the mixed chloridohydroxido complex, if it exists, is at least 180 times smaller. The formation constant from this paper [1972KOR/PER] is not credited because of the indirect proof of existence of $FeClOH^+$ provided by the kinetics, as opposed to the very straightforward interpretation of the spectrophotometric data in [1981BYR/KES].

[1972LAN/CAR]

In this paper, as part of a study of magnetic transitions in $FeCl_2$ and $FeBr_2$ the authors discussed their measurements of the heat capacities of single crystals. The Néel temperatures were reported as 23.8 K for $FeCl_2$ and 14.2 K for $FeBr_2$. The authors' Figure 1 shows the data points (5 to 50 K) for $FeCl_2$. In the present review the data points have been digitized. In the region of the maximum in the anomaly, the heat capacities are in excellent agreement with those of Westrum [1961STO]. Except at the lowest and highest temperatures, the experimental heat-capacity values are similar to the values determined by Trapeznikowa and Schubnikow [1935TRA/SCH], but there is much less scatter. For the purposes of fitting functions to the calorimetry results, the uncertainties in the individual values for the heat capacities were estimated in the present review as $\pm 0.2\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. For $FeBr_2$, measurements were done from 4 to 60 K, though the measurements were only indicated as data points (on the authors' Figure 3) to 24 K. Digitization of the points from that figure and integration of $C^{\circ}_{p,\mathrm{m}} / T$ from 6 t 24 K indicates ~ 6 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ for the difference between S°_{m} ($FeBr_2$, 24 K) and S°_{m} ($FeBr_2$, 6 K).

[1972RAO/TAR]

Eleven measurements are reported for the potential differences of magnetite-hematite *vs*. Cu-Cu_2O at temperatures from 915 to 1310 K. An Ar-atmosphere, stacked-pellet cell configuration was used. The copper oxide reference electrode was chosen to minimize problems (mixed potential) with gas-phase oxygen transport.

Separate regression equations are given for data above and below the "transformation" (= Néel transition) temperature of ~950 K, though only two measurements were made below this point. Note that the two expressions differ by 1.10 mV at 950 K, and they actually intersect at 1060 K.

$$E/\mathrm{mV} = -415.9 + 0.3656(T/\mathrm{K}) \quad (915\ \mathrm{K} < T < 950\ \mathrm{K})$$

$$E/\mathrm{mV} = -426.5 + 0.3756(T/\mathrm{K}) \quad (950\ \mathrm{K} < T < 1310\ \mathrm{K})$$

The authors noted that initial equilibration at ~1270 K resulted in very long equilibration times (up to 12 hours) for subsequent measurements at lower temperatures; a pre-equilibration temperature of ~1100 K was therefore selected.

The results, which are in excellent agreement with those of [1969BRY/SME] and [1968CHA/FLE] but not with those of [1988NEI], are discussed further in Section VII.2.2.1.

[1972RAU]

Equilibrium measurements were made on the following four gas-solid equilibria in the Fe-O-H system:

$$\tfrac{1}{4}\,Fe_3O_4(s) + H_2(g) \rightleftharpoons \tfrac{3}{4}\,Fe(s) + H_2O(g) \qquad (A.81)$$

$$3\,Fe_2O_3(s) + H_2(g) \rightleftharpoons 2\,Fe_3O_4(s) + H_2O(g) \qquad (A.82)$$

$$\text{“FeO”}(s) + H_2(g) \rightleftharpoons Fe(s) + H_2O(g) \qquad (A.83)$$

$$\tfrac{1}{3}\,Fe_3O_4(s) + \tfrac{1}{3}\,H_2(g) \rightleftharpoons \text{“FeO”}(s) + \tfrac{1}{3}\,H_2O(g) \qquad (A.84)$$

Use of a hydrogen-permeable Pd membrane permitted control and measurement of p_{H_2} and separate measurement of the total gas pressure. Solid reagents were prepared from ~99.7% pure α-FeOOH powder precursors, doped in some tests with 0.36% Sn, dehydrated *in vacuo* at 573 K to form α-Fe_2O_3 and reduced as required in H_2 at 583 K. The original FeOOH powder consisted of acicular crystals ~0.1 - 0.5 μm long; after equilibrium measurements the solid mixtures were agglomerates of roughly spherical particles ~0.1 - 0.3 μm in diameter.

The most useful results are 17 measurements on equilibrium (A.81) at 583 to 839 K without Sn dopant; they are probably the most accurate data available on this reaction. Third-law analysis of the 10 measurements between 683 and 839 K yields $\Delta_f H^\circ_m$ (Fe_3O_4, cr, 298.15 K) = − (1114.95 ± 0.40) kJ·mol^{-1}, while seven less precise, lower-temperature measurements (down to 583 K), give a value of − (1115.10 ± 1.67) kJ·mol^{-1}. These values exclude uncertainties in the thermal data. There is a typesetting error in the $\log_{10} K_p$ column of Table 1 (an erroneous minus sign for all but 6 of the tabulated data).

The data also include 11 measurements on equilibrium (A.81) with Sn dopant at 573 to 795 K; though no dopant effect was detected, these data were not used in the current review. Also given are 6 measurements on equilibrium (A.82) at 767 to 840 K, which appear to be close to the experimental limits of the method ($p_{H_2} \approx 3 - 4$ Pa) and are therefore not included in the evaluation of $\Delta_f H^\circ_m$ (Fe_2O_3, α, 298.15 K) in Section VII.2.2.1. Finally there are 11 measurements on equilibrium (A.83) at 860 to 978 K and 5 on equilibrium (A.84) at 859 to 882 K, adding relatively little to the huge quantity of data for these two reactions (see Sections VII.2.7.2.3 and VII.2.8). The Fe-wüstite-magnetite eutectoid temperature obtained in this study was 843 K, in good agreement with the most reliable literature values (see Section VII.2.8.3).

[1972REZ/FIL]

Reznitskii and Filippova made over 300 C_p measurements and complementary DTA studies on natural and synthetic specimens of α-Fe_2O_3. Unfortunately their publication includes only 11 fitted values, plus derived enthalpy and entropy increments, for temperatures between 298.15 and 1000 K. A full review for inclusion in the current assessment (Section VII.2.2.2) is therefore not possible. Overall, relative to the assessed values, their C_p values were slightly lower (within 1.3 $J \cdot K^{-1} \cdot mol^{-1}$) up to 600 K, slightly higher (within 3.3 $J \cdot K^{-1} \cdot mol^{-1}$) up to 900 K, and much lower (by 28.6 $J \cdot K^{-1} \cdot mol^{-1}$ at 950 K) near the peak of the Néel transition. Their measured transition peak temperature was (958 ± 5) K by DTA and (943 ± 1) K by "true specific heat" measurements made over temperature intervals of 1 - 2 K.

These differences illlustrate the difficulty of applying third-law calculations to equilibrium data obtained in the vicinity of large λ-type C_p anomalies (see Sections VII.2.2.1 and VII.2.7.2.2). Note, however, that the integrated enthalpy and entropy increments agree with the current assessment within about 0.6 $kJ \cdot mol^{-1}$ and 0.8 $J \cdot K^{-1} \cdot mol^{-1}$, respectively, up to 1000 K.

The authors also calculated the magnetic contributions to the overall enthalpy and entropy increments to 1000 K, but with large uncertainties: (10.1 ± 5.1) $kJ \cdot mol^{-1}$ and (15.1 ± 7.6) $J \cdot K^{-1} \cdot mol^{-1}$.

[1972SAI/NIS]

Numerous solid-state cell-potential measurements were made on metal–oxide and oxide–oxide couples in the Fe-O, Co-O, and Ni-O systems, using both stacked-pellet and closed-end electrolye-tube cell configurations and a ZrO_2-15%CaO electrolyte. Resulting potential relationships include the following, which are discussed further in Sections VII.2.2.1 and VII.2.7.2.3 of this review.

(Fe-wüstite *vs*. Ni-NiO) $E/\text{mV} = 154.7 + 0.1047(T/\text{K})$, $\sim 910 \text{ K} < T < 1370 \text{ K}$

(Fe-wüstite *vs*. Co-CoO) $E/\text{mV} = 165.3 + 0.02231(T/\text{K})$, $\sim 920 \text{ K} < T < 1330 \text{ K}$

(wüstite-magnetite *vs*. Ni-NiO) $E/\text{mV} = 419.1 - 0.2123(T/\text{K})$, $\sim 940 \text{ K} < T < 1350 \text{ K}$

(magnetite-hematite *vs*. Ni-NiO) $E/\text{mV} = -68.31 + 0.2966(T/\text{K})$, $\sim 930 \text{ K} < T < 1340 \text{ K}$

Overall reproducibility of the potential-diffrence measurements was about ±3 mV.

[1972SEK/TET]

In this study, solvent extraction was used to determine the formation constants of iron(III) chlorido and bromido complexes. Two extractants were used, thenoyl trifluoroacetone (TTA) in carbon tetrachloride and trioctylphosphine oxide (TOPO) in hexane. TTA acts as a cation exchanger; it easily exchanges the proton of its mesomeric form HTTA. TOPO extracts neutral molecules by replacing the water surrounding aqueous metallic ions.

The aqueous phases were mixed perchlorate solutions, 1 M $HClO_4$ plus 3 M $NaClO_4$ (I_c = 4 M), and varying amounts of the ClO_4^- ions were replaced by Cl^- or Br^-. The solutions contained radioactive ^{59}Fe, which was used for the radiometric analysis for iron in the two phases after equilibrium was attained. The distribution ratios for the variation of iron(III) between HTTA and these aqueous phases showed that two chlorido complexes are formed in the aqueous phases, $FeCl^{2+}$ and $FeCl_2^+$. In 4 M ionic strength solutions $\log_{10}\beta_1 = 0.88$ and $\log_{10}\beta_2 = 0.8$.

These values are in moderate agreement with other literature data and have been obtained from data in high ionic strength solutions which are at the limits of validity of the SIT model. However, the value of K_1 has been included in those used for the overall fit of literature data with the SIT formalism because the method of investigation has not been used as frequently as the others. Conversion to the molal scale produces: $I_m \approx 4.713$ mol·kg^{-1} and K_{1m} = (6.44 ± 1.00) mol^{-1}·kg. The density of the solutions varies with the sequential replacement of $NaClO_4$ by NaCl, and the density value for the median composition 1 M $HClO_4$ + 1.5 M $NaClO_4$ + 1.5 M NaCl has been used. The value of the ξ coefficient for the molar to molal conversion for this solution has been found by averaging the values 1.2323 dm^3 of solution per kg of H_2O (= ¼(ξ($HClO_4$ at 4 M)) + ¾ξ($NaClO_4$ at 4 M)) and 1.1240 dm^3 of solution per kg of H_2O (= ¼(ξ($HClO_4$ at 4 M)) + ¾(ξ(NaCl at 4 M))), which yielded 1.178 dm^3 of solution per kg of H_2O. The ξ values of $HClO_4$, $NaClO_4$, and NaCl solutions were from Table II-5. As already explained for other investigations [1969MOR/WIL], [1969NIK/PAL] for which the medium was mixed ClO_4^-,Cl^- solutions at constant ionic strength in the molar scale, we used the approximation that Cl^- is equivalent to ClO_4^- for the ionic strength effects.

The extraction of iron(III) by TOPO was less useful for chlorido complex speciation and determination of formation constant values. The extraction by HTTA of Fe(III) species in similar solutions suggested that three neutral species were extracted into the organic phase TOPO-hexane, $Fe(ClO_4)_3$, $Fe(ClO_4)_2L$ and $Fe(ClO_4)L_2$ (L = Cl^- or Br^-). The quantitative interpretation of the TOPO distribution data is very difficult because of the numerous iron(III) species in the organic phases in the presence of aqueous perchlorate.

The results from this paper were not taken into account in the overall SIT treatment for the evaluation of the formation constants of $FeCl_2^+$. Nevertheless, because these data are scarce, an initial attempt was made to include the stability constant value from the present paper in the SIT analysis. The introduction of the relatively low value of K_2 changes the sign of $\Delta\varepsilon = \varepsilon(FeCl_2^+, ClO_4^-) - \varepsilon(FeCl^{2+}, ClO_4^-)$, which becomes positive. It is expected to be negative because generally the singly-charged cation interaction coefficients are lower than those for doubly-charged cations. The rejection of this K_2 [1972SEK/TET] value in the $\log_{10}K_2 + 4D$ *vs.* $m_{ClO_4^-}$ plot made $\Delta\varepsilon$ negative, which is the usual behaviour.

[1972WHI/LAN]

This paper reported the results of an investigation of the temperature effect on the standard potential of the Fe(III)/Fe(II) couple. Measurements were carried out at temperatures between 5 and 35 °C using a set of samples with identical Fe(III)/Fe(II) ratios, and ClO_4^- concentrations. The pH of the solutions at equilibrium is given. For each temperature only one ionic strength was investigated.

The cell used was:

$$Ag|AgCl|sat.\ KCl \vdots\vdots\ HClO_4(m),\ Fe(ClO_4)_2(x),\ Fe(ClO_4)_3(y)\ |\ Pt$$

m, *x*, *y* were low to insure low junction potentials, estimated to be of the order of 0.001 V.

1.Standard potential:

The original data analysis used a Debye-Hückel equation to calculate ion activities, and took into account hydrolysis of Fe^{3+}. At 25 °C the value determined, E^{o} = (0.770 ± 0.002) V, is close to the standard potential of the other major papers analysed in this review. We applied the SIT treatment to try to incorporate the measured potential difference at 0.056 m (ClO_4^-) and 0.082 m ionic strength and its calculated value of $E^{\ddagger}$ + $(5D)(RT(\ln(10))/F)$ at 298.15 K into the selected points shown in Figure VI-3 of Section VI.1.2.1.1 of the main text. Equation (A.85) was used to calculate $E^{\ddagger}$:

$$E^{\ddagger}/V = E_{corr} + (5D)(RT(\ln(10))/F)\log_{10}(m_{Fe^{2+}}/m_{Fe^{3+}}) = 0.7677 - 0.0155 = 0.7522 \qquad (A.85)$$

where E_{corr} is the experimental potential (*vs.* the SHE) given by the authors, after correction for their reference electrode potential. This yields a value of 0.7823 V for $E^{\ddagger}$ + $(5D)(0.05916)$.

This point is significantly off the curve formed by the selected points as shown in Figure VI-2, So the high value of $E^{\ddagger}$ + $(5D)(0.05916)$ from the Whittemore and Langmuir work, was not included in the data which were selected for the SIT determination of the E^{o} and the $\varepsilon(Fe^{3+}, ClO_4^-)$ values.

The results at 25 °C were reanalyzed in the present review using the SIT model. The activity coefficients of Fe^{2+} and Fe^{3+} were recalculated by applying the equation

$$\log_{10}\gamma_M = -Dz_M^2 + \varepsilon(M,X)\,m_X. \qquad (A.86)$$

As the pH of the solution used by the authors was rather high, hydrolysis of Fe^{3+} has been taken into account using the formation constants of $FeOH^{2+}$ and $Fe_2(OH)_2^{4+}$ selected in the present review (Section VII.1.3).

$$\log_{10}\beta_{11} = \log_{10}\beta_{11}^{o} - 4D - \Delta\varepsilon(m_{ClO_4^-}) + \log_{10} a_w \qquad (A.87)$$

$$\log_{10}\beta_{22} = \log_{10}\beta_{22}^{o} - \Delta\varepsilon(m_{ClO_4^-}) + 2\log_{10} a_w \qquad (A.88)$$

Because of the non-linearity of the function $\log_{10}\beta_{11} + 4D - \log_{10} a_{\text{w}} = \text{f}(m_{\text{ClO}_4^-})$ two sets of adjustments have been carried out. One with a forced constant value for $\Delta\varepsilon$, and one with $\Delta\varepsilon = \Delta\varepsilon_1 + \Delta\varepsilon_2\cdot\log_{10} I_m$ which better fits the experimental data, taking into account the strong curvature at low ionic strength.

With $\log_{10}\beta^{\circ}_{11} = -(2.15 \pm 0.03)$, $\Delta\varepsilon_1 = -(0.22 \pm 0.05)$ kg·mol^{-1}; $\Delta\varepsilon_2 = (0.21 \pm 0.08)$ kg·mol^{-1}, $\log_{10} a_{\text{w}} = -0.00147$ the value from the three-term SIT$_2$ formulation is $\log_{10}\beta_{11} = -(2.56 \pm 0.03)$ at $I_m = 0.082$ (25 °C).

With $\log_{10}\beta^{\circ}_{22} = -(2.82 \pm 0.11)$, $\Delta\varepsilon = -(0.14 \pm 0.08)$ kg·mol^{-1}, $\log_{10} a_{\text{w}} = -0.00147$, the value of $\log_{10}\beta_{22}$ is $-(2.81 \pm 0.12)$. K_{22} $(= \beta_{22}\beta_{11}^{\ 2})$ is the equilibrium constant of the reaction $2\,\text{FeOH}^{2+} \rightleftharpoons \text{Fe}_2(\text{OH})_2^{4+}$ and $\log_{10} K_{22} = (2.31 \pm 0.13)$ at 25.0 °C and $I_m = 0.082$.

Our results and those of [1972WHI/LAN] are compared in Table A-25. It can be seen that there is a substantial difference in the value obtained for $E^{\circ}(\text{Fe}^{3+}/\text{Fe}^{2+})$. The ionic strength here is low ≈ 0.082 m, and the value used for the Fe^{3+} activity coefficient is mainly responsible for the discrepancy. The authors used an extended Debye-Hückel formulation with adjusted distance parameters. Because of the low ClO_4^- concentration, there will be a limited influence of the $\varepsilon([\text{Fe}^{3+},\text{Fe}^{2+}], \text{ClO}_4^-)$ values upon the standard potential value calculated using the SIT. So the SIT cannot compensate for the overly large variations in the calculated activity coefficients due to the use of the square of the ionic charge for the highly charged ion Fe^{3+}.

Table A-25: Comparison of the $E^{\circ}(\text{Fe}^{3+}/\text{Fe}^{2+})$ value of [1972WHI/LAN] with the results of the SIT application to the original data using TDB constants (25 °C).

Method *	$[\text{Fe}^{3+}]$/M	$\gamma_{\text{Fe}^{3+}}$	$\gamma_{\text{Fe}^{2+}}$	$E^{\circ}(\text{Fe}^{3+}/\text{Fe}^{2+})$/V *vs.* SHE
Original paper	0.00657	0.193	0.421	0.770 ± 0.002
Recalculated with the original model using the TDB hydrolysis constants	0.00607	0.193	0.421	0.768 ± 0.002**
Recalculated with SIT$_1$				
$\varepsilon(\text{Fe}^{2+}, \text{ClO}_4^-) = 0.37 \pm 0.04$ $\varepsilon(\text{Fe}^{3+}, \text{ClO}_4^-) = 0.73 \pm 0.05$	0.00607	0.133	0.410	0.777 ± 0.002
Recalculated with SIT$_2$				
$\varepsilon(\text{Fe}^{2+}, \text{ClO}_4^-) = 0.37 \pm 0.04$ $\varepsilon(\text{Fe}^{3+}, \text{ClO}_4^-) = (0.78 \pm 0.05)$ $- (0.41 \pm 0.05)\log_{10} I_m$	0.00607	0.142	0.410	0.775 ± 0.002

* Units of ε are kg·mol^{-1}; ** Average of two original values.

Another source of a smaller discrepancy is found in the values used for the hydrolysis constants in the SIT calculation above and in the original paper. The self consistency of the H^+ concentrations in the original paper is rather poor if we compare the concentrations obtained from the pH values and those calculated from the hydrogen-ion balance Equation (A.89):

$$H^+ = \text{added } HClO_4 + FeOH^{2+} + 2Fe_2(OH)_2^{4+} \quad (A.89)$$

It has been seen above that there is a rather large discrepancy between the values of $E^o_{298.15\,K}(Fe^{3+}/Fe^{2+})$ calculated by the authors and as recalculated using the SIT_1 or SIT_2. As the TDB selected value (0.37 kg·mol^{-1}) for $\varepsilon(Fe^{2+}, ClO_4^-)$ has been selected by analogy, we also have tried using a slightly different value, $\varepsilon(Fe^{2+}, ClO_4^-)$ = 0.34 kg·mol^{-1}, to assess the effect of our selection. This would have given a value of 0.7769 V for $E^{\ddagger}(Fe^{3+}/Fe^{2+})$ using SIT_1; the difference from the Table A-25 value is 0.0001 V.

In summary, the effect of the Fe(III) hydrolysis on the potentials is minimal if hydrolysis constants accepted in the present review are used. However, extrapolation of the results to zero ionic strength by using the SIT_1 and SIT_2 formulations led to substantial differences in the E^o values, 0.007 V and 0.005 V respectively, mainly attributable to differences in the Fe^{3+} activity coefficients. The value of E^o for 298.15 K was not used further in this review.

Variation of the standard potential with temperature

The authors reported the following equation for the temperature dependence of E^o ($E(T)$ was E^o_T in the notation originally used by the authors)

$$E^o(T)\,/\text{V} = -1.23\times10^{-2} + 4.147\times10^{-3}(T/\text{K}) - 5.111\times10^{-6}(T/\text{K})^2 \quad (A.90)$$

and, hence, the $\Delta_r G^o$ and $\Delta_r S^o$ values at 298.15 K were – (74.266 ± 0.167) kJ·mol^{-1} and (106.27 ± 6.28) J·K^{-1}·mol^{-1}, respectively. A recalculation by Parker and Khodakovskii [1995PAR/KHO] gave – (74.266 ± 0.167) kJ·mol^{-1}, and (120.08 ± 6.28) J·K^{-1}·mol^{-1}, using a linear relationship ($E(T)$ = a + bT, *i.e.*, $\Delta_r C_p$ = 0) instead of Equation (A.90). Also, using the $\Delta_r C_p$ value published by Hovey [1988HOV], they obtained $\Delta_r H^o$ (298.15 K) = – (42.75 ± 1.50) kJ·mol^{-1}.

The results of this paper [1972WHI/LAN] have not been used in the present review in the determination of the standard potential of the Fe^{3+}/Fe^{2+} couple and the SIT interaction coefficients of Fe^{3+}, but the straight lines representing the variation of $E^o(T)$ as a function of the temperature (original and SIT_2 calculations) are almost parallel to the straight lines representing the data of the other publications. So the data of this paper were used to obtain an estimate of the value of $\Delta_r S^o$ (298.15 K).

The $E^o(T)$ (Fe^{3+}/Fe^{2+}) values were recalculated using the SIT_2 formalism for the activity coefficients of Fe^{3+} and Fe^{2+}. They are listed in Table A-26. The values of the original paper corrected for hydrolysis using the constants of this TDB review are also shown for comparison. The $E^o(T)$ values are quite different, but the slopes, $\mathrm{d}E^o(T)/\mathrm{d}T$, are similar, as can be seen in Figure A-19.

Table A-26: Variation of $E^{\circ}(T)$ (Fe^{3+}/Fe^{2+}) with the temperature [1972WHI/LAN] data and recalculation with the SIT_2 formulation. Corrections of $E^{\circ}(T)$ using the selected TDB hydrolysis constants for 298.15 K and $\Delta_{r}C_{p}$ = 57.2 $J\cdot K^{-1}\cdot mol^{-1}$ are listed. All samples had compositions 0.00667 M Fe(III), 0.00301 M Fe(II), 0.0569 M ClO_4^-, $m_{H^+} \approx 0.0335$.

T/K	$E^{\circ}(T)^{*}$ [1972WHI/LAN] V *vs.* SHE	$E^{\circ}(T)^{*}$ SIT_2 V *vs.* SHE	Hydrolysis* Correction V *vs.* SHE	Effect (V) of $\Delta_{r}C_{p}$ = 57.2 $J\cdot K^{-1}\cdot mol^{-1}$ correction to $E^{\circ}(T)$
278.55	0.7462	0.7526	– 0.000096	– 0.000391
283.15	0.7522	0.7587	– 0.000171	– 0.000228
288.15	0.7581	0.7656	– 0.000231	– 0.000101
292.45	0.7645	0.7725	– 0.000326	– 0.0000325
293.15	0.7633	0.7714	– 0.000240	– 0.0000250
298.15	0.7700	0.7770	– 0.000008	0.000000
298.15	0.7693	0.7764	– 0.000023	0.000000
303.15	0.7752	0.7823	0.000093	– 0.0000247
308.15	0.7802	0.7872	0.000388	– 0.0000983

* Use of recalculated Fe^{3+} concentrations using the hydrolysis constants of Fe^{3+} given in the present review rather than those in the original paper. The values for D at the different temperatures were calculated using the Debye-Hückel $A(T)$ values in Table B-2 of the present volume, and the recommended temperature-independent value of 1.5 $kg^{1/2}\cdot mol^{-1/2}$ for Ba_j.

The variation of the hydrolysis constants with the temperature was calculated applying Eqs. (A.91) and (A.92). The values of the enthalpy changes for the hydrolysis reactions are those given in this review (Section VII.1.3).

$$\Delta H^{\circ}_{11} = (36 \pm 3)\ kJ\cdot mol^{-1}\ (SIT_1 \text{ or } SIT_2 \text{ calculations}).$$

$$\Delta H^{\circ}_{22} = (44 \pm 3)\ kJ\cdot mol^{-1}\ (SIT_1 \text{ calculations})$$

$$\log_{10} \beta_{11}(T) = \log_{10} \beta^{\circ}_{11}(298.15\ K) - (\Delta H^{\circ}_{11}/(R \ln(10)))(1/T - 1/298.15) \quad (A.91)$$

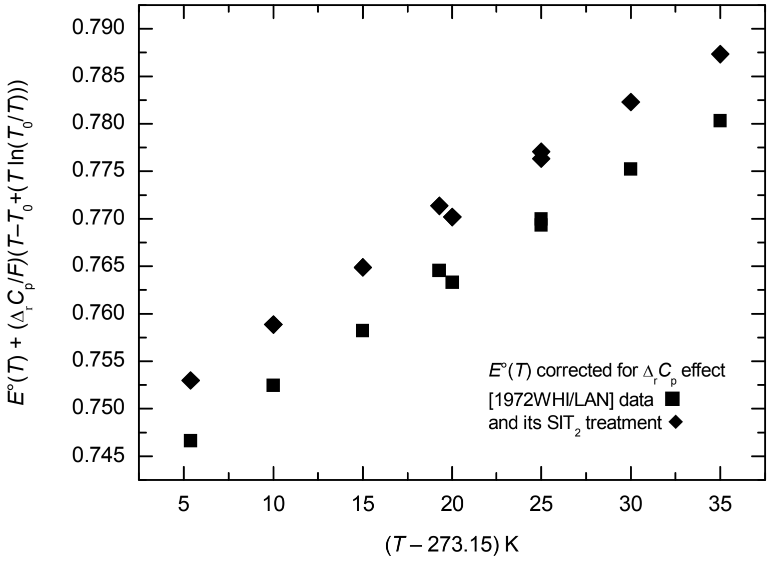
$$\log_{10} \beta^{\circ}_{11}(T) = - 2.56 - 1880(1/T - 1/298.15)$$

$$\log_{10} \beta_{22}(T) = \log_{10} \beta^{\circ}_{22}(298.15\ K) - (\Delta H^{\circ}_{22}/(R \ln(10)))(1/T - 1/298.15) \quad (A.92)$$

$$\log_{10} \beta^{\circ}_{22}(T) = - 2.81 - 2298(1/T - 1/298.15)$$

For the reaction $2FeOH^{2+} \rightleftharpoons (FeOH)_2^{4+}$, the value of $\log_{10} K_{22}$ is 2.31 at an ionic strength of ~0.082, m, and ΔH° = – 28 $kJ\cdot mol^{-1}$. So a temperature increase favours the formation of $FeOH^{2+}$, but is unfavourable for the dimerization.

Figure A-19: Influence of the temperature on the $E^{\mathrm{o}}(T)$ values corrected for a constant $\Delta_{\mathrm{r}}C_p$ value (57.2 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$) for data from Whittemore and Langmuir [1972WHI/LAN] as interpreted by the authors ■ and with the SIT$_2$ formalism ◆. Slope: Whittemore and Langmuir (0.00116 ± 0.003) $\mathrm{V{\cdot}K^{-1}}$; SIT$_2$ recalculation (0.00118 ± 0.003) $\mathrm{V{\cdot}K^{-1}}$.



The influence of $\Delta_{\mathrm{r}}C^{\mathrm{o}}_{p,\mathrm{m}}$ has been considered by introducing values for $\Delta_{\mathrm{r}}C^{\mathrm{o}}_{p,\mathrm{m}}$ [1988HOV]. As discussed in the main text, the experimental work of Hovey (the $C_{p,2,\mathrm{m}}$ values on pg. 263 of Hovey's thesis [1988]) with C^{o}_{p}(H$_2$(g) for 298.15 K) served to establish a function $\Delta_{\mathrm{r}}C_p$ = f(t) for temperatures (t/ °C) between 10 and 55 °C (only).

$$\Delta_{\mathrm{r}}C^{\mathrm{o}}_{p}\,/\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}} = \mathrm{P}_1 + \mathrm{P}_2t + \mathrm{P}_3t^2 + \mathrm{P}_4t^{-1} + \mathrm{P}_5\,t^{-2} \qquad \text{(A.93)}$$

or

$$\begin{aligned}\Delta_{\mathrm{r}}C^{\mathrm{o}}_{p,\mathrm{m}}\ (T) = {} & \mathrm{P}_1 + \mathrm{P}_2(T - 273.15) + \mathrm{P}_3(T - 273.15)^2 \\ & + \mathrm{P}_4(T - 273.15)^{-1} + \mathrm{P}_5(T - 273.15)^{-2} \qquad \text{(A.94)}\end{aligned}$$

A five-parameter equation (Eq. (A.93)) was fitted to the experimental variation of $\Delta_{\mathrm{r}}C^{\mathrm{o}}_{p,\mathrm{m}}$ as a function of the temperature. In the Hovey thesis, values of $\Delta_{\mathrm{r}}C^{\mathrm{o}}_{p,\mathrm{m}}$ are given for only four temperatures. Therefore additional values were determined by interpolation between the experimental points and were used to determine the following values for the parameters:

$P_1 = -(364.30 \pm 43.73)\ \text{J·K}^{-1}\text{·mol}^{-1}$

$P_2 = (11.746 \pm 1.14)\ \text{J·K}^{-2}\text{·mol}^{-1}$

$P_3 = -(0.1149 \pm 0.0101)\ \text{J·K}^{-3}\text{·mol}^{-1}$

$P_4 = (6082.2 \pm 664.3)\ \text{J·mol}^{-1}$

$P_5 = -(24470 \pm 3342)\ \text{J·K·mol}^{-1}$.

Equation (A.95) was used to calculate the $\mathrm{d}E(T)/\mathrm{d}T$ $(= \mathrm{d}E(T)/\mathrm{d}t)$ value at each temperature.

$$F(\mathrm{d}E(T)/\mathrm{d}T) - \int_{T_0}^{T}(\Delta_r C_p^\circ(T)/T)\mathrm{d}T = \Delta_r S^\circ(T) \qquad \text{(A.95)}$$

If $\Delta_r C_p$ is considered to be constant over the temperature range investigated, Eq. (A.95) becomes :

$$F(\mathrm{d}E(T)/\mathrm{d}T) = \Delta_r S^\circ(T) + \Delta_r C_p \ln(T/T_0) \qquad \text{(A.96)}$$

And if $\Delta_r C_p = 0$

$$F(\mathrm{d}E(T)/\mathrm{d}T) = \Delta_r S^\circ(T_0) \qquad \text{(A.97)}$$

For the average of the $\Delta_r C_p$ values reported by Hovey for temperatures near 298.15 K, ~ (57.2 $\text{J·K}^{-1}\text{·mol}^{-1}$), the value of the term $\int_{T_0}^{T}(\Delta_r C_p^\circ(T)/T)\mathrm{d}T$ and $\Delta_r C_p \cdot \ln(T/T_0)$ for a temperature difference of 10 K is approximately 2 $\text{J·K}^{-1}\text{·mol}^{-1}$. As the value of $\Delta_r S^\circ(T)$, is in the range of 120 $\text{J·K}^{-1}\text{·mol}^{-1}$, the approximation introduced by the use of Eq. (A.96) or (A.97) instead of (A.95) has a rather small influence on $\mathrm{d}E(T)/\mathrm{d}T$ and cannot clearly characterize the non-linearity of the function $E^\circ(T)$ = f(t). Other influences on the value of $E^\circ(T)$ such as those resulting from different methods of extrapolations of E'° (or similarly $E^\ddagger$ as defined in Section VI.1.2.1.1.1) to zero ionic strength or uncertainties in the junction-potential values are likely much greater than the effect of the temperature dependence of $\Delta_r C_p$. That explains the quasi-linear variation of $E^\circ(T)$ as a function of temperature found in the present work and in other papers analysed in this review (see Section VI.1.2). The mean slope is determined with fairly good precision. Equations (A.95) and (A.96) indicate that this mean slope is lower than the slope at 298.15 K for temperatures lower than 298.15 K, and higher for temperatures higher than 298.15 K. The overall slope correction for a constant $\Delta_r C_p$ value is then ($\Delta_r C_p/F$)ln(T_h/T_l), where T_l and T_h designate the lowest and highest temperatures of the study, respectively.

The slope correction $\Delta(\mathrm{d}E^\circ(T)/\mathrm{d}T)$ for 298.15 K, necessary for the determination of $\Delta_r S^\circ$, can be estimated by applying Eq. (A.98) with T = 298.15 K. Equation (A.98) is based on the assumption that for the mid temperature $(T_h + T_l)/2 = T_{½}$ the correction value is zero.

$$\Delta(\mathrm{d}E^\circ(T)/\mathrm{d}T) = (\Delta_r \mathrm{C_p}/F)\ln(T/T_{½})) \qquad \text{(A.98)}$$

According to Eq. (A.98) the correction to 298.15 K for the work of Whittemore and Langmuir, with $T_h = 308.15$ and $T_l = 278.55$ K, is:

$$\Delta(\mathrm{d}E°(T)/\mathrm{d}T) = (57.2/96485.3)\ln(298.15/293.35) = 9.6\times10^{-6}\ \mathrm{V\cdot K^{-1}}.$$

This correction increases the calculated value of $\Delta_r S_0^o$ for 298.15 K by 0.93 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, which is less than 1% of the value calculated by considering $\Delta_r C_p^o = 0$.

Another way to correct the slope $\mathrm{d}E°(T)/\mathrm{d}T$ value to 298.15 K (T_0) is to consider the contribution of a constant $\Delta_r C_p^o$ to $E^o(T)$ values as expressed by Eqs. (A.99) and (A.100).

$$E^o(T) = -\Delta_r H^o_{298.15}/F + T\Delta_r S^o_{298.15}/F + (\Delta_r C_p^o/F)(T_0 - T) + T(\Delta_r C_p^o/F)\ln(T/T_0) \quad \text{(A.99)}$$

$$E^o(T) + (\Delta_r C_p^o/F)(T - T_0 + T\ln(T_0/T)) = -\Delta_r H^o_{298.15}/F + T\Delta_r S^o_{298.15}/F \quad \text{(A.100)}$$

Equation (A.100) can be used to calculate $\Delta_r S^o$ using the slope of the curve $E^o(T) + (\Delta_r C_p^o/F)(T - T_0 + T\ln(T_0/T)) = \mathrm{f}(T)$ (see Figure A-19). This has been done, and the slopes obtained were compared to the slope calculated and corrected as explained above; they are identical within the uncertainties. For the two methods the increase of the slope after correction to 298.15 K is 0.00001 $\mathrm{V\cdot K^{-1}}$ and the effect of $\Delta_r C_p^o = 57.2\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ on the value of $\Delta_r S^o$ (298.15 K) is less than 1%.

As shown in Table A-26, correction for hydrolysis using the values of the hydrolysis constants recommended in this review introduces a correction to $E^o(T_0)$ as important as assuming a constant, non-zero $\Delta_r C_p^o$ value.

The value of $\Delta_r S^o$ (298.15 K) calculated by using the value of $\mathrm{d}E°(T)/\mathrm{d}T$ determined by applying the $\mathrm{SIT_2}$ formalism to the data of [1972WHI/LAN], and then Eq. (A.98), or Eq. (A.100) is:

$$\Delta_r S^o\ (298.15\ \mathrm{K}) = (0.00118 \pm 0.00003)\ F = (113.6 \pm 2.9)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

The uncertainty given by the statistical treatment is surely an underestimate and increasing it to ± 6.0 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ gives a value that agrees better with uncertainty values generally reported from this type of data. Therefore,

$$\Delta_r S^o\ (298.15\ \mathrm{K}) = (113.6 \pm 6.0)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

In summary, the results of the original paper with calculations using the $\mathrm{SIT_2}$ formalism to determine $E^o(T)$ give values of $\mathrm{d}E^o(T)/\mathrm{d}T$ similar to those of the authors, values which also are consistent with those obtained by others [1951CON/MCV], [1953MAG/HUI]. This is due to a discrepancy in the evaluated $\mathrm{Fe^{3+}}$ activity coefficients that is not very sensitive to temperature changes. Thus the value of $\mathrm{d}E^o(T)/\mathrm{d}T$ is used in this review, even though the value of E^o at 298.15 K is not.

[1973DAN/CHI]

This is another precipitation study carried out at 25 °C in 1 M $\mathrm{NaNO_3}$ where the pH of the solution was monitored as the reaction-progress variable. Four weeks after preparation involving five sets of ten solutions with initial [Fe^{3+}] ranging from 0.001 to 0.1 M, the pH was found to be constant, although the final values were taken after six weeks. The pH was measured with a glass electrode relative to a calomel reference electrode. The measurements are all rationalized in terms of the reaction:

$$Fe^{3+} + NO_3^- + 2\,H_2O(l) \rightleftharpoons Fe(OH)_2NO_3(s) + 2\,H^+.$$

A mean value of $\log_{10} {}^*K^\circ_{121} = -(2.20 \pm 0.03)$ is given with effects of other hydrolysis reactions having been ignored, which is a reasonable assumption in light of the relative independence of the value of $\log_{10} {}^*K^\circ_{121}$ on the initial iron(III) concentrations and the linearity and slope of the initial $\log_{10}$ [Fe^{3+}] values *vs.* the final $\log_{10}$ [H^+].

The authors made no attempt to isolate the solid phase formed nor did they vary the nitrate concentration or perform much longer experiments to verify that they had reached a final equilibrium state. Therefore, this result cannot be considered further in this review.

[1973GID/GOR]

The literature on oxygen activities and composition limits for wüstite is reviewed. The authors conclude that the partial molal Gibbs energy of oxygen has accurately linear relationships with composition (O/Fe) at fixed T and with $1/T$ at fixed composition. They conclude that “no reliable thermodynamic data exist to support the occurrence of phase transitions within the wüstite phase boundaries”. The authors suggest that previous reports of non-linear potential-composition behaviour can be attributed to either (a) measurements in flowing gas systems where sufficiently low oxygen potentials cannot be maintained [1964BAR2], [1969RIZ/GOR] or (b) compositional drift due to oxygen permeation through the solid electrolyte, especially at $T > \sim 1273$ K [1969FEN/RIL]. A table of recommended boundary compositions for the wüstite field, and corresponding relationships between $\log_{10} p_{O_2}$ and $1/T$, are given. The same authors published a complementary experimental study [1974GID/GOR].

[1973HAS/MIS]

Solubility measurements are reported for γ-FeOOH deposited on Pt electrodes as described by [1974HAS/COH]. The film was only a few microns thick. The solid was resuspended ultrasonically for 8 days at 25 °C in sealed tubes containing 0.010 to 0.032 M $HClO_4$. Mass- or surface-area-to-volume ratios are not given. Seven solubility values (mM Fe) range from 4.150 at pH 1.65 to 0.613 at pH 1.94. Solution samples were removed after two days without agitation. Based on a linear plot of [Fe_{total}]/[H^+]^2 *vs.* [H^+] it was concluded that only two equilibria were predominant, namely:

$$\gamma\text{-FeOOH} + 3\,H^+ \rightleftharpoons Fe^{3+} + 2\,H_2O(l)$$

$$Fe^{3+} + H_2O(l) \rightleftharpoons FeOH^{2+} + H^+$$

for which they report ${}^{*}K^{\circ}_{s,0}$ = (325 ± 13) M^{-2} and ${}^{*}\beta_{1,1}$ = (3.1 ± 0.8) × 10^{-3} M, respectively.

A value of $\Delta_f G^{\circ}_m$ (FeOOH, γ, 298.15 K) = −470.7 kJ·mol^{-1} is derived, but this appears not to include any activity correction. There was no discussion of the characterization of the solid phase, or consideration of the kinetics of dissolution, or the formation of fine particulates, or activity coefficients, or calibration of the pH electrode. No reliable thermodynamic information can be gleaned from this work, but it may be of interest to compare these results with the limited amount of data available elsewhere for this phase.

[1973NIK/ANT]

The authors reported potential-difference measurements for the cell

$$\mathrm{Tl(Hg)} \mid \text{saturated KCl(sln)} \ \vdots\vdots\ \mathrm{Fe(ClO_4)_2, Fe(ClO_4)_3, HClO_4} \mid \mathrm{Pt}$$

at seven temperatures from 298 to 423 K. The total molar concentrations of iron were less than 0.013 M, and the ratios of Fe(II) to Fe(III) were varied from 0.12 to 4.54. Acid molarities ranged from 0.125 to 1.913 M. The reported potentials lead to $E^{\prime\circ}$ values at 298.15 K that are outside the range of values found by other investigators [1937SCH/SHE], [1951CON/MCV], [2000TAG/DIA] for similar solutions —lower by more than 0.02 V except at the highest acid molalities. The discrepancies have been attributed by Tagirov *et al.* to the nature of the reference electrode used (Tl/TlCl/saturated KCl) for which $KClO_4$ precipitation at the junction is probable. Although Parker and Khodakovskii [1995PAR/KHO] claimed that on recalculation the results lead to a value of E° of 0.770 V at 298.15 K, application of the SIT to the data from the original paper indicated a value of E° of ~0.74 V (or perhaps 0.01 to 0.02 V greater if the results from the lowest acid molalities are omitted). The values from this paper were rejected by [2000TAG/DIA], and also are not used in the present review.

[1973NIK/PAL]

This paper is a report of a potentiometric investigation of iron(III) sulfato complexes, and focused on $\mathrm{Fe(SO_4)_2^-}$ and $\mathrm{FeHSO_4^{2+}}$ for which it was considered that the values of the formation constants were not well known.

Two cells were used:

For moderately acidic solutions,

$$\mathrm{Pt} \mid \mathrm{Fe(II,III), HClO_4, NaClO_4, Na_2SO_4} \vdots \mathrm{HClO_4, NaClO_4, Na_2SO_4, NaCl\ 0.001\ M} \mid \mathrm{Ag/AgCl}$$

and for more acidic solutions

$$\text{Glass electrode} \mid \mathrm{Fe(II,III), HClO_4, NaClO_4, Na_2SO_4} \mid \mathrm{Pt.}$$

The ionic strength was maintained constant, I_c = 3, at 25 °C. The following results (in the nomenclature used by the authors) were reported:

$$^{*}\beta_{1,1} = (85 \pm 8)\ \mathrm{M}^{-1};\ ^{*}\beta_{1,2} = (130 \pm 20)\ \mathrm{M}^{-2};\ ^{*}\beta_{1,1,0,1} = (1.0 \pm 0.5)\ \mathrm{M}^{-1}$$

where $^{*}\beta_{1,1}$, $^{*}\beta_{1,2}$ and $^{*}\beta_{1,1,0,1}$ were used to designate the formation constants of: $FeSO_4^{+}$, $Fe(SO_4)_2^{-}$ and $FeHSO_4^{2+}$ from Fe^{3+} and HSO_4^{-}. In the following text we adopted the nomenclature

$$K_{1FeSO_4^+} = {}^{*}\beta_{1,1},\ K_{2Fe(SO_4)_2^-} = {}^{*}\beta_{1,2}/{}^{*}\beta_{1,1},\ K_{1FeHSO_4^{2+}} = {}^{*}\beta_{1,1,0,1}$$

So $K_{1FeHSO_4^{2+}}$ is the formation constant of $FeHSO_4^{2+}$ from Fe^{3+}, SO_4^{2-} and H^+. All of the formation constants discussed below have been calculated in molal units.

As in the work of Mattoo [1959MAT], the quantities of Fe^{2+} sulfato complexes were considered to be negligible.

There were no attempts to extrapolate the values to zero ionic strength. No tables of experimental values are available from this paper, so in our recalculations the original formation constant values given by the authors were used to back-calculate the values of E. The influence of the interaction between Fe^{2+} and sulfate on the formation constants of $FeSO_4^{+}$, $Fe(SO_4)_2^{-}$ and $FeHSO_4^{2+}$ has been calculated by using the $FeSO_4$(aq) formation constant value suggested in the present TDB review.

The influence of the Fe^{2+} complexes has been taken into account by replacing the constant Fe^{2+}molality, 1.16×10^{-4} m of the original paper, in the Nernst equation by the free Fe^{2+} concentration given by Eq. (A.101).

$$m_{Fe^{2+}} = 1.16 \times 10^{-4} / \{1 + K_{1FeSO_4} m_{SO_4^{2-}}\} \qquad (A.101)$$

The very unstable Fe(II) species $Fe(SO_4)_2^{2-}$ and $FeHSO_4^{+}$ have been neglected.

The value of K_{1FeSO_4} was calculated by applying Eqs. (A.102) and (A.103).

$$\log_{10} K_{1FeSO_4} = (2.44 \pm 0.03) - 8D - m_{ClO_4^-}\,\Delta\varepsilon \qquad (A.102)$$

$$\Delta\varepsilon = -\,\varepsilon(Fe^{2+}, ClO_4^-) - \varepsilon(M^+, SO_4^{2-}) = -\,(0.25 \pm 0.07)\ \mathrm{kg{\cdot}mol^{-1}} \qquad (A.103)$$

For the sake of consistency we used: $\varepsilon(Fe^{2+}, ClO_4^-) = (0.37 \pm 0.04)\ \mathrm{kg{\cdot}mol^{-1}}$; M^+ in Eq. (A.103) stands for (Na^+ + H^+) and assuming that $\varepsilon(Na^+, SO_4^{2-}) \approx \varepsilon(H^+, SO_4^{2-}) = -\,(0.12 \pm 0.06)\ \mathrm{kg{\cdot}mol^{-1}}$ [1], Eq. (A.102) for I_m = 3.5 yields:

---

[1] Here the ratio m_{H^+}/m_{Na^+} is not known, and the assumption $\varepsilon(H^+, SO_4^{2-}) \approx \varepsilon(Na^+, SO_4^{2-})$ is used to avoid introducing other even less-warranted assumptions. A different value for $\varepsilon(H^+, SO_4^{2-}) \approx \varepsilon(Li^+, SO_4^{2-}) = -\,(0.03 \pm 0.04)\ \mathrm{kg{\cdot}mol^{-1}}$ was chosen in other parts of the review. If the latter value were used, the $\Delta\varepsilon$ values would be a function of the m_{H^+}/m_{Na^+} ratio and vary between $-$ 0.25 $\mathrm{kg{\cdot}mol^{-1}}$ ($NaClO_4$ solutions) and $-$ 0.34 $\mathrm{kg{\cdot}mol^{-1}}$ ($HClO_4$ solutions). Thus, values of $\log_{10} K_{1FeSO_4}$ would be between (1.314 ± 0.245) $\mathrm{mol^{-1}{\cdot}kg}$ and (1.629 ± 0.368) $\mathrm{mol^{-1}{\cdot}kg}$, with substantial overlap within the uncertainties.

$$\log_{10} K_{1\mathrm{FeSO_4}} = (1.31 \pm 0.24)\ \mathrm{mol^{-1}\cdot kg}.$$

The correction for the effect of the Fe^{2+} sulfato complex on the formation constant of the Fe^{3+} complexes has been carried out by applying Eq. (A.104).

$$(1 + K_{1\mathrm{FeSO_4}} m_{\mathrm{SO_4^{2-}}})(1 + m_{\mathrm{SO_4^{2-}}}[K_1 + m_{\mathrm{H^+}} K_{m1,1(\mathrm{HSO_4^-})} K_{1\mathrm{FeHSO_4^+}}]) + (m_{\mathrm{SO_4^{2-}}})^2 K_{1\mathrm{FeSO_4^+}} K_{2\mathrm{Fe(SO_4)_2^-}} =$$

$$(1 + m_{\mathrm{SO_4^{2-}}}[K'_{1\mathrm{FeSO_4^+}} + m_{\mathrm{H^+}} K_{m1,1(\mathrm{HSO_4^-})} K_{1\mathrm{FeHSO_4^+}}]) + (m_{\mathrm{SO_4^{2-}}})^2 K'_{1\mathrm{FeSO_4^+}}\ K'_{2\mathrm{Fe(SO_4)_2^-}} \qquad \text{(A.104)}$$

The calculation is based on the back-calculation of the *E* values from the formation constants of the Fe^{3+} complexes given in the original paper. These *E* values are used to determine corrected values of the formation constants values when the formation constant $K_{1\mathrm{FeSO4}}$ of the complex $FeSO_4$ is introduced in the Nernst equation. These corrected constants are designated here as $K'_{1\mathrm{FeSO_4^+}}$, $K'_{2\mathrm{Fe(SO_4)_2^-}}$ and $K'_{1\mathrm{FeHSO_4^{2+}}}$ where $K_{m1,1(\mathrm{HSO_4^-})}$ is the value of the formation constant of HSO_4^-, $10^{1.085\pm0.20}$, (value calculated by applying the SIT (Eq. (A.105)).

$$\log_{10} K_{m1,1(\mathrm{HSO_4^-})} = \log_{10} K^{\mathrm{o}}_{1,1(\mathrm{HSO_4^-})} - 4D - \Delta\varepsilon I_m \qquad \text{(A.105)}$$

Therefore, values of the constants, $K'_{n\ \mathrm{species}}$, can be derived from the plot of the left hand side (LHS) of Eq. (A.104) as a function of $m_{\mathrm{SO_4^{2-}}}$. The LHS values plotted are calculated by using the formation constants of the original paper plus the formation constant of $FeSO_4$, the iron(II) sulfate associate.

However, a general fit according to Eq. (A.104) in a single step is very complicated, because the complexes of Fe^{3+} are predominent in different regions of $m_{\mathrm{SO_4^{2-}}}$ and $m_{\mathrm{H^+}}$. So the fit has been carried out in three steps. The three graphs of Figure A-20 to Figure A-22 illustrate the three steps of the correction process used to take into account the influence of the $FeSO_4(aq)$ complex on the Fe^{3+} formation constants determined by potentiometry.

First the lower sulfate concentration results were used to obtain the value of the $m_{\mathrm{SO_4^{2-}}}$ first degree coefficients $[K'_{1\mathrm{FeSO_4^+}} + m_{\mathrm{H^+}}\ K_{m1,1(\mathrm{HSO_4^-})}\ K'_{1\mathrm{FeHSO_4^{2+}}}]$ from a linear fit of {the LHS of Eq. (A.104) – 1} at constant acidity as a function of $m_{\mathrm{SO_4^{2-}}}$ (the fit for 0.2 $m_{\mathrm{H^+}}$ is shown in Figure A-20).

The corrected values were used in the overall optimization of the formation constants and the related $\Delta\varepsilon$ values.

Then the values of $[K'_{1\mathrm{FeSO_4^+}} + m_{\mathrm{H^+}}\ K_{m1,1(\mathrm{HSO_4^-})}\ K'_{1\mathrm{FeHSO_4^{2+}}}]$ produced in the first step for four acidities have been plotted as a function of the acid molality (Figure A-21). The linear fit intercept with the y axis gives the value of $K'_{1\mathrm{FeSO_4^+}}$, and the slope the value of $K_{m1,1(\mathrm{HSO_4^-})}\ K'_{1\mathrm{FeHSO_4^{2+}}}$. That yields: $K'_{1\mathrm{FeSO_4^+}}$ = (102.5 ± 11.0) and $K_{m1,1(\mathrm{HSO_4^-})}\ K'_{1\mathrm{FeHSO_4^{2+}}}$ = (58.5 ± 10.0), and thus, $K'_{1\mathrm{FeHSO_4^{2+}}}$ = (4.8 ± 2.4) $\mathrm{mol^{-1}\cdot kg}$.

Figure A-20: Determination of $K'_{1\mathrm{FeSO}_4^+}$ + m_{H^+} $K_{m1,1(\mathrm{HSO}_4^-)}$ $K'_{1\mathrm{FeHSO}_4^{2+}}$. Data points are those at low $m_{\mathrm{SO}_4^{2-}}$. The y-axis values are $\{(1+K_{1\mathrm{FeSO}_4} m_{\mathrm{SO}_4^{2-}})(1+(m_{\mathrm{SO}_4^{2-}}[K_1$ + m_{H^+} $K_{m1,1(\mathrm{HSO}_4^-)}$ $K_{1\mathrm{FeHSO}_4^{2+}}]) + (m_{\mathrm{SO}_4^{2-}})^2 K'_{1\mathrm{FeSO}_4^+}$ $K'_{2\mathrm{Fe(SO}_4)_2^-} -1\}$ for $m_{\mathrm{H}^+} = 0.2$.

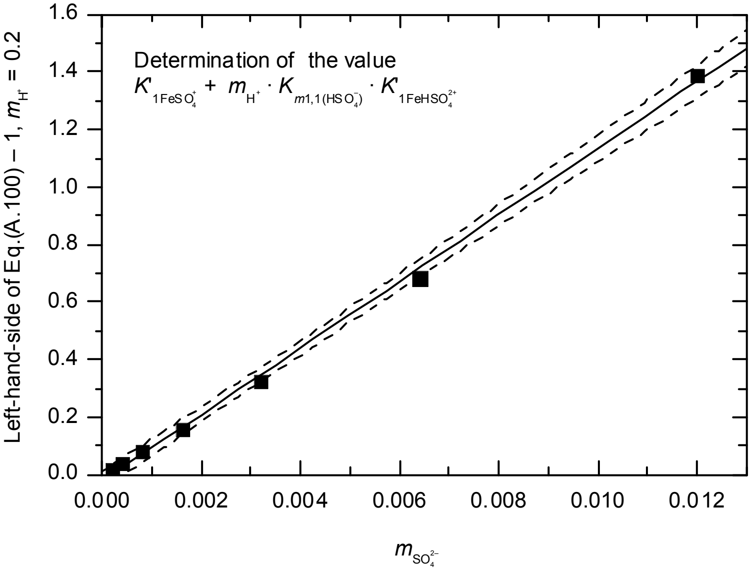


Figure A-21: Determination of $K'_{1\mathrm{FeSO}_4^+}$ and $K_{m1,1(\mathrm{HSO}_4^-)}$ $K'_{\mathrm{FeHSO}_4^+}$ values. The y-axis intercept with the linear fit gives the value of $K'_{1\mathrm{FeSO}_4^+}$ and the slope of the straight line the product $K_{m1,1(\mathrm{HSO}_4^-)}$ $K'_{\mathrm{FeHSO}_4^+}$.

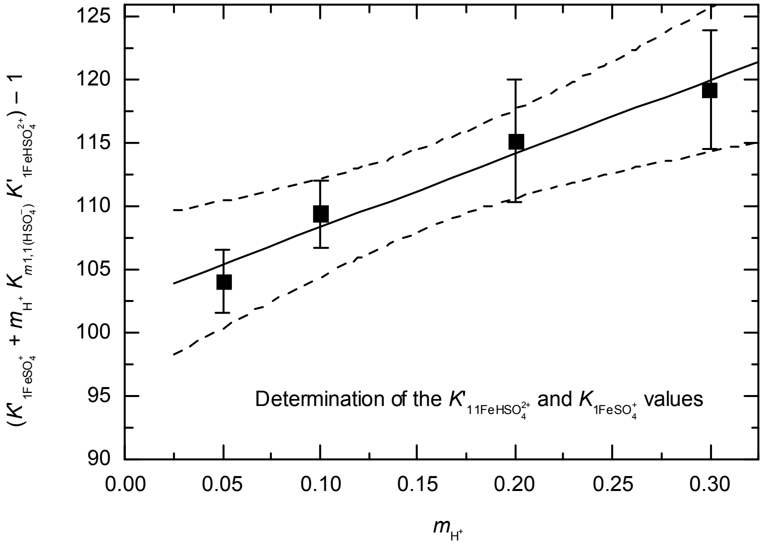
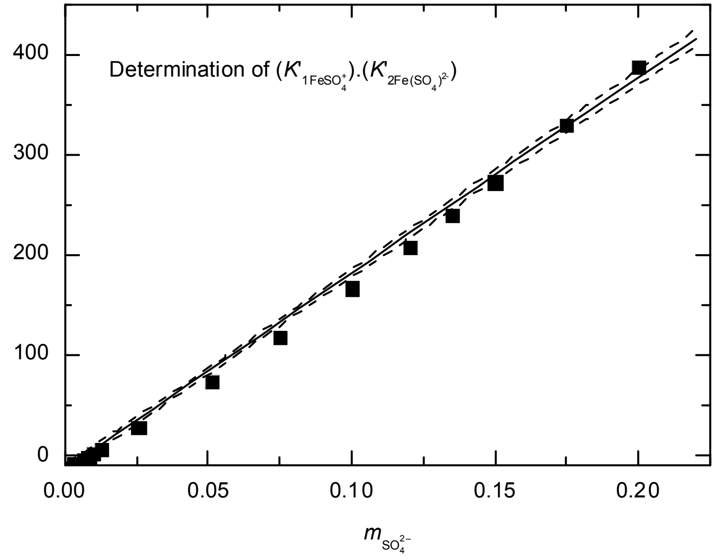


Figure A-22: Determination of $K'_{1\mathrm{FeSO}_4^+}\,K'_{2\mathrm{Fe(SO_4)}_2^-}$, which is the slope of the linear fit straight line. Y = $\{[(1 + K_{1\mathrm{FeSO}_4}\, m_{\mathrm{SO}_4^{2-}}\, (1 + (m_{\mathrm{SO}_4^{2-}}\, K_{\mathrm{FeHSO}_4^+} + m_{\mathrm{H}^+}\, K_{m1,1(\mathrm{HSO}_4^-)}\, K_{\mathrm{FeHSO}_4^{2+}}\,] - [(1 + (m_{\mathrm{SO}_4^{2-}}\, K_{\mathrm{FeHSO}_4^+}) + (m_{\mathrm{H}^+}\, K_{m1,1(\mathrm{HSO}_4^-)}\, K_{\mathrm{FeHSO}_4^{2+}}\,)]\}/\, m_{\mathrm{SO}_4^{2-}}$.



The value of $K'_{1\mathrm{FeSO}_4^+}\,K'_{2\mathrm{Fe(SO_4)}_2^-}$ has been obtained (Figure A-22) by plotting $\{(1 + K_{1\mathrm{FeSO}_4})\, m_{\mathrm{SO}_4^{2-}})\ (1 + (m_{\mathrm{SO}_4^{2-}}\, [K_1 + m_{\mathrm{H}^+}\, K_{m1,1(\mathrm{HSO}_4^-)}\, K_{1\mathrm{FeHSO}_4^{2+}}\,]) + (m_{\mathrm{SO}_4^{2-}})^2\, K'_{1\mathrm{FeSO}_4^+}\, K'_{2\mathrm{Fe(SO_4)}_2^-}\} - \{(1 + m_{\mathrm{SO}_4^{2-}}\, [K'_{1\mathrm{FeSO}_4^+} + m_{\mathrm{H}^+}\, K_{m1,1(\mathrm{HSO}_4^-)}\, K'_{1\mathrm{FeHSO}_4^{2+}}\,])\}/ m_{\mathrm{SO}_4^{2-}}$ as a function of $m_{\mathrm{SO}_4^{2-}}$. The slope of the linear fit gives the value of $K'_{1\mathrm{FeSO}_4^+}\,K'_{2\mathrm{Fe(SO_4)}_2^-}$ = (1952 ± 350) $\mathrm{mol}^{-2}\cdot\mathrm{kg}^2$. Using $K'_{1\mathrm{FeSO}_4^+}$ = (102.5 ± 11.0) $\mathrm{mol}^{-1}\cdot\mathrm{kg}$ yields a value for $K'_{2\mathrm{Fe(SO_4)}_2^-}$, (19 ± 4) $\mathrm{mol}^{-1}\cdot\mathrm{kg}$.

In summary, the corrected value for the formation constant for FeSO_4^+ is (102.5 ± 11.0) $\mathrm{mol}^{-1}\cdot\mathrm{kg}$ instead of (72.8 ± 6.9) $\mathrm{mol}^{-1}\cdot\mathrm{kg}$, the formation constant for FeHSO_4^{2+} is (4.8 ± 2.4) $\mathrm{mol}^{-1}\cdot\mathrm{kg}$ instead of (0.86 ± 0.4) $\mathrm{mol}^{-1}\cdot\mathrm{kg}$ and, more importantly, the second stepwise formation constant to form $\mathrm{Fe(SO_4)}_2^-$ is more than a factor of ten greater than the original value, (19 ± 4) $\mathrm{mol}^{-1}\cdot\mathrm{kg}$ instead of (1.32 ± 0.24) $\mathrm{mol}^{-1}\cdot\mathrm{kg}$.

[1973SKE/ESP]

Skeaff and Espelund carried out a set of measurements with an electrochemical cell with a zirconia-calcia electrolyte used to separate a sulfate-oxide mixture from an oxygen electrode. A gas-stream of SO_2 at atmospheric pressure was maintained over the reaction mixture. Under these conditions, below 913 K FeSO_4(cr) was found to decompose to Fe_2O_3(cr), and $Fe_2(SO_4)_3$(cr) decomposed to $FeSO_4$(cr). At higher temperatures, $Fe_2(SO_4)_3$(cr) decomposed to Fe_2O_3(cr), and $FeSO_4$(cr) is not a stable solid in the system. The potential-difference values for the reaction:

$$Fe_2(SO_4)_3(cr) \rightleftharpoons Fe_2O_3(cr) + 3\,SO_2(g) + 1\tfrac{1}{2}\,O_2(g)$$

are claimed to be within 2 mV of those that were derived in Kellogg's assessment [1964KEL] of vapour-pressure measurements (920 to 1020 K). However, the slopes of the equations in the two papers are not the same. The authors also provide X-ray diffraction data for $FeSO_4$(cr) that indicate that at the temperatures of the experiments, from ~ 700 to ~ 900 K, a high-temperature modification of $FeSO_4$(cr) is formed (the pattern for the lower-temperature solid was reported by Coing-Boyat [1959COI]). The synthetic procedures are not well documented.

A third-law analysis using the entropy value (305.6 $J\cdot K^{-1}\cdot mol^{-1}$) from Majzlan *et al.* [2005MAJ/NAV], which properly incorporates the magnetic contribution, gives $-$ 2576 $kJ\cdot mol^{-1}$ for $\Delta_f H^\circ_m$ ($Fe_2(SO_4)_3$, cr, 298.15 K) based on $\Delta_r G(900\,K)$. This value is not in particularly good agreement with calorimetry data for the system (see Section IX.1.2.2.3.1).

[1973SKE/PAT]

Skelton and Patterson carried out measurements for the cell Ni, NiF_2 | CaF_2 | FeF_2,Fe at temperatures from 741 to 1030 K.

The results were not tabulated, and only a poor plot was provided. The results were reported in the form of a linear equation:

$$E(A.106)/mV = 296.8 + 0.089\,(T/K)$$

for

$$NiF_2(cr) + Fe(cr) \rightleftharpoons FeF_2(cr) + Ni(cr). \qquad (A.106)$$

A third-law analysis of the results was done using auxiliary values from the present review, and thermodynamic quantities for Ni(cr) and NiF_2(cr) from Gamsjäger *et al.* [2005GAM/BUG]. This leads to values of $-$ 713.4 and $-$ 711.3 $kJ\cdot mol^{-1}$ for $\Delta_f H^\circ_m$ (FeF_2, cr, 298.15 K) based on the potentials at 741 K and 1030 K.

[1973VER/RAN]

These authors used Mössbauer spectroscopy to determine the Fe(II)/^{57}Fe(III) electron-exchange reaction (0.04 to 0.14 $mol\cdot dm^{-3}$ Fe(III)) as a function of pH in the presence of ClO_4^-, SO_4^{2-}, NO_3^- and Cl^-, and also determined the formation constant of the dimer according to:

$$2\,Fe^{3+} + 2\,H_2O(l) \rightleftharpoons Fe_2(OH)_2^{4+} + 2\,H^+ \qquad (A.107)$$

at 25 °C in the 3 $mol\cdot dm^{-3}$ media, *viz.*, (0.0135 ± 0.005) (on a molal scale: $\log_{10}{}^*\beta_{2,2}$ = $-$ (1.80 ± 0.16) at $I = 3.50\ mol\cdot kg^{-1}$). They noted that the dimer did not participate in the exchange reaction but did not provide the experimental data used to derive the dimerization constant. Moreover, there was no mention of how the pH of their solutions was measured. From measurements made at 25, 35, 45 and 55 °C they report $\Delta_r H_{2,2}$ (A.107) = 18.0 kJ·mol^{-1} as being to be "accepted only with reservation".

Interestingly, they reported dimer decomposition rates using a pH-jump technique coupled with Mössbauer spectroscopy in which they started with a 0.05 mol·dm^{-3} Fe(III) and 1.0 mol·dm^{-3} (anion) solution at pH 2.2 or 2.3, whereupon the acid concentration was increased to 2.0 mol·dm^{-3} and the following comparatively slow rate constants were reported: 8×10^{-4} s^{-1}, ClO_4^-; 1.5×10^{-3} s^{-1}, SO_4^{2-}; 1.7×10^{-3} s^{-1}, NO_3^-; 1.7×10^{-3} s^{-1}, Cl^- at 25 °C. They pointed out that these rates are *ca.* 100 times slower than that reported earlier [1971PO/SUT] using stopped-flow spectroscopy. The explanation given was that spectrophotometry responds to the change in absorbance due to the initial protonation of the dimer, whereas Mössbauer spectroscopy is sensitive to the breakdown of the dimer into monomers.

The lack of experimental details including the experimental results themselves renders the $\log_{10} {}^*\beta_{2,2}$ value only useful for comparison purposes. However, the rate constants for the decomposition of the dimer are noteworthy, but appear to be too slow to allow the many investigations of the dimer formation constant to have achieved equilibrium.

[1973WHI]

A series of aging experiments were performed at 25 °C whereby either NaOH or $NaHCO_3$ solutions were added to $FeSO_4$ solutions. The pH (no description of the calibration of the cell containing glass and Ag/AgCl reference electrodes was given), Eh and Fe concentration were monitored. Depending on the pH, either goethite was formed (low pH) after *ca.* 100 days, whereas in neutral and basic solutions goethite and lepidocrocite were immediately (after 1 day) detected by XRD with their ratios varying with pH. Three runs with bicarbonate present were reported to result in the precipitation of siderite and from the tabulated analytical data the $\log_{10} {}^*K_{s,0}$ value is (2.2 ± 0.8) at $I =$ (0.041 ± 0.007) for the reaction: $FeCO_3(s) + H^+ \rightleftharpoons Fe^{2+} + HCO_3^-$. Subsequent oxidation was observed after the initial "apparent" precipitation of siderite. The reported stabilities of coarsely crystalline goethite and lepidocrocite are $-43.9 < \log_{10} {}^*K_{s,0} < -44.6$ and < -43.6, respectively. In keeping with the suggestions in [1962FEI/MIC], crystalline phases were found to form directly from Fe(II) solutions, whereas both amorphous and poorly crystalline oxyhydroxides were formed directly from Fe(III) solutions.

There are many interesting qualitative and semi-quantitative observations in this thesis with limited results for well-characterized phases so that no thermodynamic data could be extracted from these observations.

[1974GID/GOR]

This experimental paper complements a critical literature review by the same authors [1973GID/GOR]. Coulometric titrations of wüstite were conducted at 6 temperatures between 1253 and 1385 K, with particular attention to correcting the effects of oxygen permeation through the electrolyte on the sample composition. Results are in excellent agreement with the assessment cited above. Tabulated information includes new data on composition and potential for the wüstite-Fe_3O_4 boundary.

[1974GRO/SVE]

The heat capacity of a 68.485 g specimen of high-purity synthetic Fe_3O_4, similar but not identical in preparation and analysis to the material studied at low temperatures by [1969WES/GRO], was measured, and 100 values are reported for temperatures from 299.94 to 1044.10 K, including 24 values between 837.53 and 861.40 K. This represents a major improvement on the description of the Curie transition region by [1951COU/KIN] and others; the peak of the λ-type transition was $C^{\circ}_{p,\mathrm{m}} \approx 340$ $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ at 848.5 K. The standard deviation of individual C_p measurements was 0.51%, and the accuracy of derived enthalpy and entropy values was judged to be about ±0.3%. These high-quality data are included in the assessment of $C^{\circ}_{p,\mathrm{m}}$ (Fe_3O_4, cr, T) in Section VII.2.7.1.

The paper includes a detailed discussion of lattice, dilation, and magnetic contributions to the heat capacity, which is beyond the scope of the current review. The question of zero-point entropy of Fe_3O_4 (see Section VII.2.7.1.3) is addressed, and the equilibrium measurements of [1972RAU] on the reaction $\frac{1}{4}Fe_3O_4(s) + H_2(g) \rightleftharpoons \frac{3}{4}Fe(s) + H_2O(g)$ are shown by third-law calculations to be consistent with a zero-point entropy of ~4 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, but not accurate enough to settle the question unequivocally.

[1974MAC/BAR]

Differential calorimetry was used to determine the heat-capacity values of FeF_2(cr) and FeF_3(cr) at 200 °C, 300 °C and 400 °C. For the purpose of fitting a single function to the calorimetry results from this study for FeF_2(cr) and the earlier work of Catalano and Stout [1955CAT/STO2], the individual values for the heat-capacity uncertainties were estimated as suggested by the authors.

The value of $C^{\circ}_{p,\mathrm{m}}$ (FeF_3, cr) for 473.15 K does not mesh especially well with those for temperatures above 420 K from [1965BIZ/MAI], being ~ 5 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ greater than would be expected based on the earlier work.

[1974OYK/BAL]

The basic aim of this study was to investigate the thermodynamics of the Mg(II) and Fe(II) sulfate water system at 298.15 K. These results were the ones used by Reardon and Beckie [1987REA/BEC] to establish Pitzer parameters for the aqueous $FeSO_4$ system.

Subsequently, Nikolaev *et al.* [1989NIK/DIK] also measured the osmotic coefficients of iron(II) sulfate solutions at 298.15 K, but their results were in poor agreement with those reported by Oykova and Balarew [1974OYK/BAL]. The latter are summarized in Table A-27 where the first three columns provide the *rounded* molalities of $FeSO_4$, the activities of water and the osmotic coefficients, respectively, as given by the authors who obviously used water activities derived from NaCl standards. The authors used $\ln a_{H_2O} = 18\nu m_i\phi/1000$ to evaluate the activity of water (note that here a minus sign seems to be missing). In their Table 1 the authors give four significant digits for a_{H_2O} and ϕ, but only one or two significant digits for the molality of $FeSO_4$. The review used the four digits for a_{H_2O} and ϕ, and the authors (corrected) equation to reconstruct the given molalities to 3 or 4 significant digits (listed in column 4). Then, from these reconstructed molalities the osmotic coefficients were re-evaluated using the correct relative molar mass of water (18.0153 g·mol^{-1}) (column 5). However, these corrections to the osmotic coefficient values were minor.

Table A-27: Molality, water activity and osmotic coefficients as provided in the paper. Corrected values are given in columns 4 and 5.

m_{FeSO_4} as given	a_{H_2O} as given	Osmotic coeff. ϕ as given	Re-evaluated m_{FeSO_4} using M_{H_2O} = 18.0 g·mol^{-1}	Re-evaluated osmotic coeff. ϕ using M_{H_2O} = 18.0153 g·mol^{-1}
0.1	0.9980	0.5757	0.097	0.5728
0.2	0.9963	0.5118	0.201	0.5119
0.3	0.9945	0.5118	0.299	0.5120
0.4	0.9927	0.5118	0.398	0.5109
0.5	0.9907	0.5246	0.495	0.5239
0.6	0.9888	0.5118	0.611	0.5116
0.7	0.9868	0.5209	0.709	0.5202
0.8	0.9848	0.5278	0.806	0.5274
0.9	0.9826	0.5402	0.903	0.5395
1.0	0.9805	0.5566	0.983	0.5560
1.1	0.9782	0.5583	1.097	0.5577
1.2	0.9760	0.5651	1.194	0.5647
1.3	0.9735	0.5757	1.296	0.5752
1.4	0.9710	0.5849	1.398	0.5843
1.5	0.9682	0.5971	1.503	0.5968
1.6	0.9651	0.6197	1.592	0.6193
1.7	0.9618	0.6360	1.701	0.6355
1.8	0.9583	0.6575	1.800	0.6568
1.9	0.9542	0.6868	1.896	0.6863
1.9641	0.9514	0.7035	1.9641	0.7040

The present review considers the formation of $FeSO_4$(aq) and the 2:1 complex $Fe(SO_4)_2^{2-}$, as proposed by Ciavatta *et al.* [2002CIA/TOM], such that the following species are assumed to be present in solution: Fe^{2+}, SO_4^{2-}, $FeSO_4(aq)$ and $Fe(SO_4)_2^{2-}$ but the protonation of sulfate as well as the hydrolysis of Fe^{2+} were not accounted for. Moreover, $Fe_2SO_4^{2+}$, as well as the higher-order complexes $Fe(SO_4)_n^{2(n-1)-}$ ($n > 2$) are not taken into account, but no evidence for these complexes was found.

By adopting this simple chemical model, the speciation in solution is obtained by solving

$$\beta_2 m^3_{SO_4^{2-}} + (\beta_1 + m_{(FeSO_4)_{total}}\beta_2) m^2_{SO_4^{2-}} + m_{(SO_4^{2-})_{total}} - m_{(FeSO_4)_{total}} = 0 \qquad (A.108)$$

where $m_{(FeSO_4)_{total}}$ is the total molality of Fe(II) sulfate (regardless of the actual speciation), $\beta_1 = m_{FeSO_4(aq)}/\left(m_{Fe^{2+}} m_{SO_4^{2-}}\right)$, and $\beta_2 = m_{Fe(SO_4)_2^{2-}}/\left(m_{Fe^{2+}} m^2_{SO_4^{2-}}\right)$. The relevant thermodynamic constants at each ionic strength are given by:

$$\log_{10}\beta_1 = \log_{10}\beta_1^o - \log_{10}\gamma_{FeSO_4(aq)} + \log_{10}\gamma_{Fe^{2+}} + \log_{10}\gamma_{SO_4^{2-}}$$

$$\log_{10}\beta_2 = \log_{10}\beta_2^o - \log_{10}\gamma_{Fe(SO_4)_2^{2-}} + \log_{10}\gamma_{Fe^{2+}} + 2\log_{10}\gamma_{SO_4^{2-}}$$

When applying the SIT formalism, the individual γ values are given by:

$$\begin{aligned}\log_{10}\gamma_{Fe^{2+}} = &-4D + \varepsilon(Fe^{2+}, SO_4^{2-}) m_{SO_4^{2-}} + \varepsilon(Fe^{2+}, Fe(SO_4)_2^{2-}) m_{Fe(SO_4)_2^{2-}} \\ &+ \varepsilon(Fe^{2+}, FeSO_4)\, m_{FeSO_4(aq)}\end{aligned}$$

$$\log_{10}\gamma_{SO_4^{2-}} = -4D + \varepsilon(Fe^{2+}, SO_4^{2-})\, m_{Fe^{2+}} + \varepsilon(FeSO_4, SO_4^{2-})\, m_{FeSO_4(aq)}$$

$$\begin{aligned}\log_{10}\gamma_{Fe(SO_4)_2^{2-}} = &-4D + \varepsilon(Fe^{2+}, Fe(SO_4)_2^{2-})\, m_{Fe^{2+}} \\ &+ \varepsilon(FeSO_4, Fe(SO_4)_2^{2-})\, m_{FeSO_4(aq)}\end{aligned}$$

$$\begin{aligned}\log_{10}\gamma_{FeSO_4(aq)} = &\ \varepsilon(Fe^{2+}, FeSO_4)\, m_{Fe^{2+}} + \varepsilon(FeSO_4, SO_4^{2-})\, m_{SO_4^{2-}} \\ &+ \varepsilon(FeSO_4, Fe(SO_4)_2^{2-})\, m_{Fe(SO_4)_2^{2-}}\end{aligned}$$

Nothing is known about these interaction coefficients including those for the neutral $FeSO_4(aq)$ complex with the other species in solution, which according to the TDB-2 guidelines should be set to zero when applying the SIT formalism. The first model considered showed that by following this guideline and ignoring the formation of the second complex, no sensible pair of parameters could accommodate these data.

A second model applied also assumed that the complex $Fe(SO_4)_2^{2-}$ is not formed, but in this case the SIT coefficients involving interactions with the neutral species were allowed finite, but equal, values. An "optimum" fit in the range $m_{totFeSO4} = 0.1$ to 1.5 $mol\cdot kg^{-1}$ was obtained with the following parameters: β_1^o ($FeSO_4$, aq) = (154 ± 3) $kg\cdot mol^{-1}$; $\varepsilon(Fe^{2+}, SO_4^{2-}) = -(0.09 \pm 0.03)$ $kg\cdot mol^{-1}$; ε(neutral,ion) = (0.16 ± 0.02) $kg\cdot mol^{-1}$. This parameter set produces a sum of squares of 0.00185 and a sum of differences of – 0.0011. However, no fit was obtained when β_1^o ($FeSO_4$, aq) was set to 275.4 $kg\cdot mol^{-1}$ as selected in this review.

In a third model use was made of data from Ciavatta *et al.* [2002CIA/TOM] which suggest that β_2^o ($Fe(SO_4)_2^{2-}$) is about twice β_1^o ($FeSO_4$, aq), and the finding from model 2 that $\varepsilon(Fe^{2+}, SO_4^{2-}) = -0.09$ $kg\cdot mol^{-1}$. Furthermore, for simplicity, this model assumed $\varepsilon(\mathrm{Fe^{2+}, Fe(SO_4)_2^{2-}})$ = $\varepsilon(\mathrm{Fe^{2+}, SO_4^{2-}})$. For $\beta_2^{\circ}(\mathrm{Fe(SO_4)_2^{2-}}) \leq 0.2\,\beta_1^{\circ}(\mathrm{FeSO_4, aq})$ a fair representation can be achieved with parameter sets very close to the optimum set of model 2 with either $\varepsilon(\mathrm{FeSO_4, Fe^{2+}}) = \varepsilon(\mathrm{FeSO_4, SO_4^{2-}}) = (0.16 \pm 0.02)$ kg·mol^{-1}, or $\varepsilon(\mathrm{FeSO_4, (Fe^{2+} + SO_4^{2-})}) = (0.32 \pm 0.03)$ kg·mol^{-1}. A sensitivity analysis shows that models 2 and 3 are very sensitive to changes in ε(neutral), and if the value of $\beta_2^{\circ}(\mathrm{Fe(SO_4)_2^{2-}})$ is decreased, the parameters tend towards those of model 2. This contradicts the suggested [2002CIA/TOM] formation of substantial amounts of $\mathrm{Fe(SO_4)_2^{2-}}$ in this system.

However, only a restricted amount of slightly scattered experimental data is available from this study [1974OYK/BAL] so that over-interpretion of the data must be avoided, and the $\varepsilon(\mathrm{Fe^{2+}, SO_4^{2-}}) = -(0.09 \pm 0.03)$ kg·mol^{-1} is not recommended in this review.

Nevertheless, it appears that an interaction coefficient with the neutral complex needs to be established. Gamsjäger *et al.* [2005GAM/BUG] defined a “neutral” SIT coefficient $\varepsilon(\mathrm{Ni(SCN)_2(aq), Na^+ + ClO_4^-}) = (0.38 \pm 0.06)$ kg·mol^{-1}, and Hummel *et al.* [2005HUM/AND] defined a series of “neutral” coefficients for the undissociated organic acids $\mathrm{H_2ox}$, $\mathrm{H_3cit}$ and $\mathrm{H_4edta}$ with electro-neutral combinations of inert electrolytes.

Osmotic coefficient data for a series of transition metal sulfates (Mg, Mn, Co, Ni, Cu, Zn) given by Libus *et al.* [1980LIB/SAD] appear, at first glance, to compare well with the iron(II) data given by [1974OYK/BAL]. From basic chemical principles one would expect that Fe(II) and Ni(II) sulfate solutions should behave similarly, but it is clear that there are differences. The Ni(II) solutions are selected here for comparison, because in a recent review [2005GAM/BUG], $\beta_1^{\circ}(\mathrm{NiSO_4, aq})$ was selected to be (226.1 ± 15.2) kg·mol^{-1} at 298.15 K. In their assessment, association constants of higher-order complexes were not required. Hence, evaluation according to model 2 as given above needs to consider only one free parameter, ε(neutral), because $\varepsilon(\mathrm{Ni^{2+}, SO_4^{2-}})$ should not substantially deviate from $\varepsilon(\mathrm{Fe^{2+}, SO_4^{2-}})$. However, the SIT formalism seems to be capable of describing the iron(II) system but not the nickel system, a situation that was unexpected. There may be several reasons for this result:

a) The SIT formalism as outlined above is not suited for describing the osmotic properties of Me(II) sulfate solutions and it is only by chance that the iron(II) system produces sensible results.

b) The unexpected difference between the osmotic coefficient data for $\mathrm{FeSO_4}$ and all the other $\mathrm{MeSO_4}$ (except $\mathrm{MgSO_4}$, which lies in between, and might be suitable for a SIT treatment) may suggest that either the iron data and/or all the other transition metal data are of questionable quality.

The present review cannot resolve these ambiguities. There is certainly a need to prove or to disprove the validity of the different data sets, and this probably would be done best by carrying out a series of additional experiments.

The osmotic coefficients can be well reproduced with a Pitzer formalism [1991PIT] as was demonstrated for $FeSO_4$ solutions by Reardon and Beckie [1987REA/BEC] and for $MgSO_4$ and $NiSO_4$ solutions by this work. The resulting parameter sets are provided in Table A-28.

Table A-28: Pitzer parameters for the representation of osmotic coefficients of Fe(II), Mg(II) and Ni(II) sulfate solutions at 298.15 K.

	$FeSO_4$		$MgSO_4$	$NiSO_4$
	[1987REA/BEC]	[this work]	[this work]	[this work]
A_ϕ(298.15 K), $kg^{1/2}\cdot mol^{-1/2}$	0.391	0.391	0.391	0.391
b-parameter, $kg^{1/2}\cdot mol^{-1/2}$	1.2	1.2	1.2	1.2
$\beta_{MX}^{(0)}$, $kg\cdot mol^{-1}$	0.2568	0.3161	0.2137	0.1768
α_1, $kg^{1/2}\cdot mol^{-1/2}$	1.4	1.4	1.4	1.4
$\beta_{MX}^{(1)}$, $kg\cdot mol^{-1}$	3.063	2.5098	3.321	2.942
α_2, $kg^{1/2}\cdot mol^{-1/2}$	12	12	9.48	29.62
$\beta_{MX}^{(2)}$, $kg\cdot mol^{-1}$	−42	−42	−37.28	−36.53
C^{ϕ}_{MX}, $kg^2\cdot mol^{-2}$	0.0209	−0.005983	0.0261	0.0331

Reardon and Beckie applied the Pitzer treatment for 2:2 electrolytes to determine $\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ}, and hence $\gamma_{\pm}(m)$. Their fit was constrained so as to force a value of ~0.161 for $\gamma_{\pm}(0.1\ mol\cdot kg^{-1})$ and the value of $\beta^{(2)}$ was fixed as −42. A fit unconstrained to a predetermined value of $\gamma_{\pm}$ led to 0.154 for $\gamma_{\pm}(0.1\ mol\cdot kg^{-1})$. Neither value of $\gamma_{\pm}$ is unreasonable. For the saturation molality [1974OYK/BAL], ϕ, $\gamma_{\pm}$ and a_w are 0.699, 0.048 and 0.952, respectively, as recalculated from the Pitzer-equation values of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^{ϕ} listed in Table 2 in the paper of Reardon and Beckie [1987REA/BEC], and hence, $\Delta_r G^{o}_{m}$ (A.109) = 12.57 $kJ\cdot mol^{-1}$ for:

$$FeSO_4\cdot 7H_2O(cr) \rightleftharpoons FeSO_4(sln) + 7\,H_2O(l). \qquad (A.109)$$

This is the source of the modified value (12.58 ± 0.30) discussed in [1995PAR/KHO]. Unfortunately, when the Pitzer osmotic equation for 2:2 electrolytes (*e.g.*, from Downes and Pitzer [1976DOW/PIT]) is used with the values of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^{ϕ} from Reardon and Beckie, the calculated values of ϕ do not correspond to those listed in their Table 1 [1987REA/BEC], especially at lower molalities. The equation for $\ln\gamma_{\pm}$ in their paper also appears to differ somewhat from the standard equation [1974PIT/MAY].

A refit of the Pitzer equation for 2:2 electrolytes to the data from [1974OYK/BAL] with the value of $\beta^{(2)}$ fixed as -42 (Table 2), results in ϕ, $\gamma_{\pm}$, and a_w values of 0.691, 0.0447 and 0.952, respectively, and 12.91 $kJ\cdot mol^{-1}$ for $\Delta_r G^{o}_{m}$ (A.109). Changing the fixed $\beta^{(2)}$ value to −48 leads to $\Delta_r G^{o}_{m}$ (A.109) = 13.02 $kJ\cdot mol^{-1}$, whereas lowering the estimated saturation molality to 1.944 as assessed by Linke [1958LIN], would raise the value of $\Delta_r G_m^o$ (A.109) slightly to 12.95 kJ·mol^{-1}. In the present review, the Pitzer-treatment refit, with an unconstrained value of $\gamma_{\pm}$ for the 0.1 m solution is used, and the uncertainty in $\Delta_r G_m^o$ (A.109) is estimated as ±0.4 kJ·mol^{-1}; thus,

$$\Delta_r G_m^o \text{ (A.109)} = (12.9 \pm 0.4) \text{ kJ·mol}^{-1}.$$

[1974SAI]

This paper is mainly concerned with oxygen chemical potential measurements on UO_{2+x}, but it includes a series of measurements on the potential of Fe-wüstite *vs*. Ni-NiO that yielded the following relationship.

$$E/\text{mV} = 154.7 + 0.1047(T/\text{K})$$

[1974VLE/BLO]

An edta-based procedure of the type developed by Lindsay and Norvell [1969LIN/NOR] was used to measure the solubility products of synthetic “amorphous $Fe(OH)_3$”, natural lepidocrocite (γ-FeOOH), and natural jarosite (nominally $KFe_3(SO_4)_2(OH)_6$) admixed with “amorphous $Fe(OH)_3$”. The method was based on measuring the competitive formation of $Fe(edta)^-$, $Fe(OH)(edta)^{2-}$, and either $Ca(edta)^{2-}$ or $Zn(edta)^{2-}$ complexes.

Equilibration times varied from 9 to 46 days with constant shaking at (25 ± 1) °C. The pH of the solutions was buffered with either phthalate or borate buffers and was measured with a glass/calomel combination electrode presumably calibrated against standard buffer solutions. Either known concentrations of calcium or zinc were added to these solutions to allow measurement of the Fe/Ca and Fe/Zn ratios as a function of pH to calculate the $[Fe^{3+}]$ based on formation constants for the edta complexes taken from Sillen and Martell [1964SIL/MAR] corrected to the working ionic strengths using the generic Debye-Hückel equation for the activity coefficients. The authors argued that by using small amounts of contaminated jarosite, the amorphous iron hydroxide was leached from the solid so that the measured iron concentrations could be due to amorphous jarosite. From the above method they also claim to have measured the solubility product of pure, crystalline lepidocrocite, γ-FeOOH. Apart from filtering the suspensions through filter paper prior to analysis, no other precautions appear to have been taken to avoid colloid contamination.

The resulting values of $-\log_{10} K$ for formation of (39.02 ± 0.35) for fresh synthetic “$Fe(OH)_3$”, 39.93 for natural “$Fe(OH)_3$”, and (42.48 ± 0.23) for lepidocrocite are all larger (*i.e.*, lower solubility) than expected (see Section VII.2), suggesting a bias in the auxiliary data used. In addition, the difference between “$Fe(OH)_3$” and lepidocrocite is larger than expected. A value of $-\log_{10} K$ of 98.56 was obtained for formation of jarosite. The authors were unable to measure the solubility products of goethite (α-FeOOH) and hematite (α-Fe_2O_3), because of extremely slow dissolution.

No thermodynamic data can be extracted from this work as generally amorphous solid phases are employed and there are numerous assumptions (*e.g.*, activity coefficients, pH calibration, ignoring colloid formation, *etc.*) and questionable formation constants were involved in the treatment of the experimental data. The authors were also limited by the sensitivity of the analytical instruments available to them at that time. Nevertheless, it is interesting that their solubility product for amorphous $Fe(OH)_3$ is in good agreement with the value of $(1.1 \pm 0.5) \times 10^{-39}$ reported in [1967BOH] where more careful and direct measurements were made. The uncertainty in the solubility product for crystalline lepidocrocite is too large to be useful, especially as the uncertainty does not include the contributions from the assumptions made in treating the data.

[1974WHI/LAN]

This paper is essentially an abbreviated version of [1971LAN/WHI].

[1975BIE]

This is an overview article presenting examples of applications of the SIT even mentioning the dependence of interaction parameters in ionic strength. Biedermann presumably cites Schumb and Sweetser (1935) for their study of the equilibrium: $\mathrm{Fe}^{3+} + \mathrm{Ag(s)} \rightleftharpoons \mathrm{Fe}^{2+} + \mathrm{Ag}^{+}$, in 0.1 to 1.2 $\mathrm{mol \cdot kg^{-1}}$ $HClO_4$, but did not provide the corresponding reference. However, this redox equilibrium leads to the following:

$$\log_{10} K + 4D = \log_{10} K^{\circ} + m_{\mathrm{ClO_4^-}} [\varepsilon(\mathrm{Fe^{2+}}, \mathrm{ClO_4^-}) + \varepsilon(\mathrm{Ag^{+}}, \mathrm{ClO_4^-}) - \varepsilon(\mathrm{Fe^{3+}}, \mathrm{ClO_4^-})].$$

No experimental values are provided from which to recalculate the values provided from this claimed linear relationship with respect to $m_{\mathrm{ClO_4^-}}$: *i.e.*, $E^{\circ}(\mathrm{Fe^{3+}},\mathrm{Fe^{2+}}) = (780 \pm 1)$ mV, $\varepsilon(\mathrm{Fe^{3+}}, \mathrm{ClO_4^-}) = 0.56\ \mathrm{kg \cdot mol^{-1}}$ based on claimed known (but not referenced) values of $\varepsilon(\mathrm{Fe^{2+}}, \mathrm{ClO_4^-})$ assumed equal to $\varepsilon(\mathrm{Mg^{2+}}, \mathrm{ClO_4^-})$ and $\varepsilon(\mathrm{Ag^{+}}, \mathrm{ClO_4^-}) = 0.0$. Presumably the temperature is 25 °C. Note the value of $\varepsilon(\mathrm{Fe^{3+}}, \mathrm{ClO_4^-})$ given in the NEA tables is $(0.56 \pm 0.03)\ \mathrm{kg \cdot mol^{-1}}$, also referenced in [1980CIA], who refer to the current paper. See [1935SCH/SWE] for treatment of a reanalysis of their results.

Although this reference is widely cited, the raw experimental results are available in [1935SCH/SWE] and can be treated there without the need for assumptions. Therefore, the above analysis is only of interest for the sake of comparison.

[1975CHA/KAR]

Chattopadhyay *et al.* carried out measurements for the cell Pt | Ni, NiF_2 | CaF_2 | FeF_2, Fe| Pt. The actual temperature range for the measurements was not specified. The results were not tabulated; only a plot was provided, and that did not extend to temperatures above 1020 K. The results were reported in the form of a linear equation:

$$\mathrm{E(A.110)/mV} = 252.4 + 0.146\ (T/\mathrm{K})$$

for the reaction

$$NiF_2(cr) + Fe(cr) \rightleftharpoons FeF_2(cr) + Ni(cr) \qquad (A.110)$$

for temperatures from 850 to 1050 K.

A third-law analysis of the results was done using auxiliary values from the present review, and thermodynamic quantities for Ni(cr) and NiF_2(cr) from Gamsjäger *et al.* [2005GAM/BUG]. This leads to values of − 713.4 and − 714.1 kJ·mol^{-1} for $\Delta_f H_m^\circ$ (FeF_2, cr, 298.15 K) based on the potentials at 850 and 1050 K.

[1975GRO/SAM]

High-precision heat-capacity measurements were performed on a 65.383-g specimen of commercial, high-purity α-Fe_2O_3 (Matthey "specpure", <6 ppm total detectable impurities (Si + Mn + Cu + Mg), heated to constant mass at 1000 °C, %Fe found 69.96%, theoretical 69.94%, Fe(II) below detection limit of 0.05%). A calorimeter with adiabatic shields and intermittent energy inputs was used, with thermal equilibration between each input. The empty calorimeter represented 56 - 64% of the total heat capacity; temperature measurements were judged accurate to ±0.002 K, and energy inputs to ±0.025%. Seven series of tabulated measurements, totaling 78 $C^\circ_{p,m}$ values, cover the temperature range from 301.92 to 1054.36 K.

We accept the authors' argument that their results are more accurate than those obtained in several earlier studies with "a cruder (continuous) measuring technique". Discussion in Section VII.2.2.2 of this review is therefore limited to fitting expressions and comparison with the high-temperature enthalpy measurements of [1951COU/KIN].

This paper includes a detailed discussion of the magnetic and lattice contributions to the heat capacity. Two anomalies are observed: a broad bump around 500 K and a large λ transition at the Néel point (955 K). Previously reported anomalies at 630 K [1926BRO/FUR] and 1050 K [1951COU/KIN] appear to be erroneous.

[1975KNI/SYL]

Spectrophotometric measurements for determining the first hydrolysis constant of Fe^{3+} were made on freshly prepared solutions with a total iron(III) concentration of $(1 - 3) \times 10^{-4}$ M and a pH of 2 to 3.1 in 0.1 M ionic strength ($NaClO_4$) at 25 °C. The pH was calibrated on the concentration scale, but no details were forthcoming. For monitoring the dimerization reaction, the total iron(III) concentration range was $(3.3 - 10) \times 10^{-3}$ M at pH values of 1.7 to 2.3 also at $I = 0.1$ M and 25 °C. Corrections were made for the presence of the three iron-containing species in these equilibria in an iterative fashion. No raw data or uncertainties were given and the values of $\log_{10} {}^*K_{1,1}$ and $\log_{10} {}^*\beta_{2,2}$ were quoted as: − 2.54 and − 3.1 in H_2O, and − 2.85 and − 3.2 in D_2O, respectively.

These hydrolysis constants are of value for comparison purposes only.

[1975KOR/FAD]

The enthalpies of transformation of lepidocrocite (γ-FeOOH), goethite (α-FeOOH), and maghemite (γ-Fe_2O_3) to hematite (α-Fe_2O_3) were estimated by thermal analysis. Diakonov [1998DIA] has commented on the large degree of scatter of the data, which he attributed to surface-area effects, specifically the heat of coarsening of the hematite product, which necessitated corrections of as much as 35 kJ·mol^{-1}. Note also that the entropies of transformation are spurious, because the enthalpy measurements do not refer to equilibrium transition points. Diakonov [1998DIA] extracted an upper (least negative) limit of -19 kJ·mol^{-1} for $\Delta_{\mathrm{trs}}H^{\circ}_{\mathrm{m}}$ (Fe_2O_3, $\gamma \rightarrow \alpha$, 298.15 K), but even this seems questionable (see synopses of [1976DEM] and [1998DIA]). This study is not included in the current assessment.

[1975NIK/TSV]

Potential-difference measurements for the cell

$$\mathrm{Tl(Hg)/TlCl}\mid \text{saturated KCl(sln)} \,\vdots\vdots\, \mathrm{FeSO_4, Fe_2(SO_4)_3, Na_2SO_4, H_2SO_4} \mid \mathrm{Pt}$$

were carried out to investigate the dependence of the association of Fe^{3+} with SO_4^{2-} as a function of temperature (25 to 150 °C). Two series of solutions were used. In one, the concentration of H_2SO_4 was constant at 0.20 M and the Na_2SO_4 concentration was varied from 0.05 to 0.40 M; in the second series no Na_2SO_4 was added, and the concentration of H_2SO_4 was varied from 0.10 to 1.81 M. Thus, unlike many studies, these measurements were not carried out at constant ionic strength. The concentrations of the iron salts were 2 to 5×10^{-3} M. It is not clear whether the reported "molar" concentrations at all temperatures were the room-temperature molar concentrations, or were adjusted to apply at the measurement temperature. The calculated formation constant values at each temperature showed considerable scatter, but for any particular solution the value of the apparent complexation constant did increase by approximately two orders of magnitude between 25 and 125 °C. The authors determined the complexation constants for $I = 0$ using an extended Debye-Hückel equation and fitted the following equation to their results:

$$\log_{10} K_1^{\circ} = 21.7130 - 8895.59/(T/\mathrm{K}) + 1115508(T/\mathrm{K})^{-2}.$$

The severe scatter in the data (also see the Appendix A entry for [1973NIK/ANT]) limits the quantitative utility of the results, but they do provide qualitative information concerning the temperature dependence of the value of the first complexation constant.

[1975SCH2]

See the entry for [1981SCH/GOK].

[1975SHI/SAN]

The authors carried out measurements of potentials of the solid-state galvanic cell

$$\mathrm{Pt|Fe,\ Fe_2SiO_4,\ SiO_2(quartz)|(CaO)_{0.15}(ZrO_2)_{0.85}|``FeO",Fe|Pt}$$

between 973 to 1273 K and determined the oxygen potentials corresponding to equilibrium.

The Gibbs energy of the reaction

$$2\,\text{“FeO(s)”} + \mathrm{SiO_2(s)} \rightleftharpoons \mathrm{Fe_2SiO_4(s)}$$

was reported in the form of an equation

$$\Delta_r G\ /\mathrm{kJ\cdot mol^{-1}} = -4EF/\mathrm{kJ\cdot mol^{-1}} = -43932 + 20.305(T/\mathrm{K}),$$

apparently based on measurements at 13 different temperatures. If this equation is combined the reference electrode values from O’Neill [1987NEI2], along with consistent auxiliary data for quartz ([1989COX/WAG], [1998CAR/SAL]) and oxygen [1989GUR/VEY], and with the values selected in this review for the heat capacity and entropy of α-Fe_2SiO_4 (Section X.2.1.1.1) and Fe(cr) (Section V.2), an average value of $-(1476.9 \pm 1.09)$ $\mathrm{kJ\cdot mol^{-1}}$ (2σ uncertainty) is obtained for $\Delta_f H_m^\circ$ (Fe_2SiO_4, α, 298.15 K). The recalculated values drift very slightly to more positive values with increasing temperature of the original measurements. This might be attributed to a change in the form of SiO_2(cr), as the authors indicate that above 1140 K tridymite is formed, and is thermodynamically stable with respect to β-quartz (which can be metastable [1994SWA/SAX]). However, in the present recalculations the thermodynamic values for quartz have been used for SiO_2(cr) and the drift in the recalculated values of $\Delta_f H_m^\circ$ (Fe_2SiO_4, α, 298.15 K) is linear with temperature over the entire temperature range of the measurements, with no inflection near 1140 K.

[1976ASH]

Ashurst measured the absorption spectrum of 1.02×10^{-3} M $Fe(ClO_4)_3$ aqueous solutions at $I = 5$ M (ClO_4^-; 1 M $HClO_4$) with various chloride concentrations (between 0.01 and 0.08 M) at 325 to 370 nm and at 22, 34, 47 and 60 °C. The values reported for K_1 (2σ uncertainties calculated in the present review from the constants as determined at several wavelengths) were (10.2 ± 0.8) M^{-1} (22 °C), (13.1 ± 0.8) M^{-1} (34 °C), (17.4 ± 1.3) M^{-1} (47 °C) and (22.3 ± 0.8) M^{-1} (60 °C). Values for β_2, 3.6, 9.1, 15.4 and 21.1 M^{-2}, were obtained for the same temperatures when solutions 0.048 M in iron(III) and chloride molarities as great as 3 M were used. Measurements of K_1 were also done using only perchloric acid as a supporting electrolyte (2, 3, 4 and 5 M) and at $I = 5$ M (ClO_4^-; 3 M $HClO_4$). The reported values for these solutions for 25, 34, 47 and 60 °C are listed in Table VIII-1 of the present review.[1]

The results of this study obtained at the lower ionic strengths ($I_m < 5\ \text{mol·kg}^{-1}$), after conversion to the molal scale (last column of TableVIII-1 of the main text) were used as part of the selection of values of K_1° and $\varepsilon(\text{FeCl}^{2+}, \text{ClO}_4^-)$. The β_2 values were obtained in media with ionic strengths too high to be included in the overall optimization by the SIT method.

A small chapter of this rather large report deals with Fe(II) chloride complexes. The absorption spectrum of 0.07 M $\text{Fe(ClO}_4)_2$ aqueous solutions at $I = 5$ M (ClO_4^-;1 M HClO_4 to inhibit hydrolysis) with various chloride concentrations (0, 0.5, 0.77, 1.0, 1.5, 2.0, 3.0 M) was examined at 204, 207, 210, 215, 220 nm at 25 and 60 °C. The spectrum was attributed to a charge-transfer complex. Values of $(0.32 \pm 0.01)\ \text{M}^{-1}$ and $(0.30 \pm 0.02)\ \text{M}^{-1}$ were reported for $\beta_1(\text{FeCl}^+;\ I = 5\ \text{M}\ (\text{ClO}_4^-))$ at 25 and 60 °C, respectively.

The authors argue that the changes in the value of β_1 are not significant over the temperature range 25 to 60 °C and, hence, that $\Delta_r H^{\circ}$ is close to zero ($\Delta_r G^{\circ} = 3.7$ kJ·mol^{-1} and $T\Delta_r S^{\circ} = -3.7$ kJ·mol^{-1}). It seems very risky to draw this conclusion based on just two points, and the conclusion is contradicted by the results from Heinrich and Seward [1990HEI/SEW], Palmer and Hyde [1993PAL/HYD], and the spectroscopic investigations of Vogel Koplitz *et al.* [1987VOG/MCC].

The reported uncertainties are from the linear regression of measured absorbances, and seem unduly optimistic. The ionic strengths and changes in medium are too high for the Fe(II) chloride formation-constant values to be used further in the present review.

[1976BAE/MES]

In this well-respected text, the authors provide a summary table of their recommended values for the hydrolysis of Fe^{2+} and Fe^{3+} ions at 25 °C based on their survey of data in the pre-1976 literature. For the hydrolysis of Fe^{2+} to yield Fe(OH)_y^{2-y} they reported the infinite dilution hydrolysis constants derived from the Pitzer and Brewer equation: $\log_{10}{}^*\beta_{1,1}^{\circ} = -9.5$; $\log_{10}{}^*\beta_{2,1}^{\circ} = -20.6$; $\log_{10}{}^*\beta_{3,1}^{\circ} = -31$; $\log_{10}{}^*\beta_{4,1}^{\circ} = -46$; and for the hydrolysis of Fe^{3+} to yield $\text{Fe}_x\text{(OH)}_y^{3x-y}$: $\log_{10}{}^*\beta_{1,1}^{\circ} = -2.19$; $\log_{10}{}^*\beta_{2,1}^{\circ} = -5.67$; $\log_{10}{}^*\beta_{3,1}^{\circ} = < -12$; $\log_{10}{}^*\beta_{4,1}^{\circ} = -21.6$; $\log_{10}{}^*\beta_{2,2}^{\circ} = -2.95$; $\log_{10}{}^*\beta_{4,3}^{\circ} = -6.3$.

This review by Baes and Mesmer provides a reliable source of recommended hydrolysis constants based on data available prior to 1976.

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[1] There are several minor discrepancies in Ashurst's report. The results of experimental measurements for K_1 at 22 °C (1 M HClO_4; I =5 M, Tables 1, 2 and 4) were later repeated (Tables 6 and 8) as values for 25 °C. The average values reported for 34 and 60 °C (3 M HClO_4; I =5 M) are not the averages of the values tabulated from the measurements at the different wavelengths.

[1976BAR/PER]

Results of a series of solubility measurements for siderite were reported. The experiments were carried out at 20 °C in water and in dilute electrolyte solutions ($NaClO_4$, NaCl, KNO_3, Na_2SO_4, $MgSO_4$, $CaSO_4$, $CaCl_2$, $MgCl_2$; 0.01 to 0.4 $mol\cdot kg^{-1}$ ionic strength). The initial $FeCO_3$ solid, prepared by mixing iron(II) sulfate and sodium hydrogen carbonate in aqueous solution, was washed under argon, and then contacted with solutions of known total carbon dioxide concentration in sealed bottles for 3 to 4 months. Dried solid was not used because there was a strong exothermic reaction on drying, even when this was done under nitrogen (also see Ptacek [1992PTA] and Jensen *et al.* [2002JEN/BOD]). The final pH, and iron and hydrogen carbonate molarities were measured. The authors reported $\log_{10} K^{\circ}_{s,p,0} = -(10.40 \pm 0.05)$.

In the present review, the results for the 11 solutions in water and with $NaClO_4$ added have been recalculated using the SIT (Appendix B), with CODATA values for $CO_2(g)$, $CO_2(aq)$, HCO_3^-, CO_3^{2-} and $H_2O(l)$ at 298.15 K. The temperature dependence of the carbonate equilibria and ion-product of water have been calculated using the equations of Nordstrom *et al.* [1990NOR/PLU]. The recalculation used only the measured carbonate concentrations (assumed to be parts per million by weight) and the measured iron concentrations. The resulting hydrogen ion concentrations are an average of 5% greater than values derived from the authors' measurements, but there is no apparent systematic difference. A value of $-(10.39 \pm 0.08)$ (2σ uncertainty) is obtained for $\log_{10} K^{\circ}_{s,p,0}$ at 20 °C. However, as the solubilities of heat-treated $FeCO_3$ and freshly precipitated $FeCO_3$ differ substantially [2002JEN/BOD], the results of Bardy and Péré are not used further in the present review.

[1976BAR/WES]

A sample of magnetite, prepared hydrothermally from high-purity Fe and Fe_2O_3 in a mechanically agitated autoclave at 573 K, was found to be slightly contaminated with manganese, giving the composition $Mn_{0.008}Fe_{2.992}O_4$. A total of 208 $C^{\circ}_{p,m}$ measurements on a 212.4474 g specimen are tabulated for temperatures from 53.37 to 345.58 K, including 91 in the Verwey transition region between 107.31 and 126.31 K. A bifurcated transition was observed, with peaks at 117.0 and 123.0 K, ~4 K higher than the values for a pure specimen obtained by Mn-free dry synthesis [1969WES/GRO]. More recent studies, *e.g.* [1991SHE/KOE], [1994TAK/AKI], indicate that this bifurcation implies a heterogeneous or partly stressed specimen; however, the data are included in the current evaluation of $C^{\circ}_{p,m}(Fe_3O_4, cr, T)$ in Section VII.2.7.1. The values $\Delta_{trs}H^{\circ}_{m} = (582 \pm 4)\ J\cdot mol^{-1}$ and $\Delta_{trs}S^{\circ}_{m} = (4.94 \pm 0.04)\ J\cdot K^{-1}\cdot mol^{-1}$ were also obtained for the Verwey transition.

[1976BAR/WES2]

This paper deals mainly with deliberately doped magnetite specimens and as such is beyond the scope of the current review; however, it also presents 155 measurements on "presumably high-purity crystals" between 63.86 and 347.25 K, including 78 measurements in the Verwey transition region between 107.56 and 127.98 K. These data are discussed in the evaluation of $C^{\circ}_{p,\mathrm{m}}$ (Fe_3O_4, cr, T) in Section VII.2.7.1.

[1976BYR/KES]

This study is similar in many respects to that reported in [1993KUM/SUZ] and involved solubility measurements at 25 °C of freshly precipitated "hydrous ferric oxide" in natural seawater also using the dialysis phase separation method and a ^{59}Fe tracer to monitor the iron(III) concentration. The one significant conclusion from this work is that the thermodynamic stabilities of the $Fe(OH)_2^+$ and $Fe(OH)_3$(aq) species are poorly defined at 25 °C; a statement that is unfortunately true at higher temperatures as well.

Due to the undefined nature of the solid phase, as well as its fine particle size, no useful results can be gleaned from this study for the purposes of this review.

[1976BYR/KES2]

Measurements were made of the potential of the Fe(III)/Fe(II) couple (Pt electrode with a calomel reference electrode) in (0.63 mol·kg^{-1} (NaCl + $NaNO_3$), 0.05 mol·kg^{-1} HCl) aqueous solutions at 25 °C. The ratio of $NaNO_3$ to NaCl was varied, but the concentrations of Fe(II) and Fe(III) are not clearly noted. The reported chlorido-complex formation constant values (I = 0.68 mol·kg^{-1}) were 2.76 M^{-1} and 0.44 M^{-2} for K_1 and β_2. No raw data were reported, and the values from this study are not used further in the present review.

[1976COR/OUW]

The heats of solution of $FeCl_2$(cr) and $FeCl_3$(cr) (~ 0.2 g) in ~ 0.2 dm^3 of solvent ($HCl\cdot100.6H_2O$, 0.5 mass-% $FeCl_3$) were reported as – (76.86 ± 0.23) kJ·mol^{-1} and – (135.23 ± 0.31) kJ·mol^{-1}, respectively. These values are consistent with other measurements, but in the absence of appropriate values for the enthalpies of dilution in the mixed electrolyte solution, the heats of solution are not used in the calculation of $\Delta_f H^{\circ}_{\mathrm{m}}$ (Fe^{2+}) or $\Delta_f H^{\circ}_{\mathrm{m}}$ (Fe^{3+}).

[1976DEM]

Only a one-paragraph abstract is available. Direct measurement of the heat of transformation of a well-ordered maghemite specimen to hematite yielded a value of $\Delta_{\mathrm{trs}} H^{\circ}_{\mathrm{m}}$ (Fe_2O_3, γ→α, 803 K) = −(15.9 ± 0.8) kJ·mol^{-1}. Diakonov [1998DIA] treated this as an upper (least negative) limit, because of large uncertainties about surface-area effects, and derived an upper limit for $\Delta_{\mathrm{trs}} H^{\circ}_{\mathrm{m}}$ (Fe_2O_3, γ→α, 298.15 K) of −18.2 kJ·mol^{-1}, based on Korobeinikova's $C^{\circ}_{p,\mathrm{m}}$ data for ordered maghemite. Recalculation with $C^{\circ}_{p,\mathrm{m}}/T$ relationships for hematite from Section VII.2.2 and for maghemite from [2003MAJ/LAN] (see Section VII.2.4.1) yields a $\Delta_{\mathrm{trs}} H^{\circ}_{\mathrm{m}}$ (Fe_2O_3, γ→α, 298.15 K) value of −15.5 kJ·mol^{-1}. The uncertainty is difficult to evaluate, because of the lack of reliable $C^{\circ}_{p,\mathrm{m}}$ data for maghemite above ~400 K, as well as surface-area effects. Because the measured enthalpy could include a negative (grain coarsening or recrystallization) term, it is not certain that this value is indeed an upper limit. A value of $\Delta_{\mathrm{trs}}H^{\circ}_{\mathrm{m}}$ (Fe_2O_3, $\gamma\rightarrow\alpha$, 298.15 K) = $-(15.5 \pm 5.0)$ kJ·mol^{-1} is probably reasonable for this study.

[1976DOU/DEB]

An interesting flow-through titration – spectrophotometric apparatus was used to investigate the hydrolysis behaviour of iron(III) nitrate solutions, and kinetics thereof, from 24 °C (one titration each was performed at 55 and 90 °C, but without added salt) with continuous pH monitoring *via* a combination glass electrode calibrated against commercial buffer solutions. Titrations were carried out between 6.25×10^{-4} and 0.0625 M Fe(III) with $NaNO_3$ making up the ionic strengths from 0.1 to 3.0 (there were also six titrations performed without the presence of a supporting electrolyte). The titrations proceeded slowly, generally from 8 to 20 or more hours. XRD patterns of the recovered solids indicated that goethite was produced in titrations with 0.0625 and 0.625 M Fe(III), whereas lower concentrations produced an amorphous solid.

No hydrolysis constants were obtained in this study nor were the titration results tabulated. The authors proposed a stepwise hydrolysis mechanism, *viz*., (1) the reversible and rapid formation of monomers and a dimer; (2) the reversible and rapid growth of small multi-nuclear species; (3) oxolation or the formation of large polynuclear species; and finally (4) the precipitation of solid phases. These steps proceed as the pH of the iron(III) solution is raised and the validity of the reversibility of steps (1) and (2) was confirmed by back titration within the early stages of the overall titration. These qualitative findings are of general interest.

[1976KAN/GRA]

Solubility experiments using a flow-through column are reported at two lithium hydroxide concentrations of 0.941 and 0.00817 mol·dm^{-3} at 150, 200, 250 and 300 °C. The iron concentrations were determined using a ^{59}Fe-doped magnetite charge which released iron into solution to be adsorbed on a second non-radioactive magnetite charge in the down-stream compartment of the reaction vessel. This necessitated cooling the vessel down to room temperature after each equilibration to remove the magnetite collection charge and count the adsorbed ^{59}Fe. The feed solutions were maintained under a hydrogen atmosphere. The magnetite was synthesized and sintered for this study and, although no XRD patterns are shown, the authors state that the material was crystalline and contained no observable hematite. The flow rate of the feed solution was varied to some extent and no dependence on flow rate could be detected.

The experimental conditions were not as well controlled as in the subsequent experiments of Tremaine and LeBlanc [1980TRE/LEB] who were more scrupulous in maintaining reducing conditions and collection of solution samples was continuous. Nevertheless, if it is assumed that at the pH of the two solutions employed in this study, only $Fe(OH)_3^-$ was present in solution (this assumption is supported by the results plotted in Figure 4 of [1980TRE/LEB]), then according to the equilibrium

$$\tfrac{1}{3}\,\mathrm{Fe_3O_4(cr)} + \tfrac{2}{3}\,\mathrm{H_2O(l)} + \mathrm{OH^-} + \tfrac{1}{3}\,\mathrm{H_2(g)} \rightleftharpoons \mathrm{Fe(OH)_3^-} \qquad \text{(A.111)}$$

the $\log_{10}\beta^{\circ}_{s,3}$ values are listed in the following table:

Table A-29: Logarithm of the solubility constants for Reaction (A.111) assuming p = 1 bar (H_2).

Run No.	t/°C	$\log_{10}\beta_{s,3}$	Run No.	t/°C	$\log_{10}\beta_{s,3}$
A-1	200	– 6.58	B-3	150	– 6.56
A-2	200	– 6.69	B-4	200	– 6.59
A-3	200	– 6.60	B-5	200	– 6.56
A-4	200	– 6.59	B-6	200	– 6.52
A-5	200	– 6.51	B-7	250	– 5.86
A-6	250	– 6.24	B-8	250	– 5.88
A-7	250	– 6.29	B-9	250	– 5.82
A-8	300	– 5.95	B-10	300	– 5.88
A-9	300	– 5.95	B-11	300	– 5.80
B-1	150	– 6.38	B-12	300	– 5.85
B-2	150	– 6.45			

These results are represented in Figure A-23 where the large experimental uncertainties observed can be traced to the inherent difficulty in carrying out these high-temperature experiments compounded, as outlined above, by the need to carefully control the oxidation state of the solid and the analytical challenges of measuring the iron(III) concentration and pH.

Reaction (A.111) is isocoulombic and as there is no trend in $\log_{10}\beta_{s,3}$ with ionic strength it is assumed that within the large uncertainty of these values, $\log_{10}\beta_{s,3}$ = $\log_{10}\beta^{\circ}_{s,3}$.

Using the $\log_{10}{}^{*}K_{w}$ values for water (for the equivalent aqueous NaCl solutions) [1978BUS/MES] the $\log_{10}\beta^{\circ}_{s,3}$ for Reaction (A.111) are converted to $\log_{10}{}^{*}\beta^{\circ}_{s,3}$ values for Reaction (A.112):

$$\tfrac{1}{3}\,\mathrm{Fe_3O_4(cr)} + \tfrac{5}{3}\,\mathrm{H_2O(l)} + \tfrac{1}{3}\,\mathrm{H_2(g)} \rightleftharpoons \mathrm{Fe(OH)_3^-} + \mathrm{H^+} \qquad \text{(A.112)}$$

The mean $\log_{10}{}^{*}\beta^{\circ}_{s,3}$ values are listed in Table A-30 with large uncertainties estimated by this review to reflect the true experimental and statistical uncertainties of these measurements.

Figure A-23: Plots of $\log_{10} \beta_{s,3}$ for Reaction (A.111) as a function of reciprocal temperature (kelvin).

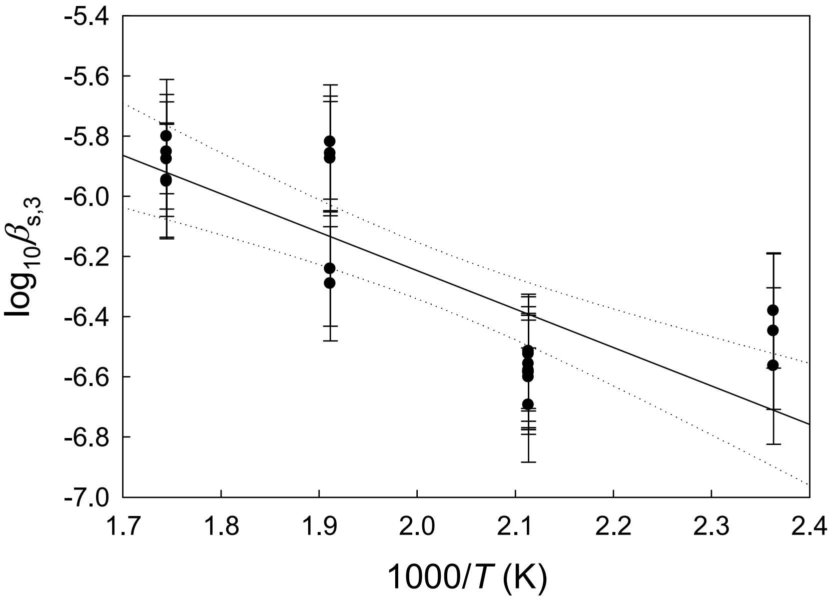


Table A-30: The mean $\log_{10}{}^{*}\beta^{\circ}_{s,3}$ values for Reaction (A.112).

t, °C	$\log_{10}{}^{*}\beta^{\circ}_{s,3}$	uncertainty
150	-17.8	0.9
200	-17.6	0.7
250	-16.9	0.6
300	-16.8	0.7

These values where used in this review together with the corresponding results reported by Tremaine and LeBlanc [1980TRE/LEB] to provide a fit of the $\log_{10}{}^{*}\beta^{\circ}_{s,3}$ values *vs*. temperature.

[1976KHA/BEL]

The main aim of the paper was to establish formation constant values for chlorido complexes of Fe(III). The potential differences for the cell Pt|Fe^{2+},Fe^{3+},$HClO_4$,HCl⋮ Fe^{2+},Fe^{3+},$HClO_4$|Pt were measured in 1.0, 3.0 and 6.0 M $HClO_4$ using variable HCl concentrations at constant ionic strength. For Fe-chlorido complexes the authors reported the concentration constants: {$\beta_1 = 3.3$ ($I = 1$ M)}; {$\beta_1 = 5.7$, K_2(Fe(III)) = 0.43

(I = 3 M)}; {β_1 = 58, K_2(Fe(III)) = 2.45, K_2'(Fe(II)) = 0.314 (I = 6 M)}.

The advantage of the method used was that there was a strongly reducing diffusion potential. The observed potential directly provided evidence of differences in chemical speciation. Unfortunately, the temperature was not given, and room temperature is assumed.

The meaning of K_2'(Fe(II)) = 0.314 at I = 6 M is not clear. In the authors' Equation 1 K_2' is expressed as $K_2' = [FeCl_2]/[FeCl^+][Cl^-]$, but in Equation 8 the same(?) K_2' is associated with a term in $[Cl^-]^2$, leading to an inconsistency. The authors do not evaluate K_1', the corresponding constant for $FeCl^+$. Obviously they seem to have assumed that only $FeCl_2$(aq) is formed.

From the independently established Fe(III) constants the cell-potential data could be re-evaluated and used to derive the Fe(II) set. However, considering the high ionic strength and the lack of temperature information, such calculations are not warranted for the purposes of the present review.

[1976RAM]

The author spectrophotometrically measured the competition between Fe(II) bipyridine and phenanthroline complexes and the $FeCl^+$ complex at pH 2, 18.0 – 43.5 °C and 2.8 M ($NaCl/KNO_3$). The basic idea of the work was that under otherwise constant conditions the easily measurable FeL_3^{2+} complexation constants can be used to evaluate the formation constant of $FeCl^+$ in systems in which the Cl^- concentration is varied:

$$K_{\text{app}} = \frac{c_{\text{FeL}_3^{2+}}}{c_{\text{Fe(II)}_{\text{total}}} c_{\text{L}}^3} = \frac{K_0}{1 + K'c_{\text{Cl}^-}} \qquad \text{(A.113)}$$

where, in the nomenclature of the authors, K_0 is the formation constant for FeL_3^{2+} and K' that of $FeCl^+$. Re-arranging Eq. (A.113) gives

$$\frac{c_{\text{Fe(II)}_{\text{total}}}}{c_{\text{FeL}_3^{2+}}} = \frac{1}{K_0 c_{\text{L}}^3} + \frac{K'c_{\text{Cl}^-}}{K_0 c_{\text{L}}^3} \qquad \text{(A.114)}$$

It was proposed that when c_L is kept constant and is in excess with respect to $c_{\text{Fe(II)}_{\text{total}}}$, the regression against c_{Cl^-} delivers the intercept $(1/K_0)/c_\text{L}^3$ and the slope $(K'/K_0)/c_\text{L}^3$. The ratio slope/intercept would then directly give the value of the sought for the formation constant (K') of $FeCl^+$.

The results were reported in tabular form for seven temperatures and for experiments done using the two organic ligands.

These constants were derived from regression against chloride concentration ($\text{mol}\cdot\text{dm}^{-3}$). As the measurements were performed in mixed $NaCl/KNO_3$ solutions, where the original 2.8 M KNO_3 was gradually replaced by NaCl, it is not possible to recalculate the author's formation constants to obtain corresponding values of β_{1m}.

Temperature/°C	K' /dm^3·mol^{-1} (2′,2-bipyridine)		K' /dm^3·mol^{-1} (1,10 phenanthroline)	
	reported	calculated[1]	reported	calculated[1]
18.0	0.45 ± 0.05	0.43 ± 0.04	0.12 ± 0.03	0.19 ± 0.06
20.0	0.38 ± 0.05		0.09 ± 0.03	
22.0	0.37 ± 0.05		0.095 ± 0.03	0.21 ± 0.05
26.0	0.29 ± 0.05	0.57 ± 0.13	0.13 ± 0.03	0.22 ± 0.05
32.0	0.37 ± 0.05	0.38 ± 0.04	0.13 ± 0.03	
37.0	0.39 ± 0.05	0.31 ± 0.03	0.12 ± 0.03	0.18 ± 0.02
43.5	0.43 ± 0.05		0.15 ± 0.03	

[1] Calculated in the present review from the author's plotted data points.

The author did provide plots from experiments at four temperatures with each of the organic ligands. However, these indicate the use of chloride concentrations greater than would be compatible with the reported total ionic strength. Furthermore, in many cases the calculated values of K' based on the plots show a marked lack of agreement with the reported values, well beyond the estimated uncertainties (and the differences appear to be systematic for the experiments done using phenanthroline).

Furthermore, such an analysis would be valid only provided that iron(II) nitrate interactions are negligible compared to iron(II) chloride interactions. There is no selected value available for the formation constant of $FeNO_3^+$ nor for $\varepsilon(Fe^{2+},NO_3^-)$, but an estimate of $\varepsilon(Fe^{2+}, NO_3^-)$, based on a correlation of existing $\varepsilon(Me^{2+}, NO_3^-)$ values with mean metal-water distances from [1988MAR] produces $\varepsilon(Fe^{2+}, NO_3^-)$ = (0.16 ± 0.09) kg·mol^{-1}. With this, the necessary correction term $-I_m\cdot\varepsilon(Fe^{2+}, NO_3^-)$ would become –(0.49 ± 0.29). The value for $\varepsilon(K^+,Cl^-)$ is 0.00 kg·mol^{-1}. Assuming no nitrato complexes are formed, the average value of $\log_{10}K$ for formation of $FeCl^+$ at ~25 °C and 3.18 m KNO_3 can be estimated from the study to be –(0.55 ± 0.16), and the value of $\log_{10} K_1^\circ$ becomes $-(0.06 \pm 0.33) + 3.18\cdot\varepsilon(FeCl^+, NO_3^-)$.

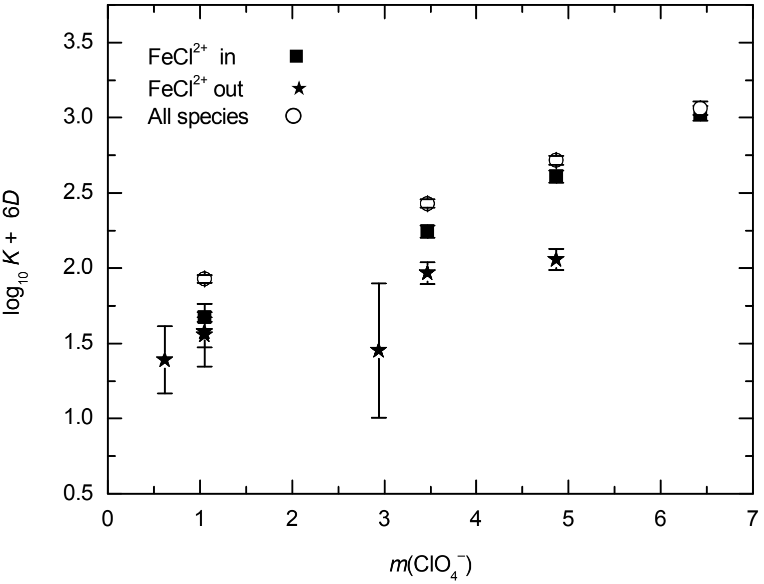
No value for $\varepsilon(FeCl^+, NO_3^-)$ is estimated here, and no value of $\log_{10} K_1^\circ$ is derived from Raman's study. No useful value of $\Delta_r H_m^\circ$ could be obtained from the reported or recalculated formation-constant values.

[1976SCH/DOD]

This paper reports another study of the chlorido complexes of iron(III) through kinetic investigations. A new approach, independent of relaxation methods, was used to follow the formation of the outer-sphere complex $Fe(H_2O)_6Cl^{2+}$ (*i.e.*, $FeCl^{2+}_{(out)}$) by spectrophotometry. The concentration decrease of the inner-sphere complex $FeCl^{2+}_{(in)}$ formed by pulse radiolysis was measured as a function of time and chloride ion concentration. That showed the occurrence of an outer-sphere complex with negligible light absorption at the wavelength of absorption by $FeCl^{2+}$.

It was demonstrated that first the Tl(II) ions produced by radiolysis in chloride media are able to oxidize Fe^{2+} to form the inner-sphere chlorido complex, $FeCl^{2+}{}_{(in)}$ [1976SCH/DOD], quantitatively. This complex then decays into a mixture of inner- plus outer-sphere complexes. The formation and the decay of $FeCl^{2+}{}_{(in)}$ can be followed by the observation of its charge-transfer band in its UV-visible spectrum.

Figure A-24: SIT treatment for the formation constants of $FeCl^{2+}{}_{(in)}$, $FeCl^{2+}{}_{(out)}$ and both 1:1 Fe^{3+} chlorido complexes from the data of [1976SCH/DOD].



This investigation allowed determination of the equilibrium formation constants of the monochlorido complexes (inner- and outer-sphere) and the inner-sphere dichlorido iron(III) complex:

At 25 °C and for $I_c = 1$ M,

$$K_{in} = m_{Fe(H_2O)_5Cl^{2+}} / (m_{Fe^{3+}} m_{Cl^-}) = 3 \text{ mol}^{-1}\cdot\text{kg}$$

$$K_{out} = m_{Fe(H_2O)_6Cl^{2+}} / (m_{Fe^{3+}} m_{Cl^-}) = 2.2 \text{ mol}^{-1}\cdot\text{kg}$$

$$K_2 = m_{FeCl_2(H_2O)_4^+} / (m_{FeCl(H_2O)_5^{2+}} m_{Cl^-}) = 1.3 \text{ mol}^{-1}\cdot\text{kg}.$$

The SIT method has been applied to the data to determine the values of $K^{\circ}_{1(out)}$ and $K^{\circ}_{1(in)}$ and the value of $\Delta\varepsilon_{(in)}$, $\Delta\varepsilon_{(out)}$ and an overall value of $\Delta\varepsilon$, $\Delta\varepsilon_{(both)}$. See Figure A-24. The linear fit produces:

$\log_{10} K^{\circ}_{1(\text{in})}$ = (1.394 ± 0.056) $\text{mol}^{-1}\cdot\text{kg}$; $\Delta\varepsilon_{(\text{in})}$ = – (0.25 ± 0.01) $\text{mol}^{-1}\cdot\text{kg}$; $R^2 = 0.998$

$\log_{10} K^{\circ}_{1(\text{out})}$ = (1.594 ± 0.340) $\text{mol}^{-1}\cdot\text{kg}$; $\Delta\varepsilon_{(\text{out})}$ = – (0.075 ± 0.078) $\text{mol}^{-1}\cdot\text{kg}$; $R^2 = 0.65$.

The variation of $\log_{10} K_{1(\text{out})} + 6D$ as a function of $m_{\text{ClO}_4^-}$ is far from linear, and the values of $\log_{10} K^{\circ}_{1(\text{out})}$ and $\Delta\varepsilon_{(\text{out})}$ must be taken with caution. Much more precise formation constant measurements are necessary.

$\log_{10} K^{\circ}_{1(\text{both})}$ = (1.65 ± 0.11) $\text{mol}^{-1}\cdot\text{kg}$; $\Delta\varepsilon_{(\text{both})}$ = – (0.23 ± 0.02) $\text{mol}^{-1}\cdot\text{kg}$; $R^2 = 0.994$

This investigation led to the conclusion that the molar absorption coefficients of $\text{FeCl}^{2+}{}_{(\text{in})}$ and FeCl_2^+ are independent of ionic strength. That contradicts the assumption of Rowley and Sutin [1970ROW/SUT], and the authors reinterpreted the data from that earlier paper using their values of the formation constants, K_{in} and K_{out}, and assuming that the outer-sphere species has a negligible absorption in the region 340 nm. Schwarz and Dodson were able to find $\text{FeCl}^{2+}{}_{(\text{in})}$ molar absorption coefficients varying from 250 to 279 $\text{m}^2\cdot\text{mol}^{-1}$ between 1 and 6 M HClO_4. K_{out} is nearly independent of the ionic strength between $I_c = 1$ and $I_c = 4$ while K_{in} increases by a factor of five.

In spite of the authors having used a rather indirect approach to determine the kinetic and thermodynamic constants for iron(III) chlorido 1:1 complex formation, the results are in fair agreement with other values in the literature, and the results of this paper limited to the ionic strengths 1.05 to 5 m have been included in the data treated together by the SIT formalism to get the recommended values of $\log_{10} K^{\circ}_1$, $\log_{10} K^{\circ}_2$, $\varepsilon(\text{FeCl}^{2+}, \text{ClO}_4^-)$ and $\varepsilon(\text{FeCl}_2^+, \text{ClO}_4^-)$.

[1976SUS/GOR]

The vapour-pressure over FeCl_2 solutions containing 5-38 wt.% was measured at 25, 40, 50, 60, 70, 85 and 100 °C by two methods referenced simply to previous publications by other authors. The vapour pressure of water was reproduced to within 1%. Small corrections were applied to compensate for temperature variations from the specified values and the molalities given in their summary table of results are rounded values rather than the primary data.

The lack of experimental details and the fact that only smoothed vapour-pressure values were tabulated led this review not to use to these results to calculate osmotic and activity coefficients of iron(II) chloride.

[1976SUS/GOR2]

This was the second of two papers published by Susarev and coworkers in 1976 providing amongst other vapour-pressure data (also see the entry for [1976SUS/GOR] above) five values for iron(II) chloride solutions at 25 °C citing a dynamic experimental method with no further details. Their original data (their Table 2) and the corresponding calculated molalities and osmotic coefficients are summarized in the following table.

There are obvious errors in the subsequently calculated osmotic coefficients by Moog *et al.*, and a miscalculation of the molality of the final solution. However, their conclusion that only the solutions with mole-% of $FeCl_2$ of 2.04 and 2.90 exhibited osmotic coefficients that are compatible with many other studies is still valid.

Table A-31: Vapour-pressure experimental data and calculated osmotic coefficients of iron(II) chloride solutions at 25 °C.

Mole-% H_2O	Mole-% $FeCl_2$	Total Vapour Pressure/mmHg	$FeCl_2$/mol·kg^{-1}*	Osmotic coefficient*	$FeCl_2$/mol·kg^{-1}**	Osmotic coefficient**
100.00	0.00	23.77	0.0	1.0000		
99.05	0.95	23.20	0.5324	0.8423		
99.01	0.99	23.15	0.5550	0.8798		
97.96	2.04	22.19	1.1560	1.0994	1.1560	1.0895
97.10	2.90	21.26	1.6578	1.2438	1.6578	1.2375
95.08	4.92	18.82	2.8723	1.5022	4.9710	1.9200

* calculated by this review; ** [2004MOO/HAG]

Despite the lack of experimental details in this paper, the two measurements indicated above are accepted for inclusion in determining the osmotic coefficient of $FeCl_2$.

[1976VAS/RAS]

The heat of oxidation of iron metal to Fe^{3+} with H_2O_2(aqueous solution, 1.0% and 1.5%) was measured in perchlorate medium (1 to 4 M, $HClO_4$). Eight to ten measurements were carried out for each peroxide concentration for four different perchloric acid concentrations. The final iron concentration was approximately 0.01 M. Hydrolysis and complexation were assumed to be negligible, and ionic strength corrections [1967VAS] were applied to provide an estimate of $-(616.09 \pm 0.63)$ kJ·mol^{-1} ($-(147.25 \pm 0.15)$ kcal·mol^{-1}), 1σ uncertainty, for the enthalpy of the reaction:

$$Fe(s) + \tfrac{3}{2}\,H_2O_2(aq) + 3\,H^+ \rightleftharpoons Fe^{3+} + 3\,H_2O(l) \qquad (A.115)$$

at $I = 0$.

Parker and Khodakovskii [1995PAR/KHO] recalculated the ionic strength dependence, and obtained $-(617.21 \pm 0.30)$ kJ·mol^{-1} for $\Delta_r H_m^\circ$. In the present review, the ionic strength corrections were again recalculated. The values for the eight sets of experiments were equally weighted, and an ion interaction model [1996PLY/GRE] was used for the extrapolation. The value obtained for $\Delta_r H_m^\circ$ is $-(618.38 \pm 0.77)$ kJ·mol^{-1} (2σ uncertainty), with $\Delta\varepsilon_L = (2.48 \pm 0.31) \times 10^{-3}$ kg·K^{-1}·mol^{-1} used for the extrapolation, and ε_L defined as $(\partial\varepsilon / \partial T)_p$ [1997GRE/PLY2]. If the results from the highest molality solutions (~4.9 mol·kg^{-1}) are omitted, $\Delta_r H_m^\circ$ is $-(617.78 \pm 0.54)$ kJ·mol^{-1} (2σ uncertainty), with $\Delta\varepsilon_L$(A.115) $= (2.90 \pm 0.29) \times 10^{-3}$ kg·K^{-1}·mol^{-1}.

The differences between values from the different calculations reflect the different limiting law assumptions, and such differences are greater than the experimental uncertainties. The interpretation of the experimental work is limited by the lack of results in perchloric acid below 1 M, and the relatively high final concentration of the Fe^{3+} ion. Also, it is not clear that appropriate experimental work has been done to determine limiting law enthalpy of dilution behaviour for mixtures of 1:1 and 3:1 electrolytes, and there are inconsistencies between results from this work [1976VAS/RAS] and work on the heat of solution of $FeCl_3$(cr) in perchloric acid [1995PAR/KHO]. Nevertheless, the various treatments are in fairly reasonable agreement (though not within the stated uncertainties). In the present review, the value from the six lower ionic strength experiments are used with the SIT extrapolation to $I = 0$; thus, − (617.8 ± 2.5) kJ·mol^{-1}, where the uncertainty is an estimate.

[1977ASH/HAN2]

A spectroscopic study was carried out with solutions containing 1 M $HClO_4$(sln) using $NaClO_4$ to provide a total ionic strength of 5 M. The total sulfate in the solutions ranged from 0.0 to 0.3 M. The reported "molar" concentrations at all temperatures were probably the room-temperature molar concentrations. In their calculations the values used by the authors for $K_{c1,1(\mathrm{HSO_4^-})}$, the protonation constant of SO_4^{2-}, were (34.3 ± 1.5), (39.1 ± 1.7), (49.0 ± 1.9) and (62.0 ± 2.0) M^{-1} for 25.0, 34.0, 47.0 and 60.0 °C, respectively. The reported molar formation constants of $FeSO_4^+$, K_1, were (210 ± 3), (265 ± 4), (324 ± 3) and (432 ± 6) M^{-1} for 25.0, 34.0, 47.0 and 60.0 °C, I_c = 5.0 M. From the formation constants found for I_c = 5.0 M, and assuming that the value of $\Delta_r C_{p1}$ was zero, the authors calculated a value of 16.4 kJ·mol^{-1} for $\Delta_r H_1$. Because the experiments involved high ionic strength from mixed electrolytes, no further use has been made of these values in the present review.

[1977CER/HEP]

These experienced authors were very meticulous in their preparation of two samples of $FeCl_2 \cdot nH_2O$(cr) with n = 0.0082 and 0.0228. They reported on a careful study of the heat of solution of $FeCl_2$(cr) in very dilute (10^{-4} m) HCl(sln) at (25.00 ± 0.05) °C. Four measurements (0.00439 to 0.01575 m $FeCl_2$ final) were done to determine the heat of solution of $FeCl_2 \cdot 0.0228H_2O$, and six measurements (0.00211 to 0.00673 m $FeCl_2$ final) to determine the heat of solution of $FeCl_2 \cdot 0.0082H_2O$. The final solution in each experiment was checked (using KSCN(sln)) to ensure that no oxidation of iron(II) to iron(III) had occurred. The enthalpy of solution values were corrected to values for $I = 0$ using estimated heats of dilution based on values for $NiCl_2$(sln) and $MgCl_2$(sln) solutions used in the USNBS compilations [1969WAG/EVA], [1971PAR/WAG]. Results from Schäfer [1949SCH] were used to correct for the small hydrate content of the solid, and this led to a consistent value for the heat of solution for $FeCl_2$(cr), – (82.9 ± 0.4) kJ·mol^{-1}.

In the present review several different procedures were attempted to estimate the heats of dilution for the 1:1 and 2:1 electrolyte mixtures. There are no good useful experimental studies for these low molalities, and differences between various theoretical treatments are generally less than 0.2 $\text{kJ}\cdot\text{mol}^{-1}$. First, Equations (IX.70) and (IX.71) from Grenthe *et al.* [1997GRE/PLY2] were used neglecting the ~ 0.0001 m HCl in the solutions. No tabulated values are available for ε as used in these equations, but at the low molalities used in the work of Cerutti and Hepler, it was found that the ε terms would make a contribution of less than 0.02 $\text{kJ}\cdot\text{mol}^{-1}$ in the final enthalpy of solution—much less than the experimental uncertainties—and these terms were neglected. Thus, the average heats of solution, corrected to $I = 0$ are $-(82.24 \pm 0.17)$ $\text{kJ}\cdot\text{mol}^{-1}$ for $\text{FeCl}_2\cdot0.0228\text{H}_2\text{O}$, and $-(82.83 \pm 0.10)$ $\text{kJ}\cdot\text{mol}^{-1}$ for $\text{FeCl}_2\cdot0.0082\text{H}_2\text{O}$. These values are approximately 0.3 $\text{kJ}\cdot\text{mol}^{-1}$ more negative than those reported originally by the authors. The uncertainty in the heat of dilution corrections is estimated here as ± 0.40 $\text{kJ}\cdot\text{mol}^{-1}$.

Using (63.86 ± 3.00) $\text{kJ}\cdot\text{mol}^{-1}$ for the enthalpy of the reaction,

$$\text{FeCl}_2\cdot\text{H}_2\text{O(cr)} \rightarrow \text{FeCl}_2\text{(cr)} + \text{H}_2\text{O(g)}$$

based on the work of Schäfer [1949SCH] as discussed in Section VIII.3.2.2, the enthalpy of

$$\text{FeCl}_2\cdot\text{H}_2\text{O(cr)} \rightarrow \text{FeCl}_2\text{(cr)} + \text{H}_2\text{O(l)}$$

is (22.83 ± 3.00) $\text{kJ}\cdot\text{mol}^{-1}$. Thus, for the heat of solution of FeCl_2(cr), values of $-(82.76 \pm 0.18)$ $\text{kJ}\cdot\text{mol}^{-1}$ and $-(83.02 \pm 0.11)$ $\text{kJ}\cdot\text{mol}^{-1}$ are calculated, and the weighted average is -82.94 $\text{kJ}\cdot\text{mol}^{-1}$—essentially identical to the -82.93 $\text{kJ}\cdot\text{mol}^{-1}$ reported by the authors.

A treatment using the equation of Silvester and Pitzer [1978SIL/PIT] for a 2:1 electrolyte, but at the total ionic strength of each solution, leads to values of $-(82.31 \pm 0.18)$ $\text{kJ}\cdot\text{mol}^{-1}$ and $-(82.86 \pm 0.10)$ $\text{kJ}\cdot\text{mol}^{-1}$ for the heats of dissolution of the hydrated solids, and $-(83.00 \pm 0.09)$ $\text{kJ}\cdot\text{mol}^{-1}$ as the heat of dissolution of FeCl_2(cr) to infinite dilution.

The SIT limiting-law heat of dilution correction for a 2:1 electrolyte in a 0.0001 m 1:1 electrolyte is -0.08 $\text{kJ}\cdot\text{mol}^{-1}$, and this might be added to the value from the SIT treatment. However, it also seems that all limiting-law heat of dilution corrections are likely to be greater than the actual correction [1959LAN]. In the present review, the result based on the Silvester and Pitzer equation [1978SIL/PIT] is used for the heat of dissolution of FeCl_2(cr) to infinite dilution, without further correction (also see the Appendix A discussion for [1979BER/MOR]), and an uncertainty of 0.40 $\text{kJ}\cdot\text{mol}^{-1}$ is assigned. The primary source of this uncertainty is the heat of dilution corrections.

[1977CHO/EUG]

The conditions explored in this study are beyond the scope of this review.

[1977SAD/KAW]

Sadakane *et al.* [1977SAD/KAW] measured the potentials of the cell

$$\mathrm{SO_2(g),\ Fe_2O_3(cr),\ Fe_2(SO_4)_3(cr),\ Pt|ZrO_2,\ CaO|Pt,\ air}$$

for temperatures between 823 and 904 K. The oxygen chemical potential corresponds to the temperature-dependent $p_{\mathrm{O_2}}$ at fixed $p_{\mathrm{SO_2}}$ for the reaction

$$\tfrac{2}{3}\,\mathrm{Fe_2(SO_4)_3(cr)} \rightleftharpoons \tfrac{2}{3}\,\mathrm{Fe_2O_3(cr)} + 2\,\mathrm{SO_2(g)} + \mathrm{O_2(g)},$$

and the $\mathrm{Fe_2(SO_4)_3(cr)/Fe_2O_3(cr)}$ boundary may intersect the boundary for the decomposition to $\mathrm{FeSO_4(cr)}$ in T-$\mathrm{O_2}$-$\mathrm{SO_2}$ partial pressure space, such that $\mathrm{FeSO_4(cr)}$ may become the thermodynamically preferred decomposition product under certain conditions:

$$\mathrm{Fe_2(SO_4)_3(cr)} \rightleftharpoons 2\,\mathrm{FeSO_4(cr)} + \mathrm{SO_2(g)} + \mathrm{O_2(g)}.$$

The results (shown only in a Figure) are scattered (uncertainties in $\Delta_{\mathrm{r}}G(T)$ are of the order of 10 $\mathrm{kJ\cdot mol^{-1}}$), and do not agree especially well with those of Skeaff and Espelund [1973SKE/ESP] or Jacob and Iyengar [1986JAC/IYE]. As the latter authors noted, in pure $\mathrm{SO_2(g)}$ at 0.1 MPa and the temperatures of the measurements by Sadakane *et al.*, $\mathrm{Fe_2(SO_4)_3(cr)}$ is unstable, and begins to decompose to $\mathrm{FeSO_4(cr)}$ [1973SKE/ESP]. Therefore the results from the study of Sadakane *et al.* are not used further in the present review.

[1977SAP/PAT]

This study of the hydroxido and sulfato complexes of Fe(III) at temperatures from 25 to 80 °C was designed to improve understanding of the mechanism of the formation of mono-dispersed basic iron(III) sulfate hydrosols.

Several investigation techniques were used: UV-visible spectroscopy for the sulfato complexes and hydroxido complexes, potentiometry for the hydroxido species, temperature-jump for the kinetics of formation of the mixed hydroxidosulfato-precipitate precursors, potentiometry with a $\mathrm{Na^+}$ ion selective electrode for $\mathrm{Na^+}$, $\mathrm{SO_4^{2-}}$ ion pairing.

Equilibrium constants for the formation of $\mathrm{HSO_4^-}$ and $\mathrm{NaSO_4^-}$ were determined (*e.g.*, at 25 °C for $I_c = 2.67$ M, $K_{c1,1(\mathrm{HSO_4^-})} = (13.7 \pm 2.6)\ \mathrm{M^{-1}}$; $K_{\mathrm{NaSO_4^-}} = (2.7 \pm 0.5)\ \mathrm{M^{-1}}$). The authors considered that failure to take $\mathrm{Na^+, SO_4^{2-}}$ ion pairing into account was the main source of uncertainty for their formation constants for the 1:1 sulfato complex. The formation constant of $\mathrm{HSO_4^-}$ given in this paper is in rough agreement with the value contained in the Table IX-6 of [1997GRE/PLY2].

The sulfato complexes of Fe(III) were investigated by spectrophotometry. The basic equation used for interpreting the absorption data was:

$$\Delta\mathrm{A} = \varepsilon_1\, K_{\mathrm{ML}}\, C_{\mathrm{M}}^0\ m_{\mathrm{SO_4^{2-}}} + \varepsilon_{1\mathrm{H}}\, K_{\mathrm{ML}}\, C_{\mathrm{M}}^0\ m_{\mathrm{SO_4^{2-}}} m_{\mathrm{H^+}} / K_{c1,1(\mathrm{HSO_4^-})}$$

where ΔA is the absorption due to Fe(III) sulfato complexes ($FeSO_4^+$ + $FeHSO_4^{2+}$), K_{ML} is the formation constant of $FeSO_4^+$, C_M^0 is the total Fe(III), and $K_{c1,1(HSO_4^-)}$ is the protonation constant of SO_4^{2-}.

The results were: K_1 = (84 ± 7) M^{-1} ($FeSO_4^+$) for I_c = 2.67 M and 25 °C, K_1 = (245 ± 20) ($FeSO_4^+$) at 55 °C and (1020 ± 110) M^{-1} at 80 °C ($FeSO_4^+$). An approximate value of (4 ± 1) M^{-1} ($FeHSO_4^{2+}$) was reported for K_{MHL} at all temperatures (with Na^+, SO_4^{2-} ion pairing taken into account in that calculation).

A total of 840 measurements were carried out to cover the variation of the relevant parameters.

Species distribution diagrams for sulfates and hydroxides were given as a function of temperature and pH.

This paper shows the complicated character of the iron-sulfate system and the difficulty in obtaining a complete set of thermodynamic equilibrium constants for the metal complexes. The formation of the Fe(III) hydrogensulfato species $FeHSO_4^{2+}$, which has been challenged elsewhere [1953WHI/DAV], [1959MAT], [1990STI], was confirmed. However, it is possible that because of the weakness of the interaction, the presence of this species can be masked by interferences.

Primarily the investigation was undertaken to define aqueous precursors to precipitation of solid mixed hydroxidosulfato complexes, such as $Fe_3(SO_4)_2(OH)_5 \cdot 2H_2O$ which precipitates at 25 °C from a 0.18 M $Fe(NO_3)_3$ solution containing 0.53 M Na_2SO_4 at pH 1.7. Calculation of the supernatant composition has been carried out (TableVII of the original paper) and no mixed hydroxidosulfato aqueous species were identified. This is in contrast with assertions in other papers [1988KHO/ROB], [1969ZVY/LYA] in which formation of such mixed solution species was claimed. In these last two papers the speciation claim was only based on potentiometric and pH-variation measurements, and as some $FeOH^{2+}$ and other hydrolysis products were present, but such techniques are insufficient to assess the presence of the mixed soluble complexes. This topic needs further experimental work focused on the question. For example, one might expect significant spectroscopic differences between pure sulfato- and mixed hydroxidosulfato-species.

No tables of experimental values are available in this paper. However as the formation constants are reasonable when compared with others in the literature, for example [1953WHI/DAV], [1959MAT], [1973NIK/PAL], the results have been taken into account in calculation of recommended values in the present review. Concentrations and equilibrium constants in molarities have been converted to molalities using the conversion factors given in Table II-5.

In this case, the value of the conversion factor molar to molal scale ξ = 1.14 was calculated by using the values of $NaClO_4$ and $HClO_4$ in two steps: first, calculation of the ξ factor for 2.67 M $NaClO_4$ and $HClO_4$ by interpolation between the 2 and 3 M values of the table. The difference between the ξ factors for 2.67 M $NaClO_4$ and $HClO_4$, Δξ, was further used as shown by Eq. (A.116).

$$\xi_{\text{solution}} = \xi_{\text{HClO}_4} + (1.00/2.67)\Delta\xi_{\text{HClO}_4} \text{ or } \xi_{\text{solution}} = \xi_{\text{NaClO}_4} - (1.67/2.67)\Delta\xi \qquad \text{(A.116)}$$

This type of calculation, though not described in as much detail in the other entries, also was used for all the other Fe(III)-sulfate papers.

The authors took into account Na^+, SO_4^{2-} interaction by introducing a formation constant for the species $NaFeSO_4^{2+}$. This is contrary to what is done in the SIT method, in which the Na^+, SO_4^{2-} interaction is taken into account in using an ion-interaction coefficient. The molal formation constant of $FeHSO_4^{2+}$ has been divided by (1.31 ± 0.24) to maintain consistency with the use of the SIT method considering the consequential higher concentration of free sulfate. That yields

$$K_{1\text{HFeSO}_4^{2+}} = (2.7 \pm 0.8)\ \text{mol}^{-1}\cdot\text{kg}$$

For calculation of $K_{1\text{FeSO}_4^+}$ the authors did not use the Na^+/SO_4^{2-} association constant and only the molar to molal conversion was applied to yield (73.8 ± 6.0) $\text{mol}^{-1}\cdot\text{kg}$ as the value of $K_{1\text{FeSO}_4^+}$.

As already mentioned above, Sapiesko *et al.* determined the formation constant of $FeSO_4^+$ at 25, 55 and 80 °C, a much greater temperature range than that investigated by other authors [1960KUM], [1962DAV/SMI], [1963WIL] who worked in the region 0 to 35 °C. A plot of $\ln K_{1\text{cFeSO}_4^+}$ as a function of $1/T$ showed that $\ln K_{1\text{cFeSO}_4^+}$ is not a linear function of $1/T$. The forced linear fitting leads to a value of (39 ± 9) $\text{kJ}\cdot\text{mol}^{-1}$ for $\Delta_r H$, a much greater value much than the ≈ (26 ± 6) $\text{kJ}\cdot\text{mol}^{-1}$ found for the values obtained from data at lower temperatures. In view of the limited number of data points, no additional attempts have been made to interpret the results of this analysis, and the $\Delta_r H$ value from this paper is not considered further in the present review.

Regarding the hydrolysis data presented in this paper, the relaxation method was able to provide a measurement of $\Delta_r H_{1,1}$ (VII.9) due to the much slower rate of dimerization. The spectrophotometric measurements were conducted at 340 nm at six ionic strengths ($NaClO_4$), whereas the potentiometric titrations were only carried out at an ionic strength of 2.67 M. No raw experimental data were provided for any of the techniques used.

The “static” spectrophotometric measurement of ${}^*K_{1,1}$ using 5.0×10^{-4} M total Fe(III) involves the assumptions that only one hydrolysis species was formed ($[H^+]$ was apparently maintained at ≥ 0.04 M) and that the molar decadic absorption coefficient of Fe^{3+} can be ignored compared to that of $FeOH^{2+}$ (given as 5 and 922 $\text{cm}^2\cdot\text{mol}^{-1}$ at 340 nm, respectively, and therefore this appears to be a reasonable assumption[1]). The

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[1] Although the authors indicated that the units were $\text{cm}^2\cdot\text{mol}^{-1}$, the actual units likely should have been $\text{mol}^{-1}\cdot\text{dm}^3\cdot\text{cm}^{-1}$, as based on comparison with other reported measurements, *e.g.*, [1955MIL/VOS].

authors estimated the uncertainty in $^{*}K_{1,1}$ to be ± 10% and gave a $\Delta_r H_{1,1}$ (VII.9) value of (32.2 ± 1.3) kJ·mol^{-1} at I = 2.67 M which can be compared with (34 ± 3) kJ·mol^{-1} for the same conditions using the $^{*}K_{1,1}$ values obtained from spectrophotometry ($\Delta C_{p1,1}$ (VII.9) = 0), as tabulated in Table A-32.

Table A-32: Molal $\log_{10}{}^{*}K_{1,1}$ values (uncertainties reported at < 10%).

I	t, °C	$\log_{10}{}^{*}K_{1,1}$	I	t, °C	$\log_{10}{}^{*}K_{1,1}$
0.10	25.0	– 2.61	2.07	25.0	– 2.87
	33.0	– 2.45		33.0	– 2.74
	40.0	– 2.31		40.0	– 2.47
	55.0	– 2.05		55.0	– 2.61
	70.0	– 1.81		70.0	– 2.12
	80.0	– 1.63		80.0	– 1.94
0.51	25.0	– 2.75	2.51	25.0	– 2.86
	33.0	– 2.61		33.0	– 2.74
	40.0	– 2.57		40.0	– 2.61
	55.0	– 2.32		55.0	– 2.36
	70.0	– 2.06		70.0	– 2.13
	80.0	– 1.79		80.0	– 1.97
1.05	25.0	– 2.81	3.05	25.0	– 2.88
	33.0	– 2.69		33.0	– 2.75
	40.0	– 2.56		40.0	– 2.61
	55.0	– 2.31		55.0	– 2.39
	70.0	– 2.05		70.0	– 2.15
	80.0	– 1.90		80.0	– 2.00

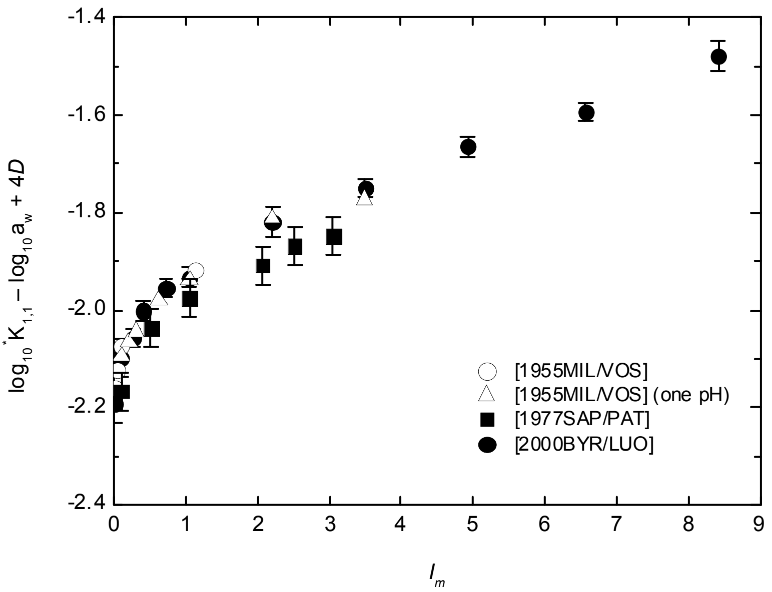
No mention was made of the iron(III) ion concentrations employed in the titrations or of the calibration of their electrodes, other than to state that the procedure of [1953HED2] was used. Consequently, these results for $^{*}\beta_{2,1}$ {(2.0 ± 1.3) × 10^{-6}} M^{-2} and $^{*}\beta_{2,2}$ {(6.0 ± 1.7) × 10^{-4}} M^{-2} at 25 °C and I = 2.67 M can only be used for comparison purposes; it is noted that in their data analysis $^{*}K_{1,1}$ was taken from their spectrophotometric study. These results are summarized in Table A-33 where they are converted to molal units.

Table A-33: Molal equilibrium constants at I = 3.05 (mol·kg^{-1}).

t/°C	$\log_{10}{}^{*}K_{1,1}$	$\log_{10}{}^{*}\beta_{2,1}$	$\log_{10}{}^{*}\beta_{2,2}$
25.0	– 2.88 ± 0.04	– 5.58 ± 0.28	– 3.16 ± 0.12
55.0	– 2.39 ± 0.04	– 4.42 ± 0.21	– 2.69 ± 0.31
80.0	– 2.00 ± 0.04	– 3.08 ± 0.14	– 2.40 ± 0.16

The hydrolysis constants listed in Table A-32 at 25 °C are shown in Figure A-25 plotted according to the SIT method. The values tend to deviate from the results of two other comprehensive studies, although they almost agree within the combined uncertainties. The hydrolysis constants for the other temperatures were treated similarly, and results are listed in Table VII-8.

Figure A-25: SIT treatment of the first hydrolysis constants at 25 °C.



[1977SCH/SOH]

The authors measured potentials of the solid-state galvanic cells

$$\mathrm{Pt|Fe,\ Fe_2SiO_4,\ SiO_2(cristobalite)|(CaO)ZrO_2|\text{“FeO”},Fe|Pt}$$

at 1233 to 1428 K to determine the oxygen chemical potentials corresponding to equilibrium.

To calculate values of $\Delta_f H_m^o$ (Fe_2SiO_4, α, 298.15 K), the measured potentials for the reference electrode from [1987NEI2] are used, along with consistent auxiliary data for cristobalite ([1982RIC/BOT], [1998CAR/SAL]) and oxygen [1989GUR/VEY], and with the values selected in this review for the heat capacity and entropy of α-Fe_2SiO_4 (Section X.2.1.1.1) and Fe(cr) (Section V.2). Values ranging from − 1472.3 to − 1477.7 $kJ \cdot mol^{-1}$ are obtained, and show a drift to more negative values at the higher temperatures. The average value is $-(1475.6 \pm 4.2)$ kJ·mol^{-1}, where the uncertainty represents 2σ.

[1978BEN/FER]

The authors carried out heat of solution measurements (HF solution calorimetry), adiabatic-calorimetry measurements (7.76 to 309.33 K) and drop-calorimetry measurements (402.9 to 851.7 K, reference temperature 298.15 K) on a solid with the analysed composition $(\mathrm{Fe}^{2+}_{5.2766}\mathrm{Fe}^{3+}_{0.1200}\mathrm{Mn}_{0.0825}\mathrm{Mg}_{1.5209})$ $(\mathrm{Si}_{7.9163}\mathrm{Al}_{0.0837}\mathrm{O}_{22.0363})(\mathrm{OH})_{1.9637}$.

In the present review, a single equation was fit to the adiabatic-calorimetry results for temperatures above 240 K and the drop-calorimetry results.

$$[C^{\circ}_{p,\mathrm{m}}]^{850\,\mathrm{K}}_{240\,\mathrm{K}}\,(\text{“amosite”})/\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}} = 614.27 + 0.57172(T/\mathrm{K}) - 8.88035\times10^{6}(T/\mathrm{K})^{-2}$$

i.e.,

$$[H^{\circ}_{\mathrm{m},T} - H^{\circ}_{\mathrm{m,\,298.15\,K}}]^{850\,\mathrm{K}}_{240\,\mathrm{K}}\,(\text{“amosite”})/\mathrm{kJ{\cdot}mol^{-1}} = 0.614265(T/\mathrm{K}) + 2.8586\times10^{-4}(T/\mathrm{K})^{2} + 8.80348\times10^{3}\,(T/\mathrm{K})^{-1} - 2.3834\times10^{2}.$$

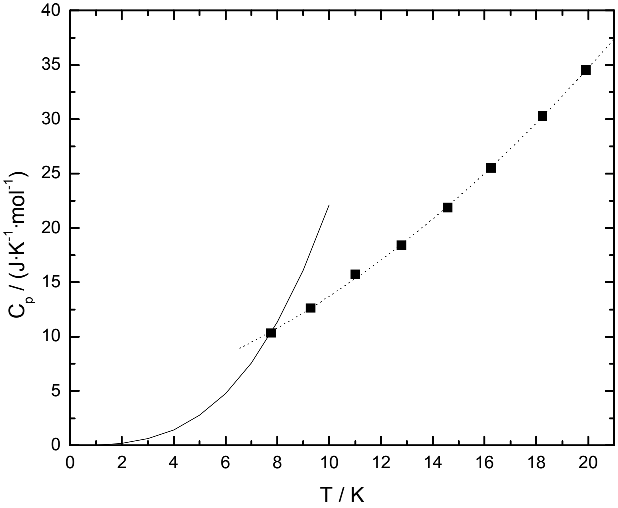
The uncertainties used to weight the drop-calorimetry results were assumed to be 0.4% of the enthalpy changes. Adiabatic-calorimetry results were assumed to have uncertainties 0.1% for temperatures below 273 K, and 0.2% at higher temperatures.

The authors reported 706.0 J·K^{-1}·mol^{-1} for the value of S°_{m} at 298.15 K. However, the heat-capacity values at low temperatures do not extrapolate smoothly to 0 J·K^{-1}·mol^{-1} at 0 K (Figure A-26), which suggests a thermal anomaly below 7 K, and thus a large uncertainty in this entropy value (also, see the Appendix A entry for a discussion of results for a somewhat different grunerite [1995KOM/WES]).

The calorimetric measurements of the heat of dissolution of the amosite sample, α-$\mathrm{SiO_2}$, $\mathrm{H_2O}$(l), $\mathrm{Al_2(SO_4)_3{\cdot}12H_2O}$(cr), $\mathrm{Fe_2O_3}$(cr), $\mathrm{FeSO_4{\cdot}7H_2O}$(cr), $\mathrm{Mg(OH)_2}$(cr), MnO(cr) and $\mathrm{H_2SO_4{\cdot}7H_2O}$(l) were carried out using 20.1% aqueous HF at 346.85 K. With then-current values of $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$(298.15 K) for α-$\mathrm{SiO_2}$, $\mathrm{Al_2(SO_4)_3{\cdot}12H_2O}$(cr), $\mathrm{Fe_2O_3}$(cr), $\mathrm{FeSO_4{\cdot}7H_2O}$(cr), $\mathrm{Mg(OH)_2}$(cr), MnO(cr), $\mathrm{H_2O}$(l) and $\mathrm{H_2SO_4}$(sln), the reported value of $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($\mathrm{Fe_2SiO_4}$, α, 298.15 K) was -10122 kJ·mol^{-1}. Re-evaluation of the required auxiliary data, especially for $\mathrm{Al_2(SO_4)_3{\cdot}12H_2O}$(cr), $\mathrm{Mg(OH)_2}$(cr) and MnO(cr) is beyond the scope of the present review.

Although the sample was properly analysed, the derived stoichiometry was only for a specific example of a mineral which has a range of compositions, and especially a variable Fe:Mg ratio. Thermodynamic quantities for a single composition, in isolation, are not particularly useful for modelling purposes. Thus, also considering the other difficulties noted above, no recalculations have been done to derive values of the enthalpy of formation and entropy for amosite.

Figure A-26: Heat-capacity measurements for amosite [1978BEN/FER] (■: experimental measurements, dotted line: smooth extrapolation of the experimental measurements, solid line: $C_p = aT^3$).



[1978BON/PER]

Solid-state potential-difference measurements are reported for several oxide cells; results include the following potential relationships.

For Fe-wüstite *vs*. Ni-NiO: $E/\text{mV} = \{173.4 + 0.089(T/\text{K})\} \pm 0.9$ at 1093 to 1273 K.

For wüstite-Fe_3O_4 *vs*. Ni-NiO: $E/\text{mV} = \{400.1 - 0.194(T/\text{K})\} \pm 1.8$ at 1073 to 1273 K.

For Fe-wüstite *vs*. Ni-NiO: $E/\text{mV} = \{-331.7 + 0.299(T/\text{K})\} \pm 2.0$ at 1123 to 1273 K.

These expressions are difficult to evaluate because of limited experimental details.

[1978CHO]

An H_2-fugacity sensor technique was used to investigate several O_2-fugacity buffers, including magnetite-hematite (MH) and quartz-iron-fayalite (QIF), in hydrothermal experiments at p = 2 kbar and 4 kbar and T = 873 - 1073 K. The author extracted the following relationships, adjusted to p = 1 bar, for this temperature range.

$$\text{MH: } \log_{10} f_{O_2} = \{0.0317 + 4381/(T/\text{K}) - 15720000/(T/\text{K})^2\} \pm 0.12$$

$$\text{QIF: } \log_{10} f_{O_2} = \{7.991 - 23973/(T/\text{K})\} \pm 0.08$$

The MH result is discussed further in Section VII.2.2.1 of this review, but is not fully evaluated because of the combination of elevated pressure and novel sensor design, which was based on post-test analysis of Ag-AgCl-HCl solution equilibria. In effect, for the magnetite–hematite case, the author measured the following equilibrium:

$$2\,\mathrm{AgCl(cr)} + 2\,\mathrm{Fe_3O_4(cr)} + \mathrm{H_2O(g)} \rightleftharpoons 2\,\mathrm{Ag(cr)} + 2\,\mathrm{HCl(g)} + 3\,\alpha\text{-}\mathrm{Fe_2O_3}.$$

The paper is of particular interest because it is a hydrothermal study performed at comparable temperatures to many solid-state cell-potential measurements of oxygen buffers.

[1978JOH/BAU]

To get the standard potential of the couple $Fe^{2+}/Fe(0)$, Johnson and Bauman measured potential-difference values of the cell:

$$\mathrm{Fe(s)}\,|\,\mathrm{FeCl_2(0.02\ m)}+x\mathrm{HCl} \ \vdots\vdots\ \mathrm{sat.KCl}\,|\,\mathrm{AgCl,Ag(s)}.$$

Vacuum-annealed iron (99.9999% pure) was used. $FeCl_2$(sln) was generated by coulometric oxidation of iron metal and care was taken to exclude O_2 and CO_2 throughout the solution transfer and titrations. The pH value was varied between 1.42 and 7.6. Stable potential-difference values were found after several hours, but the measured potentials, recalculated as values of $E^\circ(\mathrm{Fe^{2+}/Fe(0)})$ *vs.* SHE, varied from -0.2 to -0.417 V. For pH values greater than 5.8, more stable potentials from -0.417 to -0.415 V *vs.* SHE were obtained ($\Delta_f G_m^\circ(\mathrm{Fe^{2+}}) = -80.08\ \mathrm{kJ\cdot mol^{-1}}$).

The authors used activity coefficients of Fe^{2+} calculated using a Debye-Hückel relationship with the A and B values given by Robinson and Stokes [1959ROB/STO]. Junction potentials were estimated to be of the order of $2-3$ mV [1952MIL], but were not taken into account in the calculations. The results from this paper were not used further in the present review. However, this investigation of the influence of pH on the cell-potential values helped lead to reconsideration of the work of Hurlen and, hence, to the value of $E^\circ(\mathrm{Fe^{2+}/Fe(0)})$ proposed in the main text (Section VI.1.1.2.4).

For the measurements of the first hydrolysis constant at 25 °C a simple titration procedure was employed using the following solutions: 0.024 m $Fe(ClO_4)_2$; 0.024 m $Fe(ClO_4)_2$, 0.048 m NaCl; 0.022 m $Fe(ClO_4)_2$, 0.028 m NaCl. The combination glass electrode was standardized against commercial buffers and as the ionic strength of the solutions was < 0.1 m no liquid-junction potential corrections were applied. No experimental data were tabulated. The $-\log_{10}{}^*K_{1,1}^\circ$ values are reported in a small figure as a function of pH that when taken graphically and reconverted to the $-\log_{10}{}^*K_{1,1}^\circ$ using the same Debye-Hückel function yielded: $-(9.12 \pm 0.02)$ (I_m = 0.072); $-(8.98 \pm 0.08)$ (I_m = 0.120, excluding three points for which the solutions were considered to be supersaturated); and $-(8.85 \pm 0.03)$ (I_m = 0.09). Titrations were also carried out at 1 and 40 °C, but no corresponding solution compositions were reported.

Addition of excess NaOH to the above-mentioned titration "end-points" resulted in precipitation of amorphous iron(II) hydroxide for which an average solubility product of the unaged solid is given as $10^{-14.39}$ at 25 °C.

The $-\log_{10}{}^{*}K^{\circ}_{1,1}$ values appear to be significantly smaller than those reported by [1971MES], but otherwise they cannot be discounted *a priori* considering the large scatter in the all the values reported in the literature.

Consider:

$$\mathrm{Fe^{2+} + H_2O(l) \rightleftharpoons FeOH^{+} + H^{+}}$$

$$\log_{10}{}^{*}\beta_{1,1} + 2D = \log_{10}{}^{*}\beta^{\circ}_{1,1}$$

$$I_m = 0.072, D = 0.10;\ \log_{10}{}^{*}\beta^{\circ}_{1,1} = -(8.93 \pm 0.12)$$

$$I_m = 0.120, D = 0.12;\ \log_{10}{}^{*}\beta^{\circ}_{1,1} = -(8.86 \pm 0.15)$$

$$I_m = 0.09, D = 0.11;\ \log_{10}{}^{*}\beta^{\circ}_{1,1} = -(8.74 \pm 0.14).$$

The expanded uncertainty ranges were estimated by this review and an average value of $\log_{10}{}^{*}\beta^{\circ}_{1,1} = -(8.84 \pm 0.10)$ was derived.

Analysis of [1971MES] yielded $\log_{10}{}^{*}\beta^{\circ}_{1,1} = -(9.49 \pm 0.16)$ based on an unknown number of titrations. Despite the large variation in these results, this review cannot distinguish between the reliability of these two studies and therefore assigns a provisional value of $\log_{10}{}^{*}\beta^{\circ}_{1,1} = -(9.1 \pm 0.4)$ at 25 °C.

[1978PER/TAP]

This paper reports on a kinetics (T-jump) investigation of complexation of $\mathrm{Fe^{3+}}$ with $\mathrm{Cl^{-}}$ in aqueous solution. The stoichiometric Fe(III) concentration in each experimental solution was between 1.1×10^{-2} and 9.0×10^{-2} M and was always in excess over the $\mathrm{Cl^{-}}$ concentration, 5×10^{-3} to 8×10^{-2} M. The solution also contained sufficient $\mathrm{HClO_4}$ such that the ionic strength was 1.0 M. The rather high acidity 0.5 M prevented any significant hydrolysis. The authors used their measurements to determine the value of $K_{\mathrm{(in)}}$ to be $(2.95 \pm 0.14)\ \mathrm{M^{-1}}$. They also determined the value of $K_{\mathrm{(out)}}$ in the same solutions, and in accordance with the results of Wendt and Strehlow [1962WEN/STR] they found $K_{1\mathrm{(out)}} \leq 2.2\ \mathrm{M^{-1}}$. The K_1 values from this paper were not introduced into the set of literature data used in this review for the determination of K°_{1} because of the indirect method in which they were obtained.

[1978SPE/KUB]

This review emphasizes the evaluation of high-temperature (> 1000 K) thermodynamic properties of wüstite, magnetite, hematite, and liquid Fe-O.

[1978TEW/WAL]

The solubilities and rates of dissolution of several iron sulfides, mackinawite $\mathrm{FeS_{(1-x)}}$, troilite FeS, pyrrhotite $\mathrm{Fe_{(1-x)}S}$ (monoclinic and hexagonal), and pyrite $\mathrm{FeS_2}$ have been determined in aqueous H_2S solution at 0.1 MPa and 1.8 MPa H_2S pressure between 25 and 125 °C. The dependence of solubility on the pH of the medium has also been studied. Single crystals of FeS troilite, pyrrhotite (monoclinic) and pyrite were used for the solubility and rate of dissolution studies. Mackinawite powder was prepared electrochemically (≈ 20 mA, three days) using a carbon-steel anode and platinum cathode in 0.1 $\text{mol}\cdot\text{kg}^{-1}$ NaOH while H_2S was bubbled continuously. Hexagonal pyrrhotite was prepared by the reaction of the required amounts of deoxygenated iron powder and sulfur at 800 °C for three days. All samples were analyzed by X-ray powder diffraction before and after the dissolution experiments. It was reported that whereas the solubility of troilite was achieved within hours, for pyrrhotite it took at least seven days of vigorous agitation. In the dissolution experiment of hexagonal pyrrhotite, small amounts of pyrite were reported to be present after the experiment. Also, for mackinawite experiments, many samples contained various amounts of other sulfides such as marcasite, greigite and pyrite. The solubilities of the iron sulfides (Fe^{2+} in $\mu\text{mol}\cdot\text{kg}^{-1}$) at 0.1 MPa H_2S and 25 °C were determined to be,

pH	Troilite	Mackinawite	Pyrrhotite (Monoclinic)	Pyrrhotite (Hexagonal)
3.5	66	2700	9 ± 0.5	0.56 ± 0.05
4.0	6.0 ± 0.5	560	2.5 ± 0.5	0.25 ± 0.05

and approximately 0.1 $\mu\text{mol}\cdot\text{kg}^{-1}$ for pyrite (independent of pH). The slopes of plots of the logarithm of solubility *vs*. pH were approximately -2.1 for troilite, -1.4 for mackinawite, -1.1 for monoclinic pyrrhotite and -0.8 for hexagonal pyrrhotite. If we assume that the reaction $\text{FeS(s)} + 2\text{H}^+ \rightleftharpoons \text{Fe}^{2+} + \text{H}_2\text{S(aq)}$ controls the solubility regardless of these slopes, $\log_{10} K$ for the reaction can be estimated with using $\log_{10} K = -1.02$ for $\text{H}_2\text{S(g)} \rightleftharpoons \text{H}_2\text{S(aq)}$ (CODATA) from the above solubilities as:

pH	Troilite	Mackinawite	Pyrrhotite (Monoclinic)	Pyrrhotite (Hexagonal)
3.5	1.80	3.42	0.94 ± 0.01	−0.27 ± 0.09
4.0	1.76 ± 0.08	3.73	0.38 ± 0.02	−0.62 ± 0.20

The differences between results for the 0.1 MPa and 1.8 MPa H_2S pressures were found to be less than 10 %. The solubilities decreased at higher temperatures but the changes were also small. The rates of dissolution at various acidities have also been determined. For mackinawite and troilite the rate of dissolution was first order in H^+, but for pyrrhotite and pyrite it was essentially independent of H^+ concentration. The rates varied widely. At 25 °C and pH ≈ 3.5, the rates of dissolution differed by a ratio $\approx 10^5{:}10^4{:}50{:}10{:}1$ for mackinawite, troilite, hexagonal pyrrhotite, monoclinic pyrrhotite and pyrite, respectively. These differences were even greater at higher acidities. Solubilities and the rates were obtained from the results of the dissolution experiment (undersaturation only), and the equilibrium state was judged from the attainment of a constant solubility. However, the direct product precipitated from the solution of Fe(II) and H_2S is known to be nanoparticulate mackinawite ([2000BEN/WIL], [2006OHF/RIC], [2006RIC]). Thus, it is necessary to confirm that the reverse reaction rate is not affected by mackinawite formation and controlled solely by the crystal. The X-ray powder-diffraction method cannot detect the minor amount of the surface nanoparticlulate mackinawite. The slopes of the logarithm of solubility *vs*. pH do not always give the expected slope of – 2. Although this paper gives qualitative information on the solubilities and rates of dissolution of these iron sulfides, no attempts to obtain equilibrium constants were carried out. The results of this paper are not considered further in this review.

[1978VAS/VAS2]

Enthalpy of solution measurements for $(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$ in 1, 2, 3 and 4 M $HClO_4$ containing H_2O_2 were reported. Using the heats of dissolution of Fe(cr) and $(NH_4)_2SO_4$(cr), and heats of dilution of H_2O_2(aq, 0.2988 weight fraction H_2O_2) and concentrated aqueous sulfuric acid (0.9265 weight fraction H_2SO_4)[1] in similar solutions, the enthalpy of formation of $(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$ was calculated. As discussed by the authors (also see [1985VAS/DMI2]), in the reactions in 1 M and 2 M $HClO_4$ there was likely to have been some dissociation of the HSO_4^- product in the final solutions, and this complicates the calculations. Although the results calculated assuming deprotonation of 4% of the sulfate in the 2 M $HClO_4$ solutions [1978VAS/VAS2] are reasonably consistent with those calculated assuming no deprotonation in the 3 M and 4 M perchloric acid solutions, only the results from the measurements in the 3 M and 4 M solutions are used in the present review. The aqueous solutions used for determining the heat of dissolution of the iron contained 0.0133 M H_2SO_4, 0.0133 M $(NH_4)_2SO_4$ and either 1.0 or 1.5 weight-% H_2O_2(aqueous solution). The average results from experiments with the two different peroxide concentrations were generally statistically indistinguishable at the 95% confidence limits. In the recalculation of the enthalpy of formation of $(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$, the value for the enthalpy of formation of the concentrated aqueous solution of H_2O_2 was taken from Wagman *et al.* [1982WAG/EVA], as was the value for the enthalpy of formation of the concentrated sulfuric acid solution[2]. There is only a moderate consensus as to the value of $\Delta_f H_m^\circ$ ($(NH_4)_2SO_4$, cr, 298.15 K). The authors used – (1180.3 ± 0.6) $kJ\cdot mol^{-1}$, whereas Naumov *et al.* [1971NAU/RYZ] list – 1180.0 $kJ\cdot mol^{-1}$. In their assessment Robie and Hemingway [1995ROB/HEM] report – (1182.7 ± 1.3) $kJ\cdot mol^{-1}$. The latter value was

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[1] Thus, this is $H_2SO_4\cdot 0.432H_2O$ (not $H_2SO_4\cdot 0.2H_2O$ as in the analysis in [1995PAR/KHO]).

[2] A re-evaluation of data for the H_2SO_4-H_2O system might lead to a somewhat different value for the enthalpy for formation of the 92.65% H_2SO_4. Results from Zeleznik's re-assessment [1991ZEL] might be used, but only with a parallel re-evaluation of any effect on the CODATA value for $\Delta_f H_m^\circ$ (SO_4^{2-}, 298.15 K).

traced to DeKock [1986DEK], – 1182.65 kJ·mol^{-1} from a tabulation by Parker *et al.* [1976PAR/WAG] (– (282.66 ± 0.14) kcal·mol^{-1}). The differences appear to have arisen primarily from use of different values of $\Delta_f H_m^o(\mathrm{NH_4^+})$ and $\Delta_f H_m^o(\mathrm{SO_4^{2-}})$, and for those species the values from Parker *et al.* [1976PAR/WAG] are consistent with Cox *et al.* [1989COX/WAG]. In the present review the CODATA-consistent value for $\Delta_f H_m^o$ ((NH$_4$)$_2$SO$_4$, cr, 298.15 K) [1976PAR/WAG]. [1989COX/WAG] is used with the uncertainty as estimated by Robie and Hemingway [1995ROB/HEM].

With these auxiliary data, the value of $\Delta_f H_m^o$ ((NH$_4$)$_2$Fe(SO$_4$)$_2$·6H$_2$O, cr, 298.15 K) is – (3925.58 ± 2.40) kJ·mol^{-1}.

[1978YAK/KUL]

Studies were conducted using solutions containing Fe(III) ions from 10^{-3} to 10^{-2}; ammonium, 0.254; copper from 0.005 to 0.5 mol·L^{-1} at 25 °C. Concentrations of sulfuric acid were varied from 0 to 0.61 mol·L^{-1}. The concentration of iron was measured by weight and/or a complexometric method, whereas that of sulfuric acid was measured by complexometry and by a method described in a previous paper. The uncertainty in the pH meter readings (there was no definition given of the pH scale used by the authors, although the Henderson equation was used to estimate liquid-junction potentials with an assumed metal sulfate concentration) was 1 mV when nitrate ion was substituted by sulfate ion. Titrations of mildly acidic solutions were conducted with more acidic titrants, and reverse titrations were done as well. The authors surmised that the concentrations of the sulfate ions were high enough to convert all Fe(III) ions into aqueous sulfatoiron(III) complexes and aqueous $\mathrm{Fe}_m(\mathrm{OH})_n(\mathrm{SO_4})_x$ species.

The values of $^*\beta_{1,1}$ and $^*\beta_{2,2}$ at a copper sulfate concentration of 0.05 mol·L^{-1} are (1.4 ± 0.15) × 10^{-4} mol·L^{-1} and (1.94 ± 0.08) × 10^{-4} mol^2·L^{-2}. $^*\beta_{2,2}$ is equal to (6.55 ± 0.60) × 10^{-4} mol^2·L^{-2} at a copper concentration of 0.5 mol·L^{-1}. The error presented above relates to the 2σ interval. The actual ionic strength is impossible to estimate within this host of species and although the presence of hydrogensulfate ions was considered in these solutions, the pH of which ranged from 2 to 3, they were ignored in the treatment of the data.

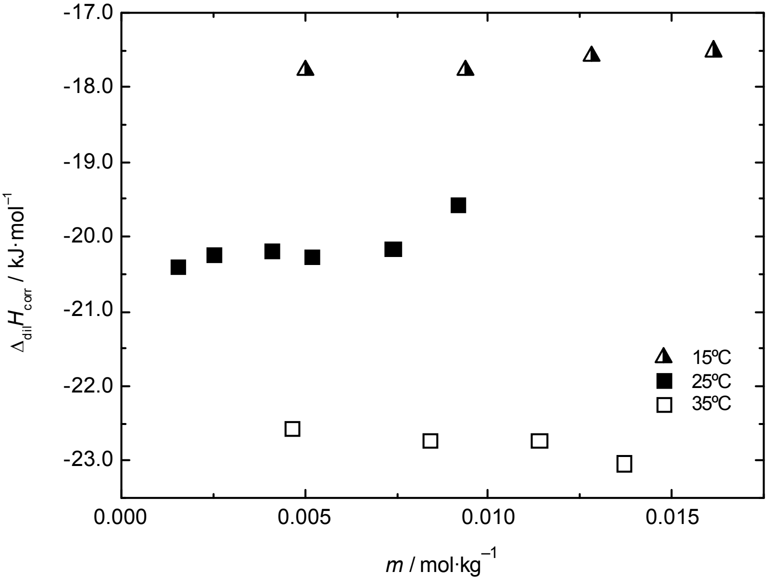
The complex solution speciation alone (*cf.* Section IX.1.2.1.3.6) renders this study useless for obtaining thermodynamic hydrolysis constants so that these data are not taken into account in this review.

[1979BER/MOR]

Measurements were reported for the sequential heats of solution of samples of 4.43 m FeCl$_2$(sln) into water and the resulting aqueous solutions. The diluted solutions ranged from 0.00502 to 0.0161 m at 15 °C, 0.00155 to 0.00916 m at 25 °C, 0.00465 to 0.0137 m at 35 °C. Although the authors suggest otherwise, the results are much too scattered to provide a reliable value for the second term in the Silvester and Pitzer [1978SIL/PIT] heat of dilution equation (*i.e.*, the values reported by the authors for

$\Delta H^{\circ}/dm$). As can be seen from the figure below, the actual values of $\Delta_{\text{dil}}H^{\circ}_{\text{m}}$ might better be estimated as the average value at each temperature (– (17.70 ± 0.22), – (20.16 ± 0.39) and – (22.78 ± 0.31) kJ·mol^{-1} at 15, 25 and 35 °C respectively, recalculated here using the Bradley and Pitzer [1979BRA/PIT] values of A_H).

Figure A-27: Enthalpies of dilution of 4.43 m $FeCl_2$(sln) at different temperatures.



The authors used their results to calculate – (303 ± 20) J·K^{-1}·mol^{-1} and – (210 ± 20) J·K^{-1}·mol^{-1} for $C^{\circ}_{p,\text{m}}$ ($FeCl_2$, aq) at 20 and 30 °C, respectively. From these, the authors estimated $C^{\circ}_{p,\text{m}}$ ($FeCl_2$, aq, 298.15 K) = – (256 ± 30) J·K^{-1}·mol^{-1} and hence $C^{\circ}_{p,\text{m}}$ (Fe^{2+} 298.15 K) = – (9 ± 30) J·K^{-1}·mol^{-1} based on the value of – 123.2 J·K^{-1}·mol^{-1} for $C^{\circ}_{p,\text{m}}$ (Cl^{-}, 298.15 K) [2002PAT/WOO].

[1979FIT]

This paper is concerned primarily with the thermodynamics of Zn-bearing magnetite solid solutions, $Zn_xFe_{3-x}O_4$, with $0 < x < 1$, *i.e.*, up to 100% substitution of Zn^{2+} for Fe^{2+} in magnetite. It includes a series of solid-state cell-potential measurements of the solid couples (α-Fe_2O_3 + Fe_3O_4) *vs.* (Cu + Cu_2O) in a galvanic cell using a CaO-stabilized zirconia electrolyte. The results yielded the following relationship for the cell potential at temperatures between about 1100 and 1250 K.

$$E/\text{mV} = \{-418.4 + 0.36768(T/\text{K})\} \pm 5$$

This in turn yielded a Gibbs energy relationship for the reaction $4Fe_3O_4(cr) + O_2(g) \rightleftharpoons 6Fe_2O_3(cr, \alpha)$ at 1100 to 1250 K (units converted from cal to J by the reviewer).

$$\Delta_r G_m^o /\text{kJ}\cdot\text{mol}^{-1} = \{-502.23 + 0.29497(T/\text{K})\} \pm 2.1$$

The potential relationship shows excellent agreement with three previous studies ([1968CHA/FLE], [1969BRY/SME], [1972RAO/TAR]), but diverges from the more recent results of O'Neill [1988NEI] by about 4 to 7 mV. The reasons for this difference have not been resolved, though this review generally favours the seemingly meticulous study by O'Neill. The studies cited here are included in the compilation shown in Figure VII-17, but are not used further in the current assessment.

[1979GOL/NUT]

These authors compiled and critically accessed data available at that time to derive the osmotic and activity coefficients for $FeCl_2$ and other selected electrolytes at 25 °C. They provided the criteria for their choice of weighing factors. However, in the case of iron(II) chloride only the isopiestic results from Stokes and Robinson [1941STO/ROB] and the vapour-pressure measurements reported in [1962KAN/GRO] were available, and Goldberg *et al.* chose to give the former unit weights whereas the results of the latter study were given zero weight.

The smoothed data tabulated in this work are shown in Figure A-28 together with all the 25 °C osmotic coefficient data now available.

Clearly the limited thermodynamic results available at the time this report was published severely limits the utility of their treatment and therefore it will not be considered further in this review.

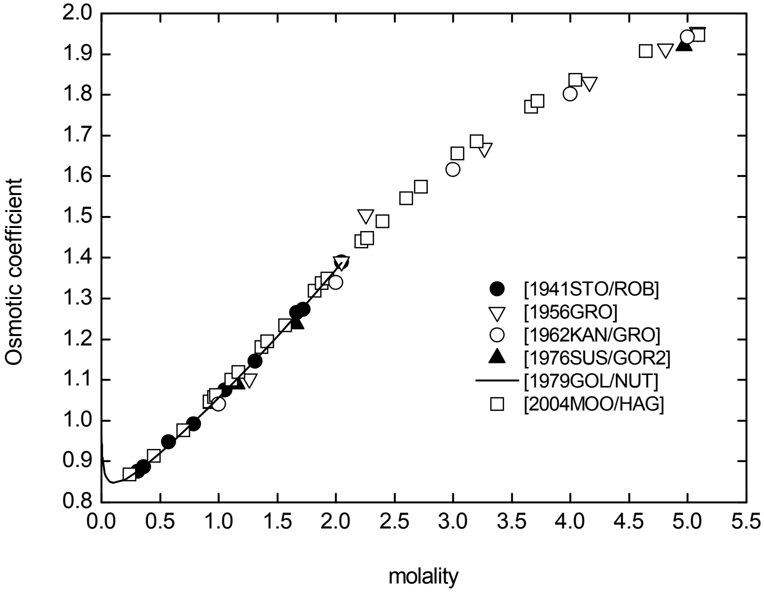
[1979MAL/DRA]

Values of the equilibrium water-vapour pressures over a mixture of $FeSO_4\cdot 7H_2O$ and a lower hydrate (identified by the authors as $FeSO_4\cdot 4H_2O$, also see [1964KOH/ZAS2]) were reported as 0.015016 bar at 21.30 °C and 0.033743 bar at 32.65 °C. The values were obtained by an isopiestic procedure using saturated aqueous solutions of $NaBr\cdot 2H_2O$ and $CuCl_2\cdot 2H_2O$, respectively [1967YOU] as standards. The results were used to estimate the enthalpy and Gibbs energy of reaction over the limited temperature range for

$$FeSO_4\cdot 7H_2O(cr) \rightleftharpoons FeSO_4\cdot 4H_2O(cr) + 3\,H_2O(g). \qquad (A.117)$$

The limited experimental results lead to $\Delta_r H_m^o$ (A.117) = 160.2 kJ·mol^{-1}. For weighting purposes, uncertainties of 50 Pa were estimated; primarily, these uncertainties arise from uncertainties in the vapour pressures assumed for the reference solutions.

Figure A-28: Summary of available osmotic coefficient data for iron(II) chloride solutions at 25 °C.



[1979MYE/GUN]

A thermogravimetric procedure in a CO-CO_2 atmosphere, using a solid-state sensor to monitor oxygen chemical potential, was calibrated with Ni-NiO and Fe-wüstite assemblages before conducting measurements on the Co-CoO couple. The following oxygen fugacity expression, adjusted by the reviewer to a standard-state pressure of 0.1 MPa, was obtained for Fe-wüstite with a standard deviation of 0.03 and a maximum deviation of 0.05 for $1073 < T < 1573$ K.

$$\log_{10} f_{O_2} = 7.190 - \frac{28040}{T}$$

[1979NAV/PIN]

Solution-calorimetry measurements were carried out for dissolution of α-Fe_2SiO_4, γ-Fe_2SiO_4 and $FeSiO_3$("orthopyroxene") into $2PbO{\cdot}B_2O_3$ as a solvent at 986 K. The reported heats of solution were (15.661 ± 1.080), (12.719 ± 1.255) and (5.732 ± 0.569) $kJ{\cdot}mol^{-1}$ ((3743 ± 258), (3040 ± 300) and (1370 ± 136) $cal{\cdot}mol^{-1}$, 2σ uncertainties). The reported heat of solution of quartz was $-(3.18 \pm 0.84)$ $kJ{\cdot}mol^{-1}$. Thus, at 986 K, the enthalpy of conversion of γ-Fe_2SiO_4 to α-Fe_2SiO_4 at 1.01 bar (1 atm) is $-(2.94 \pm 1.66)$ $kJ{\cdot}mol^{-1}$, and the enthalpy of the reaction

$$\alpha\text{-Fe}_2\text{SiO}_4 + \text{SiO}_2(\beta\text{-quartz}) \rightleftharpoons 2\,\text{FeSiO}_3(\text{“orthopyroxene”}) \qquad (A.118)$$

is (1.02 ± 1.78) $\text{kJ}\cdot\text{mol}^{-1}$. When combined with selected values for α-Fe_2SiO_4 from the present review and for quartz ([1989COX/WAG], [1998CAR/SAL]), the value of $\Delta_f H^{\circ}_{m}$ ($FeSiO_3$(“orthopyroxene”, 298.15 K)) is $-(1197.9 \pm 3.6)$ $\text{kJ}\cdot\text{mol}^{-1}$. This value is more negative than reported from evaluations of high-pressure data [1996SAX], [1997FAB/SUN].

The authors also used compressibility and thermal expansion data to estimate entropy differences between α- and γ-Fe_2SiO_4 as -20.0 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, and -4.0 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for the entropy of Reaction (A.118) at 986 K.

[1979STR/PAT]

This article deals with the thermodynamic formation constants for Fe(III) chlorido complexes as investigated by spectrophotometry and the study of the kinetics of the complexation reactions by the *T*-jump method (4.0 K rise, initial temperature 294.15 K), using both the relaxation times and the relaxation amplitudes.

This spectrophotometric investigation used the absorbances at 395, 400, 405, 410, 415 and 420 nm for the determination of the $\text{FeCl(H}_2\text{O)}_5^{2+}$ stability constant in 1 M $HClO_4$, I_c = 2.6, adjusted by additions of $NaClO_4$ and NaCl. A value of (7.6 ± 0.4) $\text{M}^{-1}$was found for K_1.

The stability constant determination for the complex FeCl_2^+, in 1 M $HClO_4$, I_c = 2.6, was also carried out by static spectrophotometry using the absorption at 430, 440, 450,and 460 nm. The value K_{2c} = (1.80 ± 0.08) M^{-1} was found.

The relaxation-time measurements in chloride solutions, 0.03 to 2 M, containing 0.086 to 0.1 M $Fe(ClO_4)_3$ with 1 M $HClO_4$, I_c = 2.6 adjusted by $NaClO_4$, showed three separate effects:

A very fast process, τ = 10 to 13 μs corresponding mostly to the formation of the 1:1 outer-sphere complex.

A slower process, τ = 100 to 200 ms corresponding mostly to the formation of the 1:1 inner-sphere complex.

The third effect occurs at high chloride concentrations. It is an additional relaxation time, τ = 540 μs, which corresponds to the formation of higher chlorido complexes.

The relaxation amplitudes and the results obtained already by static spectrophotometry were used to calculate the formation constants of the following species, all at 25 °C and 1 M $HClO_4$, I_c = 2.6 adjusted by $NaClO_4$ additions, $\text{FeCl}^{2+}{}_{(\text{out})}$, $\text{FeCl}^{2+}{}_{(\text{in})}$, FeCl_2^+, and FeCl_3^0.

The variation of the formation constants with the temperature allowed the authors to obtain values for the thermodynamic constants for the reactions. All the values found for the stability and the thermodynamic constants are collected in Table A-34. We recalculated them from the values of K and $\Delta_r H$.

They differ from the original values given in $\text{cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ or $\text{kcal}\cdot\text{mol}^{-1}$, probably because of different rounding.

Table A-34: Thermodynamic data (298.15 K) for single reaction steps [1979STR/PAT] and for the overall formation process of the Fe^{3+}-Cl^- complexes (medium: 1 M $HClO_4$ + 1.6 M $NaClO_4$ / NaCl).

Process	K	$\Delta_r G$ /kJ·mol^{-1}	$\Delta_r H$ /kJ·mol^{-1}	$\Delta_r S$ /J·K^{-1}·mol^{-1}
$Fe^{3+} + Cl^- \rightleftharpoons FeCl^{2+}_{(out)}$	1.1 (K_{1out})	– 0.2361	11.72	40.08
$Fe^{3+} + Cl^- \rightleftharpoons FeCl^{2+}_{(in)}$	6.5 (K_{1in})	– 4.64	13.39	60.46
$FeCl^{2+}_{(in)} + Cl^- \rightleftharpoons FeCl_2^+$	1.8 (K_2)	– 1.46	8.79	34.37
$FeCl_2^+ + Cl^- \rightleftharpoons FeCl_3(aq)$	6.0 (K_3)	– 4.44		

The forward rate constant k_2 for the formation of the 2:1 complex was calculated to be 324 $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ from the measured value of k_{-2} and the formation constant. This rate constant reflects rates that are larger than the rates involving the 1:1 chlorido complex.

Only K_3 = 6 has been determined for the reaction; $FeCl_2(H_2O)_4^+ + Cl^- \rightleftharpoons Fe(H_2O)_3Cl_3(aq)$. K_4 was not taken into account as it did not improve the fit to the experimental results. The value of K_3 is too large and is questionable in view of the other literature results; it has not been used further in determining the value for K_3 recommended in the present review.

In the present review the molar concentration and formation constant were converted to molal values as described the Appendix A entry for [1942RAB/STO] and in the main text. The values of K_1 and K_2 were used in the SIT treatment of the literature data to obtain the recommended values of $\log_{10} K_1^\circ$, $\log_{10} K_2^\circ$, $\varepsilon(FeCl^{2+}, ClO_4^-)$ and $\varepsilon(FeCl_2^+, ClO_4^-)$.

This paper contains only chlorido-complex formation constants, but no hydrolysis data.

[1979ZOT/KOT]

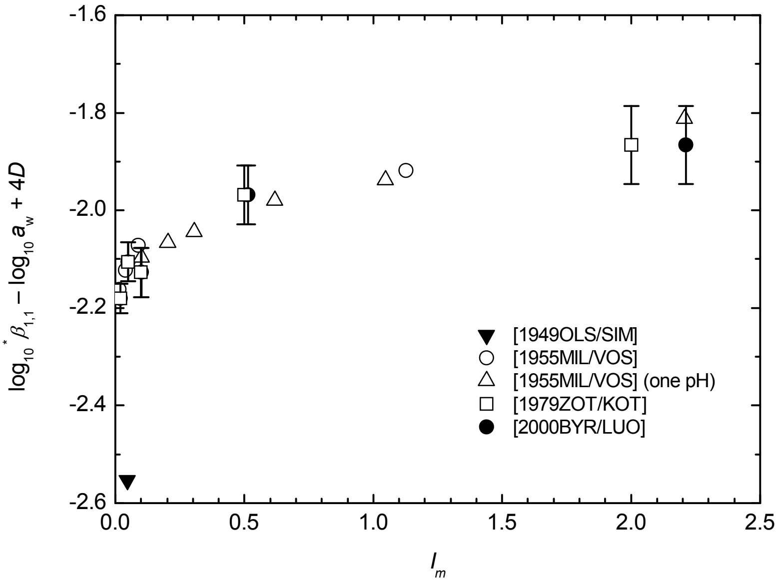
A spectrophotometric method was used to measure the first hydrolysis constant of Fe^{3+} (10^{-4} M) at 25, 50 and 80 °C in $NaClO_4$ solutions (0.02 to 2 M).

This paper was not translated by the reviewer so that details of the experiments have not been evaluated. Comparison of the 25 °C values treated with the SIT (Figure A-29) indicate that these results are in very good agreement within the given experimental uncertainties with those from selected other studies.

Table A-35: The $\log_{10} {}^*\beta_{1,1}$ values taken directly from [1979ZOT/KOT].

I_m	$-\log_{10} {}^*\beta_{1,1}$	I_m	$-\log_{10} {}^*\beta_{1,1}$	I_m	$-\log_{10} {}^*\beta_{1,1}$
25 °C		50.0 °C		80 °C	
0.0201	2.42 ± 0.03	–	–	–	–
0.0503	2.45 ± 0.04	0.0503	1.90 ± 0.06	–	–
0.101	2.57 ± 0.05	0.101	1.99 ± 0.02	0.101	1.41 ± 0.03
0.513	2.69 ± 0.06	0.514	2.22 ± 0.06	0.513	1.61 ± 0.05
2.213	2.84 ± 0.08	2.220	2.30 ± 0.05	2.209	1.75 ± 0.04

Figure A-29: SIT of the $\log_{10} {}^*\beta_{1,1}$ – $a_w + 4D$ values at 25 °C given in Table A-35 and those taken from the literature.



[1980BOC/POP]

The solubility of presumably crystalline hematite was measured in HCl solutions (0 to 0.470 mol·dm^{-3}, initial concentrations) at 400 to 600 °C and 100 to 200 MPa. A double-walled capsule technique was employed with a Ag:AgCl solid buffer (in water) in the inner platinum capsule to control the hydrogen fugacity and either hematite or magnetite in contact with a HCl solution in the outer gold capsule. The capsules were quenched and removed from the pressure vessel over time for analysis of the chloride and iron concentrations.

These highly complex solutions, which contained iron in both oxidation states and whose speciation is dominated by iron chloride complexation, provide results that are well outside the scope of this review.

[1980CIA]

Ciavatta uses the Fe^{3+}/Fe^{2+} couple as an example of the application of the SIT, *viz.*,

$$E_c^{\circ} = E^{\circ} - 59.16\{-4D + \varepsilon(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-) - \varepsilon(\mathrm{Fe}^{2+},\mathrm{ClO}_4^-) - \varepsilon(\mathrm{H}^+,\mathrm{ClO}_4^-)\}m_{\mathrm{ClO}_4^-}$$

citing Biedermann [1975BIE] to give values (25 °C) of E° = 779.6 mV, $\varepsilon(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-)$ = 0.56 kg·mol^{-1} and $\varepsilon(\mathrm{Fe}^{2+},\mathrm{ClO}_4^-)$ = 0.33 kg·mol^{-1}. However, the former interaction coefficient was in fact derived from data by [1937SCH/SHE] whereas the latter was simply ascribed to "other sources" by Biedermann. NEA lists only the value for $\varepsilon(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-)$ = (0.56 ± 0.03) kg·mol^{-1}.

The values for the interaction coefficients of Fe^{2+} and Fe^{3+} with perchlorate ion were derived as indicated above and represent only an example for calculating these coefficients. Therefore, in the present review, these values are derived from other sources.

[1980KAT/MAT]

This paper is concerned primarily with the thermodynamics of Cu-bearing magnetite solid solutions, $Cu_xFe_{3-x}O_4$, with $0 < x < 1$, *i.e.*, up to 100% substitution of Cu^{2+} for Fe^{2+} in magnetite. It includes a series of solid-state measurements of the potential of the solid couple (α-Fe_2O_3 + Fe_3O_4) *vs.* air in a galvanic cell using a CaO-stabilized zirconia electrolyte. The results yielded the relationship:

$$E/\mathrm{mV}\ (1106\ \text{to}\ 1306\ \mathrm{K}) = \{1286 - 0.7720/(T/\mathrm{K})\} \pm 1.6$$

Whence, for the reaction $4Fe_3O_4(cr) + O_2(g) \rightleftharpoons 6Fe_2O_3(cr, \alpha)$, the following Gibbs energy relationship was obtained (simply converted from units of cal to J by the reviewer).

$$\Delta_r G_m^{\circ}/\mathrm{kJ\cdot mol^{-1}} = \{-496.43 + 0.28506(T/\mathrm{K})\} \pm 0.63$$

Recalculation of the Gibbs energy from the cell potential, using current values of R and F, and assuming a constant p_{O_2} value for dry air of 21.224 kPa (20.946 vol. % at p = 101.325 kPa), gave a marginally different expression.

$$\Delta_r G_m^{\circ}/\mathrm{kJ\cdot mol^{-1}} = \{-496.32 + 0.28506(T/\mathrm{K})\} \pm 0.63$$

This expression is included in the compilation shown in Figure VII-17, and shows good agreement with several other studies, but is not used further in the current assessment.

[1980OSA]

The paper describes a set of DSC measurements (10 K·min^{-1}) on 11.0-23.4 mg samples of Fe_2SiO_4 (γ- and synthetic α- forms) and $FeSiO_3$ (orthopyroxene (ferrosilite)) at temperatures from 290 to 420 K. The results for α-Fe_2SiO_4 are in agreement within ~ 10% when compared to values from other studies [1982ROB/FIN], [1982WAT]. However, the results for all the solids are badly scattered, the differences between the specific heats of the two forms of Fe_2SiO_4 are inconsistent [1982WAT], and the molar heat capacity determined for $FeSiO_3$ at 298.15 K, 63 $J \cdot K^{-1} \cdot mol^{-1}$, is much too small when compared to values for similar solids [1995ROB/HEM]. The values from [1980OSA] are not used further in the present review.

[1980STU/FER]

The heat capacities of $FeCl_3$(cr) from 4.68 to 307.56 K and FeOCl(cr) from 6.07 to 313.10 K were measured using an adiabatic calorimeter within a helium cryostat. The heat-capacity curve for $FeCl_3$(cr) showed a sharp λ-type thermal anomaly, with a maximum at (8.34 ± 0.05) K. The heat capacity and entropy at 298.15 K were estimated by the authors to be 96.94 $J \cdot K^{-1} \cdot mol^{-1}$ and (147.82 ± 0.29) $J \cdot K^{-1} \cdot mol^{-1}$, respectively. The estimated entropy included a small contribution from 4.7 to 0 K that was calculated "using a smooth join of the low-temperature end of the heat-capacity curve to 0 K". In the present review, functions were fitted to values of $C^{\circ}_{p,m}/T$, but for temperatures below 10 K integration of the functions indicated markedly smaller contributions to S°_{m} than were estimated by the original authors. Several different fitting functions were used in the region of the thermal anomaly, and a contribution of 6.31 to 6.54 $J \cdot K^{-1} \cdot mol^{-1}$ was estimated from 5 to 10 K. Stuve *et al.* estimated 7.87 $J \cdot K^{-1} \cdot mol^{-1}$. The authors reported that "the heat capacity curve below the transition was smoothly joined to 0 K". This is equivalent to assuming that $C^{\circ}_{p,m}/T$ is constant below 4.7 K (although the value for 5.0 K in the authors' Table 3 suggests a slightly different procedure was used). Using functions that would allow $C^{\circ}_{p,m}/T$ to decrease to zero at 0 K gave a smaller estimated entropy contribution. If $C^{\circ}_{p,m}/T$ was taken as a linear function of T below 4.8 K, the entropy contribution from 0 to 5 K is estimated as 2.50 $J \cdot K^{-1} \cdot mol^{-1}$. If $C^{\circ}_{p,m}/T^2$ was taken as a linear function of T below 4.8 K, the entropy contribution from 0 to 5 K is estimated as 1.75 $J \cdot K^{-1} \cdot mol^{-1}$, though the join in the plot of $C^{\circ}_{p,m}$ against T is not particularly smooth. Stuve *et al.* reported 3.70 $J \cdot K^{-1} \cdot mol^{-1}$ (and assuming that $C^{\circ}_{p,m}/T$ is constant would give 4.87 $J \cdot K^{-1} \cdot mol^{-1}$). It is possible that the reported values of $C^{\circ}_{p,m}$ for temperatures below 5 K have a minor systematic error. In the present review the entropy contribution from 0 to 10 K is estimated as (8.5 ± 0.7) $J \cdot K^{-1} \cdot mol^{-1}$.

There were no thermal anomalies in the heat-capacity curve for FeOCl(cr). The heat capacity and entropy at 298.15 K were estimated by the authors to be 70.50 $J \cdot K^{-1} \cdot mol^{-1}$ and (82.55 ± 0.13) $J \cdot K^{-1} \cdot mol^{-1}$, respectively. Also, high-temperature drop-calorimetry measurements were carried out between 403 and 716 K (the receiver calorimeter was at 298 K). Partial decomposition of the sample was found when it was heated above 690 K, so the highest reliable temperature for the enthalpy measurements was 662.1 K.

The following function was fitted by the authors to their drop-calorimetry results (units converted from cal to J in the present review):

$$(H^{\circ}_{\mathrm{m}}(T) - H^{\circ}_{\mathrm{m}}(298.15\ \mathrm{K}))/\mathrm{J{\cdot}mol^{-1}} = 67.032(T/\mathrm{K}) + 14.518 \times 10^{-3}\,(T/\mathrm{K})^{2} + 4.619 \times 10^{5}\,(T/\mathrm{K})^{-1} - 22835$$

Differentiation of this function results in:

$$C^{\circ}_{p,\mathrm{m}}/\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}} = 67.032 + 29.037 \times 10^{-3}\,(T/\mathrm{K}) - 4.619 \times 10^{5}\,(T/\mathrm{K})^{-2}\,.$$

The enthalpy function agrees with the experimental enthalpy-difference values to within 0.1%, and was also selected so as to mesh with the adiabatic-calorimetry results near 298.15 K (the derived heat-capacity function reproduces the smoothed experimental results down to 260 K within 0.1 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$). In the present review the uncertainty in $C^{\circ}_{p,\mathrm{m}}$ (FeOCl, cr, 298.15 K) is estimated as ± 0.20 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$.

Functions were fitted to the heat-capacity data (*i.e.*, $C^{\circ}_{p,\mathrm{m}}/T$) for temperatures above and below 80 K, and extrapolation to 0 K from 6.5 K has been based on the assumption that ($C^{\circ}_{p,\mathrm{m}}/T$) varies linearly with T^2. A value of 82.70 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ is calculated for S°_{m} (FeOCl, cr, 298.15 K), in close agreement with the value of (82.55 ± 0.13) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ proposed by Stuve *et al.* The uncertainty is estimated to be ± 0.20 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$.

The enthalpy of solution of $\mathrm{FeCl_3}$(cr) into 4.360 m HCl was measured. This is the same solution molality that was used previously by Koehler and Coughlin [1959KOE/COU], but the measurement was done at 25 °C rather than at 30 °C. The measured enthalpy of solution was – (103.33 ± 0.03) $\mathrm{kJ{\cdot}mol^{-1}}$, somewhat more negative than the – (102.34 ± 0.08) $\mathrm{kJ{\cdot}mol^{-1}}$ measured by Koehler and Coughlin. If $C^{\circ}_{p,\mathrm{m}}$ ($\mathrm{FeCl_3}$, cr) is 95.4 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, the apparent molar heat capacity of $\mathrm{FeCl_3}$ in 4.36 m HCl would need to be approximately 100 $\mathrm{J{\cdot}mol^{-1}}$ for the results at 25 and 30 °C [1959KOE/COU] to be in agreement. This is discussed further in the Appendix A entry for [1959KOE/COU].

The enthalpy of formation of FeOCl(cr) was determined as – (410.99 ± 0.92) $\mathrm{kJ{\cdot}mol^{-1}}$ by comparison of the enthalpies of solution of $\mathrm{FeCl_3}$(cr) and FeOCl(cr) at 25 °C in aqueous HCl. Recalculation in the present review leads to a value of – (11.56 ± 0.24) $\mathrm{kJ{\cdot}mol^{-1}}$ for $\Delta_{\mathrm{r}}H^{\circ}_{\mathrm{m}}$ (A.119).

$$\mathrm{FeCl_3(cr)} + \tfrac{1}{2}\mathrm{O_2(g)} \rightleftharpoons \mathrm{FeOCl(cr)} + \mathrm{Cl_2(g)} \qquad \text{(A.119)}$$

[1980SUG/KUW]

This paper deals primarily with the Pb–PbO system, but includes the following potential-temperature relationships of interest for the current review.

For air *vs*. Pb-PbO: $E/\mathrm{mV} = \{1119.4 - 0.5382(T/\mathrm{K})\} \pm 2.4$ at 673 to 1160 K.

For Fe-wüstite *vs*. Pb-PbO: $E/\mathrm{mV} = \{232.8 + 0.1803(T/\mathrm{K})\} \pm 1.1$ at 823 to 1373 K.

For Fe-Fe_3O_4 *vs*. Pb-PbO: $E/\text{mV} = \{290.4 + 0.1082(T/\text{K})\} \pm 1.3$ at 673 to 811 K.

For Fe-wüstite *vs*. air: $E/\text{mV} = \{1339.2 - 0.3450(T/\text{K})\} \pm 2.7$ at 873 to 1373 K.

The third relationship is of particular interest, because of the relative scarcity of direct measurements on the Fe-Fe_3O_4 equilibrium. Combining the first and third equations yields values for $\Delta_f G_m^o$ (Fe_3O_4, cr, T) about 5.3 kJ·mol^{-1} less negative than the high-precision, direct measurements of [1988NEI], but with an almost identical temperature dependence. This difference corresponds to a bias of nearly 7 mV in the combined expressions involving the electrochemical potentials, which is more than twice the reported combined uncertainty. Given the apparently high accuracy of the data presented in [1988NEI], the expressions from [1980SUG/KUW] were excluded from the final assessment of $\Delta_f H_m^o$ (Fe_3O_4, cr, 298.15 K).

[1980TRE/LEB]

This study virtually repeated the earlier work of Sweeton and Baes [1970SWE/BAE] from 100 to 300 °C with H_2-saturated (8.57×10^{-3} mol·kg^{-1}) HCl and NaOH feed solutions over a wider range of pH than investigated previously. Precautions were also taken to rinse the sample lines to remove deposited iron and to prewash the column to remove particulates. The magnetite was well characterised before and after the experiments. The results were analysed in terms of both Fe(II) and Fe(III) aqueous species, although the latter were considered unimportant at pH(298.15 K) < 9, and activity coefficients were taken into account using the simple Debye-Hückel expression. The authors considered only the Fe^{2+} and $FeOH^+$ species at low pH and the $Fe(OH)_2(aq)$, $Fe(OH)_3^-$, $Fe(OH)_3(aq)$ and $Fe(OH)_4^-$ species at higher pH. Moreover, the Gibbs energies of reaction to form the latter two Fe(III) species were constrained by fixing, $\Delta_r G_m^o$ (298.15 K) = 74.0 and 128.8 kJ·mol^{-1}, respectively, and their preferred fit of the entire data set involved making the final assumption that $\Delta_r S_{1,1}^o$ (298.15 K) = – 57.3 J·K^{-1}·mol^{-1} [1978JOH/BAU]. The heat capacities of reaction were by necessity assumed to be zero. The following equilibrium constants for magnetite dissolution were tabulated by the authors whereby the formation of the hydrolyzed iron(II) species was represented by hydrolysis constants. The solubility equilibrium to form Fe^{2+} takes the form

$$\tfrac{1}{3}\,Fe_3O_4(cr) + 2\,H^+ + \tfrac{1}{3}\,H_2(g) \rightleftharpoons Fe^{2+} + \tfrac{4}{3}\,H_2O(l) \qquad (A.120)$$

with the generalized form to give the hydrolyzed Fe(II) species being represented by:

$$\tfrac{1}{3}\,Fe_3O_4(cr) + (2-b)H^+ + \tfrac{1}{3}\,H_2(g) \rightleftharpoons Fe(OH)_b^{2-b} + (\tfrac{4}{3}-b)\,H_2O(l) \qquad (A.121)$$

As mentioned these authors recognized the formation of $Fe(OH)_3(aq)$ and $Fe(OH)_4^-$, and tabulated solubility constants in accord with the generalized equilibrium:

$$\tfrac{1}{3}\,Fe_3O_4(cr) + (3-b)\,H^+ \rightleftharpoons Fe(OH)_b^{3-b} + \tfrac{1}{6}\,H_2(g) + (\tfrac{4}{3}-b)\,H_2O(l) \qquad (A.122)$$

This solubility study and the earlier work of Sweeton and Baes [1970SWE/BAE] still represent the best data that are available on magnetite, which is the only well-characterised solid iron(II)-bearing phase to enable thermodynamic data for the aqueous Fe(II) species to be determined (also see the discussion by Lindsay [1986LIN2]). Moreover due to the insolubility of magnetite and iron(II) hydroxides, solubility measurements still provide the only source of the second- and third-hydrolysis constants of Fe^{2+}. In this review, the solubility constants for the formation of $Fe(OH)_b^{2-b}$, $b = 0, 1$, and 2 from Tremaine and LeBlanc were combined with those of Sweeton and Baes [1970SWE/BAE]. However, for $b = 3$ the latter results were shown to be unreliable so that additional results from [1976KAN/GRA] were also used. Additional fits of the data for the equilibria represented in Eq. (A.122) for $b = 3$ and 4 were made, although these results are considered provisional at this time because of the difficulty in verifying the exact nature of the solid phase at temperature and due to the limited pH range over which these results could be obtained. Note, that as mentioned in the synopsis of the Sweeton and Baes study, pH is perhaps the least well known, but most important, variable in these investigations and was only estimated by iterative calculations that depend on the speciation of the iron in solution. The effects of adsorption, impurities, and other possible side reactions complicate the calculation of pH for the near neutral to moderately basic pH range in particular where the lowest concentrations of iron exist in solution. The following generalized equation was used to fit the solubility constants, *viz.*, using standard weighted least-squares procedures in all cases:

$$\log_{10} {}^{*}\beta^{\circ}_{x,y} = a + b/T + c\log_{10} T \qquad \text{(A.123)}$$

First solubility constant of magnetite (iron(II) system)

$$\tfrac{1}{3}\,Fe_3O_4(cr) + 2\,H^+ + \tfrac{1}{3}\,H_2(g) \rightleftharpoons Fe^{2+} + \tfrac{4}{3}\,H_2O(l)$$

The $\log_{10} {}^{*}\beta^{\circ}_{s,0}$ values were fitted in a number of ways utilizing Eq. (A.123) based on the following criteria:

Fit 1: Assuming that $\Delta_r C^{\circ}_{p,m}$ (298.15 K) = constant with no other constraints.

Fit 2: Assuming that $\Delta_r C^{\circ}_{p,m}$ (298.15 K) = 0 with no other constraints.

Fit 3: Assuming that S°_{m} (Fe^{2+}, 298.15 K) = $-$101.01 J·K^{-1}·mol^{-1} which is the entropy for Fe^{2+} recommended from the electrochemical data within this review. Both solubility studies [1970SWE/BAE] and [1980TRE/LEB] fixed the entropy term before fitting their data.

Fit 4: Assuming that $\Delta_r S^{\circ}_{m}$ (Fe^{2+}, 298.15 K) = $-$101.01 J·K^{-1}·mol^{-1} and $C^{\circ}_{p,m}$ (Fe^{2+}, 298.15 K) = $-$22 J·K^{-1}·mol^{-1} [1988HOV].

The parameters associated with these fits, which are shown in Figure A-30, are given in Table A-36.

Figure A-30: Values of $\log_{10} {}^{*}\beta^{\circ}_{s,0}$ plotted against reciprocal temperature (kelvin) showing the results of four fitting equations used to treat these data.

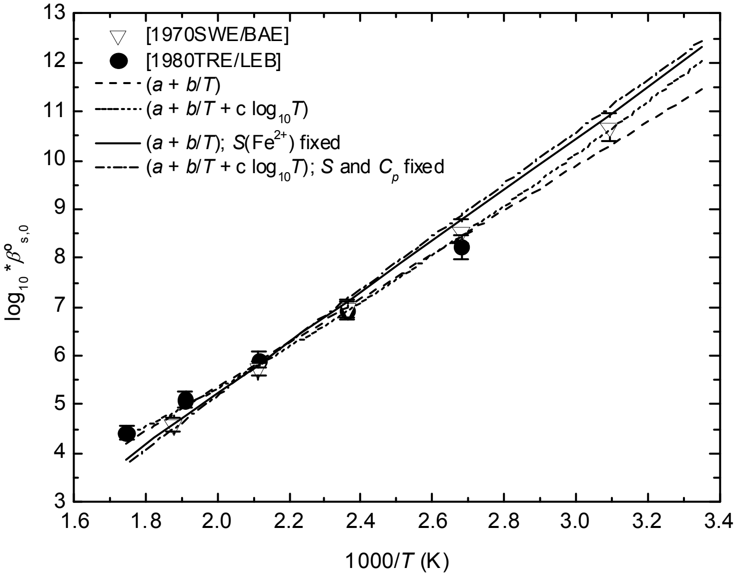


Table A-36: Parameters of Eq. (A.123) for the first solubility constant with the fixed values shown in italics.

Fit	*a*	*b*	*c*
1	−56.003 ± 27.562	7771.7 ± 1723.3	16.964 ± 8.932
2	− 3.658 ± 0.375	4511.1 ± 172.7	
3	*−5.2218*	5223.8 ± 44.1	
4	*2.4746*	4928.6 ± 54.1	*−2.6460*

The remaining thermodynamic properties at 298.15 K were determined as follows:

$$\begin{aligned}\Delta_r G^{\circ}_{m} &= \Delta_f G^{\circ}_{m}(\mathrm{Fe^{2+}}) + \tfrac{4}{3}\Delta_f G^{\circ}_{m}(\mathrm{H_2O, l}) - \tfrac{1}{3}\Delta_f G^{\circ}_{m}(\mathrm{Fe_3O_4, cr})\\ &= -RT\log_{10} {}^{*}\beta^{\circ}_{s,0}\end{aligned}$$

$$\Delta_f G^{\circ}_{m}(\mathrm{Fe^{2+}}) = \Delta_r G^{\circ}_{m} - \tfrac{4}{3}(-237140) + \tfrac{1}{3}(-1012720)\ \{\mathrm{J\cdot mol^{-1}}\}$$

$$\Delta_r H^{\circ}_{m} = \Delta_f H^{\circ}_{m}(\mathrm{Fe^{2+}, aq}) + \tfrac{4}{3}\Delta_f H^{\circ}_{m}(\mathrm{H_2O, l}) - \tfrac{1}{3}\Delta_f H^{\circ}_{m}(\mathrm{Fe_3O_4, cr})$$

$$\Delta_f H^{\circ}_{m}(\mathrm{Fe^{2+}}) = \Delta_r H^{\circ}_{m} - \tfrac{4}{3}\Delta_f H^{\circ}_{m}(\mathrm{H_2O, l}) + \tfrac{1}{3}\Delta_f H^{\circ}_{m}(\mathrm{Fe_3O_4, cr})$$

$$\Delta_f H^{\circ}_{m}(\mathrm{Fe^{2+}}) = \Delta_r H^{\circ}_{m} - \tfrac{4}{3}(-285830) + \tfrac{1}{3}(-1115780)\ \{\mathrm{J\cdot mol^{-1}}\}$$

$$\Delta_{\mathrm{r}}S^{\mathrm{o}}_{\mathrm{m}}\,(\mathrm{Fe}^{2+}) = -(\Delta_{\mathrm{r}}G^{\mathrm{o}}_{\mathrm{m}} - \Delta_{\mathrm{r}}H^{\mathrm{o}}_{\mathrm{m}})/298.15$$

$$S^{\mathrm{o}}_{\mathrm{m}}\,(\mathrm{Fe}^{2+}) = \Delta_{\mathrm{r}}S^{\mathrm{o}}_{\mathrm{m}} - \tfrac{4}{3}S^{\mathrm{o}}_{\mathrm{m}}\,(\mathrm{H_2O, l}) + \tfrac{1}{3}S^{\mathrm{o}}_{\mathrm{m}}\,(\mathrm{Fe_3O_4, cr}) + \tfrac{1}{3}S^{\mathrm{o}}_{\mathrm{m}}\,(\mathrm{H_2, g})$$

$$S^{\mathrm{o}}_{\mathrm{m}}\,(\mathrm{Fe}^{2+}) = \Delta_{\mathrm{r}}S^{\mathrm{o}}_{\mathrm{m}} - \tfrac{4}{3}\,(69.950) + \tfrac{1}{3}\,(145.89) + \tfrac{1}{3}\,(130.68)\ \{\mathrm{J\cdot K^{-1}\cdot mol^{-1}}\}$$

$$C^{\mathrm{o}}_{p,\mathrm{m}}\,(\mathrm{Fe}^{2+}) = \Delta_{\mathrm{r}}C^{\mathrm{o}}_{p,\mathrm{m}} - \tfrac{4}{3}C^{\mathrm{o}}_{p,\mathrm{m}}\,(\mathrm{H_2O, l}) + \tfrac{1}{3}C^{\mathrm{o}}_{p,\mathrm{m}}\,(\mathrm{H_2, g}) + \tfrac{1}{3}C^{\mathrm{o}}_{p,\mathrm{m}}\,(\mathrm{Fe_3O_4, cr})$$

$$C^{\mathrm{o}}_{p,\mathrm{m}}\,(\mathrm{Fe}^{2+}) = \Delta_{\mathrm{r}}C^{\mathrm{o}}_{p,\mathrm{m}} - \tfrac{4}{3}\,(75.351) + \tfrac{1}{3}\,(28.836) + \tfrac{1}{3}\,(150.78)\ \{\mathrm{J\cdot K^{-1}\cdot mol^{-1}}\}.$$

These calculated thermodynamic quantities for Fe^{2+} are given in Table A-37.

Table A-37: Thermodynamic quantities for Fe^{2+} at 298.15 K with the fixed values shown in italics.

Fit	$\log_{10}{}^{*}\beta^{\mathrm{o}}_{\mathrm{s},0}$	$\Delta_{\mathrm{f}}G^{\mathrm{o}}_{\mathrm{m}}$ /kJ·mol^{-1}	$\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ /kJ·mol^{-1}	$S^{\mathrm{o}}_{\mathrm{m}}$ /J·K^{-1}·mol^{-1}	$C^{\mathrm{o}}_{p,\mathrm{m}}$ /J·K^{-1}·mol^{-1}
1	12.04	−90	−98	−130	48
2	11.47	−87	−77	−71	0
3	12.30 ± 0.15	−91.6	−90.8	*−101.0 ±3.1*	0
4	12.46 ± 0.18	−92.5	−91.7	*−101.0 ±3.1*	*−22*

Second solubility constant of magnetite (iron(II) system)

$$\tfrac{1}{3}\,\mathrm{Fe_3O_4(cr)} + \mathrm{H^+} + \tfrac{1}{3}\,\mathrm{H_2(g)} \rightleftharpoons \mathrm{FeOH^+} + \tfrac{1}{3}\,\mathrm{H_2O(l)} \qquad \text{(A.124)}$$

The $\log_{10}{}^{*}\beta^{\mathrm{o}}_{\mathrm{s},1}$ values were fitted in a number of ways utilizing Eq. (A.123) based on the following criteria:

Fit 1: Assuming that $\Delta_{\mathrm{r}}C^{\mathrm{o}}_{p,\mathrm{m}}$ (298.15 K) = 0 with no other constraints.

Fit 2: Using the $\log_{10}{}^{*}\beta^{\mathrm{o}}_{\mathrm{s},1}$ value at 298.15 K equal to 3.2 in combination with the corresponding value of $\log_{10}{}^{*}\beta^{\mathrm{o}}_{\mathrm{s},0}$ from Fit 4 (Table A-37) to give $\log_{10}{}^{*}\beta^{\mathrm{o}}_{1,1} = -9.1$ which is compatible with the independent hydrolysis data and a $\Delta_{\mathrm{r}}C^{\mathrm{o}}_{p,\mathrm{m}}$ (298.15 K) = 0 for Reaction (A.124).

Fit 3: Same as for Fit 2, except using $\log_{10}{}^{*}\beta^{\mathrm{o}}_{\mathrm{s},0}$ from Fit 4 (Table A-37) at 25 °C.

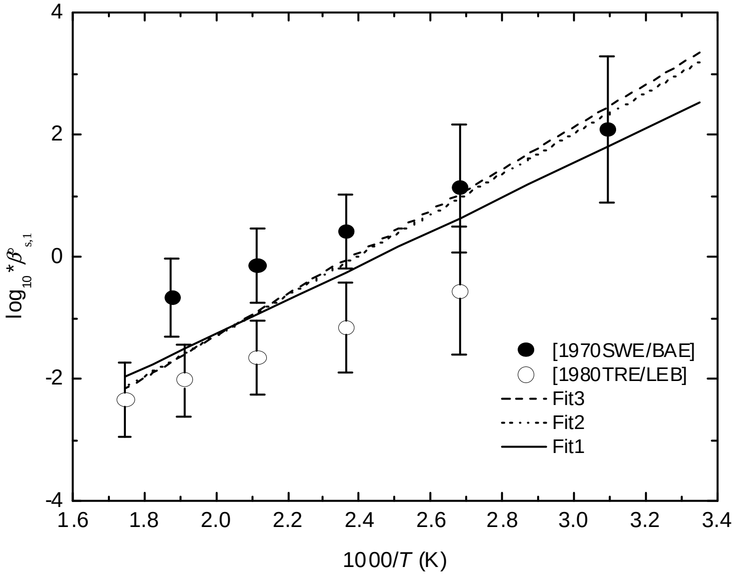
Table A-38: Parameters of Eq. (A.123) for the first solubility constant.

Fit	*a*	*b*
1	−6.848 ± 1.717	2795.35 ± 791.21
2	−7.917 ± 0.663	3314.3 ± 197.6
3	−8.170 ± 0.672	3437.1 ± 200.4

Table A-39: Thermodynamic quantities for $FeOH^+$ at 298.15 K.

Fit	$\log_{10}{}^*\beta^{\circ}_{s,0}$	$\Delta_f G^{\circ}_m$ /kJ·mol^{-1}	$\Delta_f H^{\circ}_m$ /kJ·mol^{-1}	S°_m /J·K^{-1}·mol^{-1}
1	2.5	– 273	– 330	– 62
2	*3.20*	– 277	– 340	– 82
3	*3.36*	– 278	– 343	– 88

Figure A-31: Values of $\log_{10}{}^*\beta^{\circ}_{s,1}$ plotted against reciprocal temperature (kelvin) showing the results of three fitting equations used to treat these data.



Third solubility constant of magnetite (iron(II) system)

$$\tfrac{1}{3}\,Fe_3O_4(cr) + \tfrac{1}{3}\,H_2(g) + \tfrac{2}{3}\,H_2O(l) \rightleftharpoons Fe(OH)_2(aq) \qquad (A.125)$$

The results for $\log_{10}\beta^{\circ}_{s,2}$ from [1970SWE/BAE] and [1980TRE/LEB] were combined in a weighted, but unrestrained fit using the linear version of Eq. (A.123). The parameters for this fit are: $a = -(6.700 \pm 0.911)$ and $b = -(786.38 \pm 412.73)$, which produced the straight line in Figure A-32 and a $\log_{10}\beta^{\circ}_{s,2}$ at 298.15 K = $-(8.7 \pm 1.1)$, and the thermodynamic parameters for $Fe(OH)_2(aq)$: $\Delta_f G^{\circ}_m(Fe(OH)_2, aq) = -445.8$ kJ·mol^{-1}; $\Delta_f H^{\circ}_m(Fe(OH)_2, aq) = -324.7$ kJ·mol^{-1}; $S^{\circ}_m(Fe(OH)_2, aq) = -29$ J·K^{-1}·mol^{-1}.

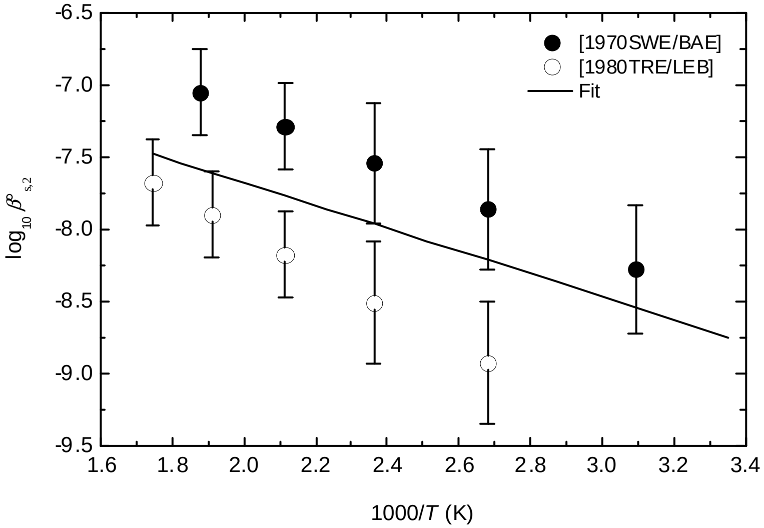
$$\Delta_r G^{\circ}_m = -R\ln(10)\{aT + b\} = 49.66\ \text{kJ·mol}^{-1}$$

$$\Delta_r H^{\circ}_m = -R\ln(10)\,b = 15.055\ \text{kJ·mol}^{-1}$$

$$\Delta_r S^{\circ}_m = R\ln(10)\,a = -116.8\ \text{J·K}^{-1}\text{·mol}^{-1}$$

$$\log_{10}{}^{*}\beta^{\circ}_{2,1} = -(21.2 \pm 1.1) \text{ at } 298.15\text{ K}.$$

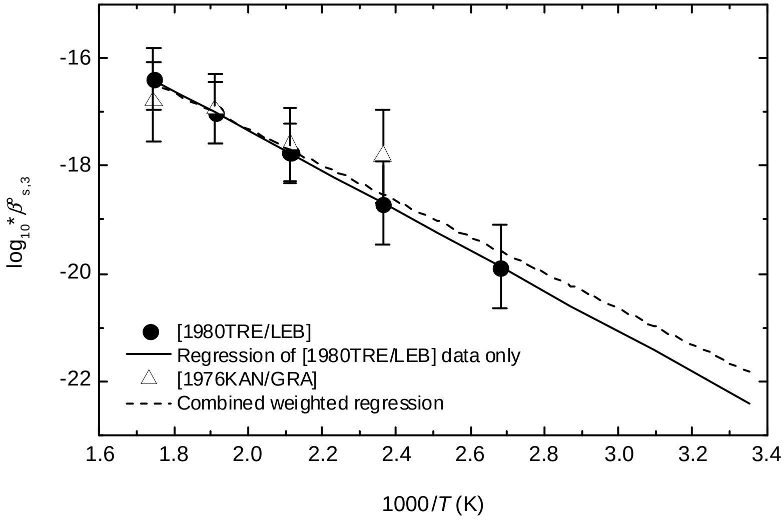
Figure A-32: Temperature dependence of $\log_{10}\beta^{\circ}_{s,2}$ using the simple unrestrained linear fit to the data in [1970SWE/BAE] and [1980TRE/LEB].



Fourth solubility constant of magnetite (iron(II) system)

$$\tfrac{1}{3}\,\mathrm{Fe_3O_4(cr)} + \tfrac{1}{3}\,\mathrm{H_2(g)} + \tfrac{5}{3}\,\mathrm{H_2O(l)} \rightleftharpoons \mathrm{Fe(OH)_3^-} + \mathrm{H^+} \qquad \text{(A.126)}$$

Figure A-33: Temperature dependence of $\log_{10}{}^{*}\beta^{\circ}_{s,3}$ using the simple unrestrained linear fit to the data in [1976KAN/GRA] and [1980TRE/LEB].



[1980ZOT/KOT]

This study represents an extension of their earlier spectrophotometric investigation carried out from 25 to 80 °C.

Table A-40: The $\log_{10} {}^*\beta_{1,1}$ values taken directly from [1980ZOT/KOT].

I_m	$\log_{10} {}^*\beta_{1,1}$	I_m	$\log_{10} {}^*\beta_{1,1}$	I_m	$\log_{10} {}^*\beta_{1,1}$
	80 °C		110 °C		140 °C
0.101	1.45 ± 0.04	0.101	0.97 ± 0.04	–	–
0.513	1.53 ± 0.05	0.511	1.08 ± 0.04	0.507	0.71 ± 0.04
1.050	1.67 ± 0.06	1.042	1.20 ± 0.05	1.028	0.79 ± 0.04
2.213	1.63 ± 0.05	2.178	1.26 ± 0.06	2.128	0.83 ± 0.06
	170 °C		200 °C		
0.502	0.39 ± 0.07	–	–		
1.009	0.50 ± 0.06	0.986	0.23 ± 0.08		
2.064	0.60 ± 0.06	1.982	0.32 ± 0.07		

As for the companion paper [1979ZOT/KOT], there is a need to translate the Russian text for details to provide a more thorough examination of the data.

[1981BYR/KES]

This paper revisits the studies of chlorido and hydroxido complexes of Fe(III) as investigated by UV-visible spectrophotometry. The authors reviewed the previous data. The literature values for the formation constant of $FeCl^{2+}$ at 1 M ionic strength and 25 °C are spread between 3 and 5. The authors tried to lower the quantitative discrepancies by using advanced computer programs for data interpretation. These programs are better able to assess the interpretation errors resulting from interferences of new species.

Their results confirm the lower values of the formation constant found by Woods *et al.* [1962WOO/GAL]. For ionic strength I_c = 2.74 M at 25 °C, they found $K_1 = (5.34 \pm 0.14)\ \text{dm}^3\cdot\text{mol}^{-1}$.

The authors also discussed the stability of the mixed FeClOH^+ complex after an assessment based on new experimental data. They carefully investigated whether the mixed complex FeClOH^+ occurs in solutions with 0.68 m ionic strength (mimicking seawater). The spectra of 5×10^{-6} M iron(III) in 0.68 m Cl^- solutions between pH 2.16 and 4.17 show only the absorption bands of inner-sphere FeCl^{2+} and FeOH^{2+} because two isosbestic points are observed at 271 and 327 nm. From that they estimated the value of $\beta_{1,1} = [\text{FeClOH}^+]\,[\text{H}^+]/[\text{Fe}^{3+}]\,[\text{Cl}^-]$ to be less than 1.8×10^{-4}, which is 200 times lower than the value proposed by Koren and Perlmutter-Hayman [1972KOR/PER].

The primary interest of this relatively modern investigation with a method used by many earlier workers seems to have been in the data treatment by currently available computer programs.

The quantitative results have to be taken into account.

Concerning the problem of the existence and the stability of the FeClOH^+ species in aqueous solution, it is proven that if this species exists, it is a marginal species and its presence has not been shown by a physical property measurement during this investigation; in spite of the rather favourable range of chemical conditions used.

The value of K_1 has been taken into account in the SIT treatment of all the literature data and contributed to the determination of the recommended values of $\log_{10} K_1^{\circ}$, $\log_{10} K_2^{\circ}$ and $\varepsilon(\text{FeCl}^{2+}, \text{ClO}_4^-)$. The value of K_2 ($0.34\ \text{dm}^3\cdot\text{mol}^{-1}$) is much lower than those in the rest of the literature and has been rejected for the same reasons as has the K_2 value of [1972SEK/TET] (also see the discussion in the main text).

[1981JAC/ROS]

This paper presents solid-state cell-potential measurements for the couples (A) (Fe + wüstite) *vs.* air, (B) (Ni + NiO) *vs.* (Fe + wüstite), (C) (Co + CoO) *vs.* (Fe + wüstite), and (D) (Co + CoO) *vs.* (Ni + NiO), at temperatures up to 1580 K, using a CaO-stabilized zirconia electrolyte. Features of the "double tube cell" design included an Al_2O_3 capillary insert to minimize gas volume in the sample compartment. When (Fe + wüstite) was used in the reference compartment, care was taken to prevent contact and possible side-reactions with the zirconia tube. The procedure was designed to minimize oxygen permeation through the tube wall during experiments. For measurements with an air reference, a constant p_{O_2} value of 21.224 kPa was assumed, with no corrections for variations in humidity or barometric pressure (*cf.* [1988NEI]).

The paper presents 26 measurements on (Fe + wüstite) *vs.* air at 753.6 to 1554.2 K, including three below the Fe-wüstite-Fe_3O_4 eutectoid, at which the stable assemblage would be (Fe + Fe_3O_4). There are also 72 measurements on (Ni + NiO) *vs.*

(Fe + wüstite) at 862.1 to 1619.3 K, and 33 measurements on (Co + CoO) *vs.* (Fe + wüstite) at 965.3 to 1595.3 K. The results are not reviewed in detail here, because of the limited discussion of high-temperature equilibria involving wüstite (see Section VII.2.7.2.3); some data are included in the compilation shown in Figure VII-32.

[1981JOH]

Johnson used fluorine bomb calorimetry to determine the enthalpy of formation of anhydrous iron(III) fluoride as − 989.6 kJ·mol^{-1} at 298.15 K.

During the reaction, tungsten foils were used to prevent the iron from contacting structural nickel in the bomb calorimeter. Unreacted tungsten was recovered and weighed, the amount of FeF_2(cr) as a by-product was determined analytically, and the reported heats were corrected for the amounts of WF_6(cr) and FeF_2(cr) that were formed. Despite these difficulties, the authors estimated that the overall 2σ uncertainty in their value of $\Delta_f H_m^o$ (FeF_3, cr, 298.15 K) was 2.2 kJ·mol^{-1}. Because of the need to determine the residual tungsten and FeF_2 at the end of each experiment, a bias in the final enthalpy of formation value cannot be ruled out. The paper provided an assessment of earlier enthalpy of formation determinations for FeF_3(cr). The value obtained by Johnson was markedly less negative than those reported from earlier work [1928JEL/RUD], [1937DOM], [1975SCH2] (also see [1981SCH/GOK]). The author noted agreement with a value, − (990.8 ± 2.1) kJ·mol^{-1}, from Pervov *et al.* [1978PER/MUR]. That result was reported only in an abstract that was unavailable to the current reviewers. However, it is likely that the work discussed in [1978PER/MUR] is part of the experimental work later described by Pervov *et al.* [1981PER/MUR] (in which a slightly more negative estimate for $\Delta_f H_m^o$ (FeF_3, cr, 298.15 K) was reported).

[1981PAR/DAY]

Parkinson and Day measured the equilibrium humidity over slightly dehydrated samples of $FeSO_4 \cdot 7H_2O$ from 10 to 40 °C. The emphasis was on the rate of the approach to equilibrium. The sparse equilibrium vapour-pressure values appear to be in fair agreement with those from earlier work [1923SCH], [1935BON/BUR], [1979MAL/DRA]. However, the primary data were not tabulated, and the results of this study are not used further in the present review.

[1981PER/MUR]

Pervov *et al.* used fluorine bomb calorimetry (initial fluorine pressure 3.5 atm.) to determine the enthalpy of formation of anhydrous iron(III) fluoride at 298.15 K.

During the reaction, tungsten foils were used to prevent the iron from contacting structural Monel in the bomb calorimeter. Unreacted tungsten was recovered and weighed, the small amount of FeF_2(c) present in some experiments as a by-product, was determined analytically, and the reported heats were corrected for the amounts of WF_6(cr) and FeF_2(cr) that were formed. After considering uncertainties from these sources and statistical uncertainties, the authors estimated the value of $\Delta_f H_m^o$ (FeF_3, cr, 298.15 K) to be $-(993.7 \pm 2.5)$ kJ·mol^{-1}. The raw experimental data are given in less detail than those provided by Johnson [1981JOH] from his similar study.

The reported value of $\Delta_f H_m^o$ (FeF$_3$, cr, 298.15 K) is markedly less negative than those from earlier work [1928JEL/RUD], [1937DOM], [1975SCH2] (also see [1981SCH/GOK]). The authors do report a recalculation of the vapour-pressure results of Jellineck and Rudat [1928JEL/RUD] that would make those results appear to be much more compatible with the calorimetry study. However, the recalculation seems to rely on a second-law (rather than a third-law) assessment of the enthalpy of formation of FeF$_2$(cr) — the difference is ~ 50 kJ·mol^{-1}, and the second-law value is incompatible with the value selected in the present review.

[1981REI/JOH]

The solubility of FeCO$_3$ in acidic solutions was measured under different partial pressures of CO$_2$(g) (~ 80 and 8 kPa), at 50 °C in I = 1 mol·kg^{-1} (NaClO$_4$(sln)). The reported[1] mean value for $\log_{10}([\mathrm{Fe}^{2+}]\, p_{\mathrm{CO}_2}/[\mathrm{H}^+]^2)$ was (7.61 ± 0.05). The authors reported $\Delta_f G^o$(FeCO$_3$, cr, 298.15 K) = $-(669.02 \pm 0.46)$ kJ·mol^{-1} (using -82.1 kJ·mol^{-1} for $\Delta_f H^o$(Fe^{2+}, I = 1 mol·kg^{-1} (NaClO$_4$(sln)), 323.15 K), a value less negative than most) — see the re-evaluation in [2002PRE/GAM].

The reported iron and hydrogen ion concentrations and p_{CO_2} values were reanalysed using CODATA values for CO$_2$(g), CO$_2$(aq), HCO_3^-, CO_3^{2-} and H$_2$O(l) at 298.15 K and the temperature dependence of the carbonate equilibria and ion-product of water from the equations of Nordstrom *et al.* [1990NOR/PLU]. The solubility product values were corrected to I = 0 using the standard TDB SIT procedure. The average value for $\log_{10} {}^*K_{p,s,0}$ (A.127) at 323.15 K is (7.28 ± 0.03) (this uncertainty represents the 95% confidence limit, not including uncertainties in the auxiliary data).

$$\mathrm{FeCO_3(cr)} + 2\,\mathrm{H}^+ \rightleftharpoons \mathrm{Fe}^{2+} + \mathrm{CO_2(g)} + \mathrm{H_2O(l)} \qquad \text{(A.127)}$$

This value is less than the value of ~ 7.36 reported from recalculations in the paper of Preis and Gamsjäger [2002PRE/GAM] (their Figure 4). The difference is traceable to their use of the Davies equation for a solution with an ionic strength of 1.0 mol·kg^{-1} (NaClO$_4$(sln)), well beyond the normal range of applicability of the equation.

[1981SCH/GOK]

This paper used the experimental results reported earlier by one of the authors [1975SCH2], but with an enhanced analysis of the data. Careful measurements of the potential for the galvanic cell Pt | Ni, NiF$_2$ | CaF$_2$(1 mole% YF$_3$) | FeF$_2$, Fe | Pt were carried out from 897.5 to 1098.7 K. The cell was purged and operated under a slow flow (20 cm^3·min^{-1}, 2.67 kPa positive pressure) of purified argon. The results were tabulated,

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[1] For the 1 atm. standard state; also (7.608 ± 0.04) in [1980REI].

and a third-law analysis was applied to obtain an average value of $-(715.5 \pm 0.5)$ kJ·mol^{-1} for $\Delta_f H^\circ_m$(FeF$_2$, cr, 298.15 K).

A third-law reanalysis of the results has been done using auxiliary values from the present review, and thermodynamic quantities for Ni(cr) and NiF$_2$(cr) from Gamsjäger *et al.* [2005GAM/BUG]. Without consideration of the uncertainties in the auxiliary data, this leads to a value of $-(712.7 \pm 0.2)$ kJ·mol^{-1} for $\Delta_f H^\circ_m$(FeF$_2$, cr, 298.15 K). The major source of uncertainty in these calculations has its origin in the value for $\Delta_f H^\circ_m$(NiF$_2$, cr, 298.15 K), $-(657.3 \pm 8.0)$ [2005GAM/BUG], though uncertainties in $C^\circ_{p,m}$(FeF$_2$, cr, T) also can introduce an uncertainty of 1-2 kJ·mol^{-1} in the value for $\Delta_f H^\circ_m$(FeF$_2$, cr, 298.15 K).

The authors also measured the potential of the galvanic cell Ni, Pt, (MgO + MgF$_2$) | CaF$_2$(1 mole% YF$_3$) | (FeF$_3$ + Fe$_2$O$_3$), Pt, Ni to study the reaction

$$3\,\text{MgO(cr)} + 2\,\text{FeF}_3\text{(cr)} \rightleftharpoons 3\,\text{MgF}_2\text{(cr)} + \text{Fe}_2\text{O}_3\text{(cr)} \qquad \text{(A.128)}$$

at 11 temperatures between 880.8 and 934.6 K.

These were really measurements of the potential difference related to the quotient of the equilibrium constants ($K = p_{F_2} / p_{O_2}{}^{½}$) for the reactions:

$$½\,\text{O}_2\text{(g)} + \text{MgF}_2\text{(cr)} \rightleftharpoons \text{MgO(cr)} + \text{F}_2\text{(g)}$$

and

$$½\,\text{O}_2\text{(g)} + ⅔\,\text{FeF}_3\text{(cr)} \rightleftharpoons ⅓\,\text{Fe}_2\text{O}_3\text{(cr)} + \text{F}_2\text{(g)}.$$

Therefore, it was necessary that p_{O_2} over the two compartments be equal and constant. This was attempted by purging the cell, and operating it under a slow flow (20 cm^3·min^{-1}, 2.67 kPa positive pressure) of commercial argon (containing "80 ppm" oxygen). It is likely that the values of p_{F_2} were too low for any interference from gas-solid reactions, something which sometimes becomes a problem in oxygen potential measurements on couples with high equilibrium values of p_{O_2}.

The results can be combined with the values selected for Fe$_2$O$_3$(cr) (Section VII.2.2) and from CODATA [1989COX/WAG] to obtain values of $G(T)$ between $-$ 1164.6 and $-$ 1167.6 kJ·mol^{-1}. These results are very roughly in agreement with those of Jellinek and Rudat [1928JEL/RUD], but are incompatible with results of Johnson [1981JOH], Pervov *et al.* [1981PER/MUR] and Domange [1937DOM].

[1981SCH/KUS]

Oxygen fugacities, f_{O_2}, of several oxide couples were obtained by cell-potential measurements of solid-state galvanic cells of the type:

$$\text{Pt}|\text{X, Y}|\text{(CaO)ZrO}_2|\text{O}_2\text{ (air)}|\text{Pt},$$

where X, Y = Fe, "FeO" [wüstite] (1040 – 1473 K); Ni, NiO (1044 – 1477 K); Co, CoO (997 – 1633 K); "FeO", Fe_3O_4 [magnetite] (1084 – 1459 K); Fe_3O_4, Fe_2O_3 [hematite] (1133 – 1373 K).

Measurements were made after pre-equilibration in the presence of a reference buffer with similar oxygen fugacity, to minimize errors arising from oxygen diffusion. The cell design, with a tubular electrolyte, resembles that of Charette and Flengas [1968CHA/FLE], but with air in the outer annulus. Potential data were converted to oxygen fugacities before plotting the results. Smoothed values for representative temperatures were tabulated along with values from numerous earlier studies. The following relationships were obtained for iron oxide couples, adjusted by the reviewer to a standard-state pressure of 0.1 MPa.

Fe, "FeO": $\log_{10}(f_{O_2}) = \{-27403/(T/K) + 6.74\} \pm 0.02$ (1040 K $< T <$ 1473 K)

"FeO", Fe_3O_4: $\log_{10}(f_{O_2}) = \{-32928/(T/K) + 13.21\} \pm 0.02$ (1084 K $< T <$ 1459 K)

Fe_3O_4, Fe_2O_3: $\log_{10}(f_{O_2}) = \{-24949/(T/K) + 14.26\} \pm 0.04$ (1133 K $< T <$ 1373 K)

These relationships are included in data compilations shown in Section VII.2. For Fe_3O_4 + Fe_2O_3, additional measurements down to ~ 970 K show increased scatter and a negative deviation from the expression given above.

The authors also measured potentials corresponding to the solid-state galvanic cells

$$\mathrm{Pt|Fe,\ Fe_2SiO_4,\ SiO_2(cristobalite)|(CaO)ZrO_2|“FeO”,Fe|Pt} \qquad \text{(A)}$$

$$\mathrm{Pt|Fe_3O_4,\ Fe_2SiO_4,\ SiO_2(cristobalite)|(CaO)ZrO_2|“FeO”,Fe|Pt} \qquad \text{(B)}$$

Smoothed results for the oxygen fugacities were tabulated for 1173, 1273 and 1373 K. The authors point out that a major source of discrepancies in values calculated from such potential measurements are inconsistencies in values used for the reference electrode.

To calculate values of $\Delta_f H_m^\circ$ (Fe_2SiO_4, α, 298.15 K), the reported f_{O_2} values have been used, along with consistent auxiliary data for cristobalite ([1982RIC/BOT], [1998CAR/SAL]) and oxygen [1989GUR/VEY], and with the values selected in this review for the heat capacity and entropy of α-Fe_2SiO_4 (Section X.2.1.1.1) and Fe(cr) (Section V.2). Enthalpy of formation values ranging from − 1473.8 to − 1474.8 $kJ \cdot mol^{-1}$ are obtained.

The reported f_{O_2} values then were used with Schwab and Küstner's equation for the oxygen fugacities for the Fe | "FeO" | O_2 cell to derive values of 50.2, 46.8 and 43.4 mV for the potential of the cell (A) at 1173, 1273 and 1373 K. If the reference electrode values from O'Neill [1987NEI2] are used, an average value of − (1476.3 ± 0.6) $kJ \cdot mol^{-1}$ is obtained for $\Delta_f H_m^\circ$ (Fe_2SiO_4, α, 298.15 K), where the uncertainty represents 2σ, and the results show about half the drift found in the analysis using the authors' values for the reference electrode.

Achieving stable results with the cell (B) can be difficult [1987NEI2] and the fayalite-SiO_2-magnetite results are not used further in the present review.

[1982ARG]

The author reported results of thermogravimetric analysis of samples of hydrated iron(II) chloride ($FeCl_2 \cdot 4H_2O$). Samples were pre-equilibrated in air with a constant partial pressure of water (done using aqueous H_2SO_4 solutions). Loss of water (in air) was found at 323 to 353 K (to form the dihydrate), 393 to 418 K (to form the monohydrate) and 428 to 453 K to form the anhydrous salt. The heating rate was not reported, but the fractional weight losses were reported to depend on sample size.

[1982COB/MUR]

This report by Cobble *et al.* is primarily a review of chemical thermodynamic data of interest to those carrying out calculations with respect to nuclear reactor water chemistry. However, Appendix B of the report describes a study done to measure the heat of solution of $FeCl_2$(cr) in 0.005 m $HClO_4$ as a function of the final solute concentration at 25.00 °C. Nine measurements (0.00218 to 0.0107 m $FeCl_2$ final) were done to determine the heat of solution of anhydrous $FeCl_2$(cr). The results cover essentially the same concentration range as the study of Cerutti and Hepler [1977CER/HEP], and are in good agreement with the results of the earlier study. The enthalpy of solution values were corrected to values for $I = 0$ using estimated heats of dilution (apparently neglecting the contribution of the perchloric acid to the ionic strength) and a further extrapolation against molality. The reported value for $I = 0$ was $-(82.89 \pm 0.33)\ \text{kJ}\cdot\text{mol}^{-1}$.

In the present review different procedures were attempted to estimate the heats of dilution for the 1:1 and 2:1 electrolyte mixtures. There are no good useful experimental studies for these moderately low molalities, and differences between various theoretical treatments are generally less than $0.3\ \text{kJ}\cdot\text{mol}^{-1}$. First, Equations (IX.70) and (IX.71) from Grenthe *et al.* [1997GRE/PLY2] were used neglecting the ~ 0.005 m $HClO_4$ in the solutions. No tabulated values are available for ε as used in these equations, and these terms were neglected. The average heat of solution, corrected to $m = 0$ in this manner is $-(82.72 \pm 0.12)\ \text{kJ}\cdot\text{mol}^{-1}$, about $0.2\ \text{kJ}\cdot\text{mol}^{-1}$ less negative than to the $-82.9\ \text{kJ}\cdot\text{mol}^{-1}$ reported by the authors. The SIT limiting-law heat of dilution correction for a 2:1 electrolyte in a 0.005 m 1:1 electrolyte is $-0.53\ \text{kJ}\cdot\text{mol}^{-1}$, and this might be added to the value from the SIT treatment. However, it also seems that all limiting-law heat of dilution corrections are likely to be greater than the actual correction [1959LAN].

A treatment using the equation of Silvester and Pitzer [1978SIL/PIT] for a 2:1 electrolyte, but at the total ionic strength of each solution, leads to values of $-(82.76 \pm 0.13)\ \text{kJ}\cdot\text{mol}^{-1}$ as the heat of dissolution of $FeCl_2$(cr) to infinite dilution.

In the present review, the result based on the Silvester and Pitzer equation [1978SIL/PIT] is used for the heat of dissolution of $FeCl_2$(cr) to infinite dilution, without further correction, and an increased uncertainty of $0.50\ \text{kJ}\cdot\text{mol}^{-1}$ is assigned. The primary source of this uncertainty is the heat of dilution corrections.

[1982GAM/REI]

The authors attempted to obtain the value of the standard potential of the couple Fe^{2+}/Fe(0) by measuring the equilibrium constant of a redox reaction between Fe(0) and Tl^+, an oxidant ion that belongs to the redox couple Tl^+/Tl(0) and which has a standard potential value close to $E^\circ(Fe^{2+}/Fe(0))$.

The progress of the reaction: $2\,Tl^+ + Fe(0) \rightleftharpoons Fe^{2+} + 2\,Tl(0)$ was followed.

Gamsjäger *et al.* reported that $E^\circ(Fe^{2+}/Fe(0)) = -(0.435 \pm 0.005)$ V. They worked at 50 °C and claimed that the equilibrium was reached after 7 to 11 days at that temperature. The increase in temperature considerably improved the approach to equilibrium. Plots of $\log_{10} m_{Fe^{2+}}$ *vs.* $\log_{10} m_{Tl^+}$ for various Tl^+ initial concentrations were used to check this. A slope value close to 2 at the end of an experiment ensured that equilibrium had been reached. However the extrapolation to standard conditions became more difficult because of the necessary temperature and ionic strength corrections. The authors used the following assumptions: the partial molal entropy of Fe^{2+} is independent of the temperature and of the ionic strength; the Davies approximation can be used to calculate the ionic strength correction. The extrapolation to standard conditions is problematic.

Because of the slow rate of the reactions in which the two solids are involved, and also because of the excessively large difference between the values of $E^\circ(Fe^{2+}/Fe(0))$ and $E^\circ(Tl^+/Tl(0))$, the standard potential derived from these experiments is not used further in the present review.

[1982NOR/LIN]

An edta complexation method was used to obtain free Fe^{3+} concentrations and hence $a_{Fe^{3+}}\,a^3_{OH^-}$ activity products for dissolved iron in equilibrium with three nearly neutral soils. Simultaneous equilibria involving $Fe(edta)^-$, $Fe(OH)(edta)^{2-}$, and $Ca(edta)^{2-}$ complexes were evaluated. An average value of $a_{Fe^{3+}}\,a^3_{OH^-} = 10^{-(39.3 \pm 0.4)}$ was obtained, which is close to the values expected for ferrihydrite or poorly crystalline FeOOH or γ-Fe_2O_3 as the saturating phase. These results have not been re-evaluated, because edta complexes are beyond the scope of the current review.

[1982ROB/FIN]

The heat-capacity values of a carefully prepared sample of fayalite (α-Fe_2SiO_4) [1980FIN/CLA] were measured between 5.11 and 381.47 K. Special care was taken to determine values near the λ-transition at (64.88 ± 0.03) K. It was reported that the iron(III) content was a maximum of 0.86%, but analysis of other samples prepared by the same method indicated [1982KOP/ABR] that the amount of iron(III) was likely much less (< 0.001% by electron paramagnetic resonance, < 0.27% by Mössbauer spectroscopy). A value of (131.9 ± 0.1) $J \cdot K^{-1} \cdot mol^{-1}$ is reported for $C^{o}_{p,m}$ at 298.15 K. For the purposes of fitting a single function to all the calorimetry results, the uncertainties in the individual values for the heat capacities between 255.09 and 381.47 K were estimated in the present review as ± 0.2 $J \cdot K^{-1} \cdot mol^{-1}$.

The heat capacities were integrated to determine values of $(S^{o}_{m,T} - S^{o}_{m,5.1})$, and the authors calculated their experimental data from 5.1 to 0 K using a linear extrapolation of $C^{o}_{p,m}/T$ *vs.* T^2 to obtain a value of (151.0 ± 0.2) $J \cdot K^{-1} \cdot mol^{-1}$ for S^{o}_{m} at 298.15 K. In the present review, a set of polynomials and exponential functions was fit to the reported $C^{o}_{p,m}/T$ values. These functions were integrated, and (with the same assumption regarding the entropy contribution below 5.1 K) a similar value for the entropy, at 298.15 K, 151.1 $J \cdot K^{-1} \cdot mol^{-1}$, was obtained. In the present review, the original value of the authors is accepted for S^{o}_{m}(Fe_2SiO_4, cr, 298.15 K), as is the uncertainty.

[1982WAT]

Differential-scanning calorimetry was used to determine values for the molar heat capacities of α-Fe_2SiO_4, γ-Fe_2SiO_4 and $FeSiO_3$ ("clinoferrosilite"). The heating rate was 20 $K \cdot min^{-1}$. Molar heat capacities were reported (graphically) at intervals of 10 K for temperatures between 350 and 700 K for the Fe_2SiO_4 solids, and to 610 K for the clinoferrosilite. Although there is some scatter, the values for α-Fe_2SiO_4 are within a few per cent of those based on the drop-calorimetry results of Orr [1953ORR]. The values for the α-form are an average of (4.8 ± 2.4) $J \cdot K^{-1} \cdot mol^{-1}$ greater than those of the γ-form. The difference (calculated in this review by digitization of the information in the authors' Figure 5) decreases slightly with increasing temperature. The authors also reported 3-parameter equations as fit to the data. For the purposes of fitting a single function to all the calorimetry results for each compound, the uncertainties in the individual (digitized) values for the heat capacities were estimated in the present review as ± 1.5 $J \cdot K^{-1} \cdot mol^{-1}$ (However, the discussion in Gamsjäger *et al.* [2005GAM/BUG] suggests that the uncertainties may be somewhat larger).

The synthesis conditions used by Watanabe to prepare clinoferrosilite (900 °C, 7.0 GPa) would be expected to lead initially to a high-pressure form (C2/c) [1997WOO/ANG]. It is not clear whether the sealed aluminium DSC pan would have been suitable for high-pressure measurements. It also seems unlikely that the X-ray diffraction and microscopic "observations" were done under pressure. Thus, the measurements may well have been done on a sample of clinoferrosilite that had been transformed to the $P2_1/c$ structure, as the high-pressure C2/c form cannot be maintained when the pressure is lowered [1997WOO/ANG] (also see [1994HUG/WOO], [1996HUG/SHA]). In the present review it is assumed that the clinoferrosilite sample had the $P2_1/c$ structure.

[1982WON/MOL]

Although not the primary focus of the paper, a curve (Figure 2 (a) A) is shown with measurements of the magnetic heat capacity for $FeCl_2$(cr) for temperatures between 16 and 28 K. The heat capacity of the sample was measured by a thermal-relaxation method, and corrected for the heat capacity of the substrate and grease used to hold the sample in place. The lattice correction was determined by comparison with a sample of $MgCl_2$(cr). The results of the measurements are similar to those reported earlier by Lanusse *et al.* [1972LAN/CAR]. They show the same temperature dependence for the heat capacities as was reported by Trapeznikowa and Schubnikow [1935TRA/SCH], but the heat-capacity maximum is about 0.5 K higher (near 23.8 K, the authors estimate a bias in their temperature measurements of ~ 0.1 K). As only the magnetic contribution is shown in the figure, the values are markedly less than those reported in the earlier work—about 50% of the Trapeznikowa and Schubnikow values at 17 and 28 K. Integration of a plot of $T^{-1}C_{p,\text{mag}}$ *vs.* temperature indicates that between 16 and 28 K the anomaly contributes approximately 3.3 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ to the value of S°_{m}.

[1983BOH/MET]

Unfortunately, this is only an extended conference abstract, and many details were omitted. The heat capacity of $FeSiO_3$(cr) was determined from 8 to 350 K by intermittent adiabatic calorimetry. The sample used had < 1 per cent Fe(III). A λ-transition was found at 39 K, attributed to antiferromagnetic ordering, and the authors reported a value of 94.56 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ (22.6 $\text{cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) for S°_{m} (298.15 K) from integration of $C^{\circ}_{p,\text{m}}/T$. However, no value for the heat capacity was published. Apparently DSC measurements also were made, but again no information was provided. The measurements themselves were probably of good quality, but characterization of the sample was not reported. The nomenclature used (with reference to "buffers in orthopyroxene-bearing systems") and contemporary work by Bohlen and Boettcher, [1981BOH/BOE] indicate that the samples were probably a quenched orthoferrosilite (space group *Pbca*?). Therefore, it is not completely clear which form of $FeSiO_3$(cr) was used, and the reported value can be used only if a large uncertainty is assigned.

[1983KHA/TAR]

Khandkar *et al.* reported potentials for the galvanic cell Ag(cr) | AgI(cr) | Fe(cr)-FeI_2(cr) from 393 to 500 K, primarily for temperatures above the AgI(β)-AgI(α) transition at 422.5 K. Since that paper was published, Shaviv *et al.* [1989SHA/WES] have published a very careful set of measurements on the heat capacity of AgI(cr). Use of their values for $C_{p,\mathrm{m}}(T)$ and S°_{m} (298.15 K) allows a more satisfactory treatment of the data of Khandkar *et al.*

The entropy of Ag(cr) at 298.15 K is taken from the CODATA compilation [1989COX/WAG], and the heat-capacity equation is from Pankratz [1984PAN]. The values for Fe(α) are from the present review (Section V.2). The Gibbs energy of dissolution of AgI(cr, 298.15 K) in water is taken as – 91.85 $\mathrm{kJ \cdot mol^{-1}}$, based on the evaluation of Parker *et al.* [1976PAR/WAG]. If the value, 114.44 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ [1989SHA/WES], is used for S°_{m} (AgI, cr, 298.15 K), then the value of $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ (AgI, cr, 298.15 K) is – 111.37 $\mathrm{kJ \cdot mol^{-1}}$. With the corresponding values for $C_p(T)$ and the transition quantities at 420 K [1989SHA/WES], G(AgI, cr) is calculable at the temperatures of the cell-potential measurements. From the cell potentials $\Delta_{\mathrm{r}}G$ (A.129) and the Gibbs energy functions for AgI(cr), Ag(cr) and Fe(cr) are calculated at each temperature, and hence, $G(T, \mathrm{FeI_2(cr)})$.

$$2\,\mathrm{Ag(cr)} + \mathrm{FeI_2(cr)} \rightleftharpoons 2\,\mathrm{AgI(cr)} + \mathrm{Fe(cr)} \qquad \text{(A.129)}$$

Shaviv *et al.* [1989SHA/WES] indicated that the heat capacities of AgI(β) and a AgI(β/γ) mixture are indistinguishable near room temperature (also see [1995YOS/INA]). Between 405 and 425 K, these forms are converted to the α-form. Most of the potential measurements were done at temperatures above the transition temperature, and for the sake of simplicity only the results above 425 K were used in the present reanalysis.

After omission of one badly discrepant data point at 476.15 K (203 °C)[1], a least-squares fit to $G(T)$ as a function of temperature, and using the equation selected in Section VIII.3.4.1.1 for $C_p(\mathrm{FeI_2}, \mathrm{cr}, T)$, the values – 114.4 $\mathrm{kJ \cdot mol^{-1}}$ and 181.6 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ are obtained for $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($\mathrm{FeI_2}$, cr, 298.15 K) and S°_{m} ($\mathrm{FeI_2}$, cr, 298.15 K), respectively. The deviations in potentials for similar temperatures in the data set are of the order of 1 mV, or ~ 0.2 $\mathrm{kJ \cdot mol^{-1}}$ in $\Delta_{\mathrm{r}}G_{\mathrm{m}}$. However, the values for $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($\mathrm{FeI_2}$, cr, 298.15 K) and S°_{m} ($\mathrm{FeI_2}$, cr, 298.15 K) are highly correlated (linear correlation coefficient greater than 0.99). For example, if only the potentials for temperatures above 450 K are used, the values – 115.5 $\mathrm{kJ \cdot mol^{-1}}$ and 179.6 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ are obtained for $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($\mathrm{FeI_2}$, cr, 298.15 K) and S°_{m} ($\mathrm{FeI_2}$, cr, 298.15 K). Nevertheless, there are considerably increased deviations if the value – 118.7 $\mathrm{kJ \cdot mol^{-1}}$ for $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($\mathrm{FeI_2}$, cr, 298.15 K) from Parker and Khodakovskii [1995PAR/KHO] is used. Therefore, in the present review, the uncertainties in the values for $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($\mathrm{FeI_2}$, cr, 298.15 K) and

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[1] In the authors' Table 1, there are two measurements reported for 203 °C, 140.77 mV and 105.05 mV. Most of their measurements are within 1 mV for similar temperatures, and it is suspected that "140.77" is a typographical error for a value between 104 and 105 mV mV. The points plotted in the authors' Figure 1 do not show this anomalous point (unless the plotted value at 203 K is an average not very different from 105 mV).

S°_{m} (FeI_2, cr, 298.15 K) from these measurements are estimated as ± 1.5 $kJ\cdot mol^{-1}$ and ± 3.0 $J\cdot K^{-1}\cdot mol^{-1}$, respectively.

If the data are reanalysed with the value for $\Delta_f H^{\circ}_{m}$ (FeI_2, cr, 298.15 K) as selected in the present review, a value of 174.0 $J\cdot K^{-1}\cdot mol^{-1}$ is obtained for S°_{m} (FeI_2, cr, 298.15 K).

[1983KNA]

Phase boundaries for wüstite were calculated from a Gibbs energy expression, developed from the partial enthalpy and entropy values for oxygen, as assessed by Giddings and Gordon [1973GID/GOR]. Results are compared with experimental values from 10 different sources. A eutectoid point of 843 K at the composition $FeO_{1.0563}$ was obtained.

[1983MYE/EUG]

The authors used an oxygen-sensor electrode of the form

$$Pt|O_2(1\ atm.)|(CaO)_{0.15}(ZrO_2)_{0.85}|O_2(f_i)|Pt$$

to measure the fugacity of oxygen in a CO_2/H_2 mixture which was equilibrated with mixtures of iron, SiO_2(quartz) and fayalite at twelve temperatures from 1241 to 1405 K. The CO_2/H_2 ratio was adjusted so that there was no oxidation or reduction of the sample as determined by weight gain or loss according to a thermogravimetric balance. The oxygen sensor was calibrated from several series of cell-potential, weight and temperature measurements on the oxidation of iron to wüstite.

Experimental values were reported for $-\log_{10} f_{O_2}$. Based on consistent auxiliary data for quartz ([1998CAR/SAL], [1989COX/WAG]) and oxygen [1989GUR/VEY], and with the values selected in this review for the heat capacity and entropy of α-Fe_2SiO_4 (Section X.2.1.1.1) and Fe(cr) (Section V.2), values between − 1464.6 $kJ\cdot mol^{-1}$ and − 1469.6 $kJ\cdot mol^{-1}$ are calculated for $\Delta_f H^{\circ}_{m}$ (Fe_2SiO_4, α, 298.15 K).

These values are 5 to 10 $kJ\cdot mol^{-1}$ less negative than those from most other measurements except those of Nafziger and Muan [1967NAF/MUA] and the lower temperature measurement of Williams [1971WIL]. However, if a back-calculation is done, and the reference-electrode potentials preferred by O'Neill [1987NEI2] are used, the values for $\Delta_f H^{\circ}_{m}$ (Fe_2SiO_4, α, 298.15 K) are between − 1471.4 and − 1475.4 $kJ\cdot mol^{-1}$ (but still show a drift to more negative values at higher temperatures; average − (1473.66 ± 2.38) $kJ\cdot mol^{-1}$, 2σ uncertainty). These values are much more consistent with the results of other experimental work [1952KIN], [1968KIT/KAT], [1977SCH/SOH], though the measurements of Myers and Eugster [1983MYE/EUG] may still have suffered from some systematic problem.

In this study, Myers and Eugster used the same electrochemical technique to measure the oxygen fugacities of the following couples: Fe-wüstite at 1073 to 1533 K; wüstite-magnetite at 1273 to 1533 K; magnetite-hematite at 1313 to 1543 K. O'Neill

[1987NEI2] concluded that these data are internally inconsistent, *e.g.*, with respect to the Fe-wüstite-magnetite eutectoid temperature. The results are therefore excluded from the current review of iron oxides (Section VII.2).

[1983ROG/KOZ]

The authors measured potentials of the solid-state galvanic cells

$$\mathrm{Pt|O_2|Fe_2SiO_4,\ SiO_2(s)|Fe(II) + \beta\text{-}alumina|``FeO",O_2|Pt}$$

at 870 to 1200 K to determine the oxygen chemical potentials corresponding to equilibrium. The composition of the electrolyte corresponded, approximately, to $Fe_{0.26}Na_{0.48}Al_9O_{14}$.

To calculate $\Delta_f H_m^\circ$ (Fe_2SiO_4, α, 298.15 K), the potentials (reported for rounded temperatures in the authors' Table 1) are used[1] along with the reference potential values from O'Neill [1987NEI2], consistent auxiliary data for quartz ([1989COX/WAG], [1998CAR/SAL]) and oxygen [1989GUR/VEY], and with the values selected in this review for the heat capacity and entropy of α-Fe_2SiO_4 (Section X.2.1.1.1) and Fe(cr) (Section V.2). Values ranging from − 1469.2 to − 1471.4 $kJ \cdot mol^{-1}$ are obtained. These rather low values showed a slight drift to more positive values at higher temperatures. The values were not used further in the present review except for comparison purposes.

[1983SOL/BON]

The authors investigated fluoride complexes of divalent transition metals in methanol and water using 0.05 M tetraethylammonium perchlorate (TEAP) as the inert electrolyte. In the case of iron(II), specific precautions were taken to avoid oxidation. Possible traces of the strongly complexing iron(III) cation were reduced electrochemically under oxygen-free conditions. The authors reported (28 ± 4) $dm^3 \cdot mol^{-1}$ as the value of β_1(298.15 K, 0.05 M $(Et)_4NClO_4$), evaluated with a value of a "mixed" HF-dissociation constant, $K' = a_{H+} \cdot [F^-]/[HF]$, of $(9.4 \pm 0.5) \times 10^{-4}$, which was previously determined potentiometrically in aqueous 0.05 M $(Et)_4NClO_4$. A sensitivity analysis was also performed in this study: the value of β_1 became (32 ± 4) $dm^3 \cdot mol^{-1}$, and (25 ± 5) $dm^3 \cdot mol^{-1}$, respectively, when values of 9.9×10^{-4} and 8.9×10^{-4} were used for K'. The present review thus accepts the reported formation constant with an increased uncertainty range, *i.e.*, β_1(298.15 K, 0.05 M $(Et)_4NClO_4$) = (28 ± 7) $dm^3 \cdot mol^{-1}$. An exact conversion to the molal scale according to Söhnel and Novotny [1985SOH/NOV] is not possible due to the lack of parameters for TEAP solutions. If parameters for NH_4ClO_4 are taken instead, the conversion factor is estimated to be 1.006 $kg \cdot dm^{-3}$ at 298.15 K and, hence, β_1(298.15 K, 0.05 m $N(Et)_4ClO_4$) = (28 ± 7) $kg \cdot mol^{-1}$.

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[1] Values of $\Delta_r G$ for 1000 K and 1200 K, calculated from the authors' Table 1, differed slightly from those calculated using the authors' equation (5) and all the values from the authors' equation (4) differed slightly from those calculated from the authors' equation (5).

For methanol solvent (with 0.05 M TEAP) a value of β_1(298.15 K, 0.05 M $(Et)_4NClO_4$ in MeOH) of (6100 ± 1000) $dm^3\cdot mol^{-1}$ was reported.

[1983TAM/ITO]

The kinetics of transformation of γ-FeOOH to stoichiometric Fe_3O_4 (Fe^{2+} + 2γ-FeOOH(s) → Fe_3O_4(s) + $2H^+$) at 25 °C were initiated by an increase in pH. As observed previously for the accelerated precipitation of goethite caused by Fe^{2+} adsorption (followed by *in situ* oxidation in that case), above pH 7.3 Tamaura *et al.* report that Fe^{2+} is adsorbed rapidly onto the γ-FeO(OH) surface according to the reaction:

$$Fe^{2+} + -s\{FeOOH\} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Fe^{2+} - s\{FeOOH\} \qquad (A.130)$$

where $-s$ represents an active surface site. In the initial period of *ca.* 2 minutes, the number of surface sites is virtually constant such that $k_1^{'}$ = 0.11 min^{-1} (k_{-1} = 1.7 × 10^{-4} min^{-1}) while virtually no Fe_3O_4 has formed. However, one hydrogen ion is shown to be released in this adsorption step and the subsequent transformation step, such that the former should be formally written as:

$$Fe^{2+} + 2\gamma - FeOOH(s) + H_2O(l) \xrightarrow{k_1'} [\gamma - FeOOH]_2FeOH^+(s) + H^+ \qquad (A.131)$$

A second transformation step is also first order in iron(II) concentration and involves release of another hydrogen ion as the intermediate product of Reaction (A.131) is converted to magnetite (allowing the rapid adsorption of another Fe^{2+} ion) according to the equivalent reaction, *viz.*,

$$[\gamma - FeOOH]_2FeOH^+(s) \xrightarrow{k_2} Fe_3O_4(s) + H_2O(l) + H^+ . \qquad (A.132)$$

The value of k_2 increases with pH indicating that the degree of hydrolysis of the adsorbed Fe^{2+} ion plays a role in the evaluation of the rate constant for this second stage. However, the values for k_2 are of a similar order of magnitude to that for $k_1^{'}$.

There appears to be some conflicting arguments regarding whether adsorption of Fe^{2+} ion also occurs on the nearly formed magnetite surfaces and the final statement that Reaction (A.132) could also include a dissolution/precipitation step seems to this reviewer to be highly unlikely. Nevertheless, this is a most interesting study that underscores the importance of adsorption of Fe^{2+} (or other divalent metal cations in the case of the formation of mixed-metal ferrites) and establishes that the rates of transformation are very rapid (on the scale of minutes) at 25 °C. No thermodynamic data are presented in this paper.

[1984HAZ/JEA]

The structure and physical properties of wüstite are reviewed with particular attention to postulated defect clusters and related structural modifications within the wüstite stability field.

[1984LAV/TIM2]

This seems to have been a very careful study of the heat of combustion of samples of Fe(cr) with chlorine gas. Measurements were done using eight samples each of two specimens of high-purity iron. Corrections were carried out for the known impurities in the samples, and a value of $\Delta_f H_m^o$ ($FeCl_3$, cr, 298.15 K) = – (396.02 ± 0.14) $kJ \cdot mol^{-1}$ was reported (95% confidence limits). With the current value of the atomic mass of iron [2003LOS], the value of $\Delta_f H_m^o$ ($FeCl_3$, cr, 298.15 K) is – (396.00 ± 0.14) $kJ \cdot mol^{-1}$.

[1984NOV/BEL]

Heats of dissolution at 298 K of $FeCl_3$(cr) (– (138.22 ± 0.27) $kJ \cdot mol^{-1}$) and $FeCl_3 \cdot nH_2O$(cr) (n = 2.0, 2.5, 3.5, 6.0) were measured in 150 mL of 0.65 N $HClO_4$ (0.67 m) to produce solutions with a final iron concentration of ~ 0.015 M. Six measurements were done for each salt.[1]

$FeCl_3 \cdot 2H_2O$	– (94.40 ± 0.29) $kJ \cdot mol^{-1}$
$FeCl_3 \cdot 2.5H_2O$	– (86.37 ± 0.42) $kJ \cdot mol^{-1}$
$FeCl_3 \cdot 3.5H_2O$	– (61.16 ± 0.32) $kJ \cdot mol^{-1}$
$FeCl_3 \cdot 6H_2O$	– (27.21 ± 0.28) $kJ \cdot mol^{-1}$

The enthalpies of formation of the hydrated salts can then be calculated using the selected enthalpy of formation of $FeCl_3$(cr) and the partial molar enthalpies of formation of H_2O in the perchloric acid medium [1965PAR], [1989COX/WAG] (– (285.826 ± 0.041) $kJ \cdot mol^{-1}$):

$$\Delta_f H_m^o (FeCl_3) - \Delta_f H_m^o\ FeCl_3 \cdot 2.0H_2O) = (615.47 \pm 0.43)\ kJ \cdot mol^{-1}$$

$$\Delta_f H_m^o (FeCl_3) - \Delta_f H_m^o\ FeCl_3 \cdot 2.5H_2O) = (766.41 \pm 0.54)\ kJ \cdot mol^{-1}$$

$$\Delta_f H_m^o (FeCl_3) - \Delta_f H_m^o\ FeCl_3 \cdot 3.5H_2O) = (1077.44 \pm 0.48)\ kJ \cdot mol^{-1}$$

$$\Delta_f H_m^o (FeCl_3) - \Delta_f H_m^o\ FeCl_3 \cdot 6.0H_2O) = (1825.95 \pm 0.49)\ kJ \cdot mol^{-1},$$

---

[1] There appear to be two typographical errors in the reported values tabulated for $FeCl_3 \cdot 2.5\ H_2O$. Based on the reported values for $-\Delta H^o$, the first value for "ΔR" for this salt is incorrect (it probably should have been 111.8), and the third value for $-\Delta H$, 86.12 $kJ \cdot mol^{-1}$, is not the value that would be calculated from the numbers in the other three columns, 86.72 $kJ \cdot mol^{-1}$ (nor would it give the reported average value). For all the hydrated salts, recalculation suggests a minor systematic difference in auxiliary molar mass values between those used in the original paper and in the present review. The differences are of the order of 0.01 to 0.02 $kJ \cdot mol^{-1}$, and have been ignored. The reported average values of $-\Delta H^o$ [1984NOV/BEL] have been accepted in the present review, and the standard deviation values were used to calculate the 95% confidence limits for the enthalpies of solution.

where the uncertainties are 95% confidence limits. Details on the syntheses and analyses are lacking, and the actual uncertainties are likely somewhat larger. In the present review the differences are assigned an uncertainty of 1.5 $\text{kJ}\cdot\text{mol}^{-1}$.

The value of the heat of solution for the anhydrous salts is inconsistent (by approximately 10 $\text{kJ}\cdot\text{mol}^{-1}$) with results from an unpublished study by Efimov *et al.* (reported by Parker and Khodakovskii [1995PAR/KHO]).

[1984ROB/HAS]

Heat-capacity measurements (specific heats) from adiabatic calorimetry (4.98 to 373.3 K) and differential-scanning calorimetry (339.8 to 449.9 K) were reported for siderite (similar measurements also were reported for $MnCO_3$(cr)). The siderite sample was reported as having the composition $(Fe_{0.956}Mn_{0.042}Mg_{0.002})CO_3$.

Heat capacities for $FeCO_3$(cr) were obtained from the specific heats by applying corrections for the $MnCO_3$(cr) content, but these corrections were small ($< 0.1\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$).

The DSC results do not mesh especially well with the adiabatic-calorimetry results. The DSC specific-heat values (for both $MnCO_3$(cr) and siderite) are systematically lower than the adiabatic-calorimetry results (by ~ 1%). The authors' equation for $C_p(T)$ (298.15 to 600 K) looks to be fitted to both types of calorimetric data, but is not constrained to match the summary values in Table 6 of their paper. The value reported for C_p($FeCO_3$, cr, 298.15 K) is 82.44 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ from adiabatic calorimetry; the authors' equation for $C_p(T)$ generates a value of 82.25 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

A least-squares treatment then was used to obtain an equation for $C^{\circ}_{p,\text{m}}(T)$ using the heat capacities weighted according to the authors' stated precision for the specific heat measurements.

$$[C^{\circ}_{p,\text{m}}]^{500\,\text{K}}_{230\,\text{K}}(\text{FeCO}_3,\text{ cr}, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 52.390 + 125.798 \times 10^{-3}\,(T/\text{K}) - 4.004 \times 10^{5}\,(T/\text{K})^{-2} - 0.3308 \times 10^{-4}\,(T/\text{K})^{2}.$$

The uncertainty in $C^{\circ}_{p,\text{m}}$($FeCO_3$, cr, 298.15 K) is estimated as ± 2 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ because of the > 4% impurities and the discrepancy between the adiabatic calorimetry and DSC calorimetry results near 350 K.

The authors reported two slightly different values for S°_{m}($FeCO_3$, cr, 298.15 K) — (95.47 ± 0.15) $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$and (95.29 ± 0.20) $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. In the present review, a set of polynomials and exponential functions was fit to the raw C_p/T values. The functions were integrated, and a similar value for the entropy, at 298.15 K, 95.52 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, was obtained.

At temperatures below 30 K the value of C_p($MnCO_3$) is much greater than that of C_p($FeCO_3$). Therefore, if the solid is 4% $MnCO_3$ there may be a major contribution from the $MnCO_3$ to the measured specific heats at the lower temperatures (or perhaps not, if the alignment of spins is destroyed by dilution of the $MnCO_3$ in the $FeCO_3$). However, no allowance for this was made in the present reintegration. The authors indicate that in their original integration, the corrections to C_p were made with a maximum effect of 0.4% (presumably on the value of $S^{\circ}_{\rm m}$ ($FeCO_3$, cr, 298.15 K).

For temperatures below 5 K the authors assumed a smooth extrapolation of $C^{\circ}_{p,\rm m}/T$ *vs.* T^2, and obtained a contribution of 0.004 $\rm J{\cdot}K^{-1}{\cdot}mol^{-1}$ to $S^{\circ}_{\rm m}$ ($FeCO_3$, cr). Based on the results of Kalinkina [1963KAL] to 1.6 K, this appears to be a reasonable assumption.

In the present review, the original integration of the authors is accepted (*i.e.*, a value of 95.47 $\rm J{\cdot}K^{-1}{\cdot}mol^{-1}$ for $S^{\circ}_{\rm m}$ ($FeCO_3$, cr, 298.15 K)), but the estimated uncertainty is increased to ± 1.00 $\rm J{\cdot}K^{-1}{\cdot}mol^{-1}$ because of the impurities in the siderite sample.

[1984STE/CAR]

A diphenyl ether drop calorimeter was used to determine enthalpy differences for α-Fe_2SiO_4 between temperatures near the (incongruent) melting point of fayalite and 300 K. Below the melting region, enthalpy differences were reported from 985 and 1351 K to 300 K. Three measurements were made at each temperature. At the higher temperature, the values mesh well with values from the earlier work of Orr [1953ORR], whereas at the lower temperature the enthalpy differences are 1-3 $\rm kJ{\cdot}mol^{-1}$ greater. Furthermore, at 985 K, the reported values span 3 $\rm kJ{\cdot}mol^{-1}$. The measurements were done with extreme care, but the authors were unable to suggest a reason for the inconsistencies. For the purposes of fitting a single function to all the calorimetry results, the individual values for the enthalpy differences were estimated (in the present review) to have uncertainties of 0.5%. Also, for the fitting, the heat-capacity values of Robie *et al.* [1982ROB/FIN] were used to increase the enthalpy differences by 0.24 $\rm kJ{\cdot}mol^{-1}$ to correspond to $H_T - H_{298.15\,\rm K}$, rather than $H_T - H_{300\,\rm K}$.

[1985AGO]

Agoshkov [1985AGO] reported Calvet immersion calorimetry results ($H_T - H_{298.15\,\rm K}$) for the (metastable high-pressure) γ- form of Fe_2SiO_4(cr) at temperatures from 240 to 1170 K. These lead to heat-capacity values for temperatures above 350 K that are approximately mid-way between those of Watanabe for γ-Fe_2SiO_4 and the results of Orr [1953ORR] for α-Fe_2SiO_4 (except above 1000 K). However, the calculated heat-capacity values at lower temperatures are close to, or greater than those for α-Fe_2SiO_4 [1941KEL], [1982ROB/FIN]. Agoshkov also reported that he had carried out a limited set of measured values of ($H_T - H_{298.15\,\rm K}$) for α-Fe_2SiO_4 and derived values for $[C^{\circ}_{p,\rm m}]^{900\,\rm K}_{400\,\rm K}$ that were within 1.2% of tabulated values for fayalite (probably based on Orr [1953ORR]). No numerical results were reported for α-Fe_2SiO_4, though it was confirmed that the heat capacity for the γ-form is less than for the α- form. For this reason, the heat-capacity values for γ-Fe_2SiO_4 based on the results of Agoshkov appear to be too positive at lower temperatures (also see the results of Watanabe [1982WAT] for several silicate solids).

Slight surface oxidation was reported for samples at temperatures below 600 K, and some conversion to the γ- form of Fe_2SiO_4 to the α- form was reported at temperatures near 1200 K [1985AGO]. It also is possible that there was a systematic error in the method used to carry out enthalpy-difference measurements at temperatures below 300 K (with cooling). In the present review, because of the inconsistency of the low-temperature results with those for α-Fe_2SiO_4, only the measurements for $T \geq 337$ K from Agoshkov's work are accepted (with the statistical uncertainties assigned by Agoshkov).

[1985CHO/PHA]

The results of solubility measurements in the $FeCl_2\cdot4H_2O$(cr)-NaCl(cr)-H_2O(l) system are reported. The measurements were done using a "visual polythermal method". The measured solubilities of $FeCl_2\cdot4H_2O$(cr) (and the values from the authors' fitted equation) are about 2% lower than reported by Schäfer [1949SCH] and by Schimmel [1928SCH], [1952SCH3] for 20 to 25 °C (~ 3% in the saturation molality), but agree to within better than 1% for 40 and 60 °C. It was found that substantial supercooling was required to initiate crystallization from solution. The dihydrate solid was suggested to be the stable iron(II) chloride phase above 74.6 °C.

[1985DYR]

By using the chemical analogue (Linear Free Energy Relationship) approach with dithizone as a model ligand and stability constants for cadmium and mercury sulfides as reference, the stability constants of sulfide complexes of Cu, Mn, Fe, Co and Ni were estimated. The values for iron sulfides were estimated to be $\log_{10} {}^*K = -4.63$ for $Fe^{2+} + 2H_2S(aq) \rightleftharpoons Fe(HS)_2(aq) + 2H^+$, $\log_{10} {}^*K = 10.91$ for $Fe^{2+} + 2H_2S(aq) \rightleftharpoons FeHS_2^- + 3H^+$, $\log_{10} {}^*K = 2.8$ for $FeS(s) + 2H^+ \rightleftharpoons Fe^{2+} + H_2S(aq)$ at $I = 0$ and 298 K, where $\log_{10} {}^*K = 6.88$ for $H^+ + HS^- \rightleftharpoons H_2S(aq)$ and $\log_{10} {}^*K = 14.15$ for $H^+ + S^{2-} \rightleftharpoons HS^-$ were used. The estimated values depend on the cadmium and mercury values and on whether dithizone is a good analogue for sulfide. Since no experimental evidence for iron sulfide complexes and their stability constants was presented, the results are not taken into consideration in this review.

[1985HIL/VIS]

This paper describes a careful Knudsen-cell mass-spectroscopic study of iron(II) iodide at 605 to 725 K. The emphasis was on determining the gas-phase speciation and establishing enthalpy of reaction values between FeI_2(cr) and the various gas-phase iodine-containing species (FeI_2(g), $(FeI_2)_2$(g), $(FeI_2)_3$(g), FeI_3(g), I(g), I_2(g)).

The experimental work appears to have been carried out very carefully, and both second-law and third-law analyses were attempted. Unfortunately, some of the third-law analyses used values for enthalpies differences from the JANAF tables [1998CHA], values which appear to be rooted in part on the second-law analyses in the work of Zaugg and Gregory [1966ZAU/GRE]. Yet, the work in this paper

[1985HIL/VIS] shows an inconsistency of approximately 20 kJ·mol^{-1} for the calculated second-law enthalpy of reaction for formation of FeI_2(g) from FeI_2(cr) when compared to the value from [1966ZAU/GRE]. Therefore, for the value of $\Delta_f H_m^o$ (FeI_2, cr, 298.15 K), the work of Hilpert *et al.* leads to – (103.1 ± 4.3) kJ·mol^{-1} from their third-law analyses, – (120.3 ± 6.5) kJ·mol^{-1} from their second-law analysis, though they report a weighted average value of – (109.5 ± 3.5) kJ·mol^{-1}. The second-law value for $\Delta_f H_m^o$ (FeI_2, cr, 298.15 K) from Hilpert *et al.* is reasonably consistent with the values determined from calorimetry [1934HIE/WOE], [1990EFI/EVD], and potential [1983KHA/TAR] measurements.

[1985HSU/MAR]

Twenty iron(III) oxyhydroxide samples were prepared by aging $Fe(ClO_4)_3$ in HCl and NaOH solutions, some of which were immediately seeded with month-old goethite crystals, at room temperature (25 ± 3 °C) for periods ranging from 9.0 to 16.5 years. Most of the aged solid samples were pure goethite, α-FeOOH. Upon completion of the aging process, samples were filtered in a centrifuge tube fitted with various grades of filter paper, multiple times when necessary. The pH of the filtrate was measured with a glass electrode *vs.* a calomel reference electrode containing saturated NaCl, because of precipitation of $KClO_4$ if KCl were employed. Calibration of the electrode system was made against three standard buffer solutions, then converted to KCl values by an empirical comparison of KCl and NaCl potential-difference readings in standardized $HClO_4$ solutions. Some samples yielded mixtures of goethite and lepidocrocite, but these were excluded from the chosen data set, as were those that appeared to contain hematite, which was present in samples at the highest NaOH concentration. However, those samples aged for at least twelve years yielded well-crystallized goethite as confirmed by XRD and TEM. The authors used a constant pK_w value for water of 14.0 to convert the measured pH to a pOH value and the Davies equation to estimate the activity coefficients. The particle size of the crystals formed varied from 0.1 to 0.8 µm.

This appears to be a unique study in that equilibrium appears to have been established and the solid phase was identified as crystalline goethite for the cases tabulated.

The activity product, $K_s = a_{Fe^{3+}} a_{OH^-}^3$, showed a strong residual dependence on ionic strength (or pH). The average values of $-\log_{10} K_s$ for clusters of experiments varied as follows: $-\log_{10} K_s$ = 39.60 to 39.95 (average 39.80) at I near 0.005 (pH 2.27 to 2.56), N = 4; $-\log_{10} K_s$ = 39.95 to 40.47 (average 40.32) at I near 0.04 (pH 1.63 to 1.73), N = 10; $-\log_{10} K_s$ = 40.77 to 40.96 (average 40.83) at I near 0.2 (pH 1.22 to 1.31), N = 4. This resembles the variation in apparent solubility of α-Fe_2O_3 and γ-Fe_2O_3 in aqueous HNO_3 described by Taylor and Owen [1997TAY/OWE].

The experimental data were recast in this review in terms of the SIT for the equilibrium.

$$\alpha\text{-FeOOH} + 3\,H^+ \rightleftharpoons Fe^{3+} + 2\,H_2O(l) \qquad (A.133)$$

The pH values are generally low enough to neglect hydrolysis as a first approximation. Considering the pH was measured on the activity scale, the equilibrium constant can be defined as:

$$^{*}K^{\circ}_{s,0} = m_{Fe^{3+}}\gamma_{Fe^{3+}}a_w^2 / a^3_{H^+} \qquad (A.134)$$

such that:

$$\log_{10} m_{Fe^{3+}} + 9D + 2\log_{10} a_w - 3\log_{10} a_{H^+} = \log_{10}\,^{*}K^{\circ}_{s,0} + \Delta\varepsilon I_m \qquad (A.135)$$

The re-treated data are shown in the following table, noting that the reviewer was unable to reproduce the reported ionic strength exactly on the reported molarity scale, but the differences were too small to be significant compared to the overall uncertainties and scatter.

Table A-41: Recalculated experimental parameters for Eq. (A.135) at 25 °C

Sample #	pH_m	$-\log_{10}m_{Fe}$	a_w	I_m
CK8	2.27	4.03	1.000	0.0059
CK7	2.38	4.36	1.000	0.0044
CK4	2.46	4.74	1.000	0.0036
CK3	2.47	4.71	1.000	0.0035
CK2	2.56	4.64	1.000	0.0029
X10	2.35	4.23	1.000	0.0048
F301	1.73	2.34	0.999	0.0461
X5	1.64	2.69	0.999	0.0353
G16	1.72	2.50	0.999	0.0379
F312	1.64	2.58	0.999	0.0387
F313	1.65	2.60	0.999	0.0375
N2	1.66	2.67	0.999	0.0347
N4	1.67	2.71	0.999	0.0322
N5	1.63	2.61	0.999	0.0383
F309	1.64	2.66	0.999	0.0361
F310	1.69	2.55	0.999	0.0372
F12	1.21	1.41	0.991	0.293
F13	1.30	1.53	0.993	0.226
F15	1.29	1.55	0.993	0.221
F16	1.30	1.56	0.993	0.217

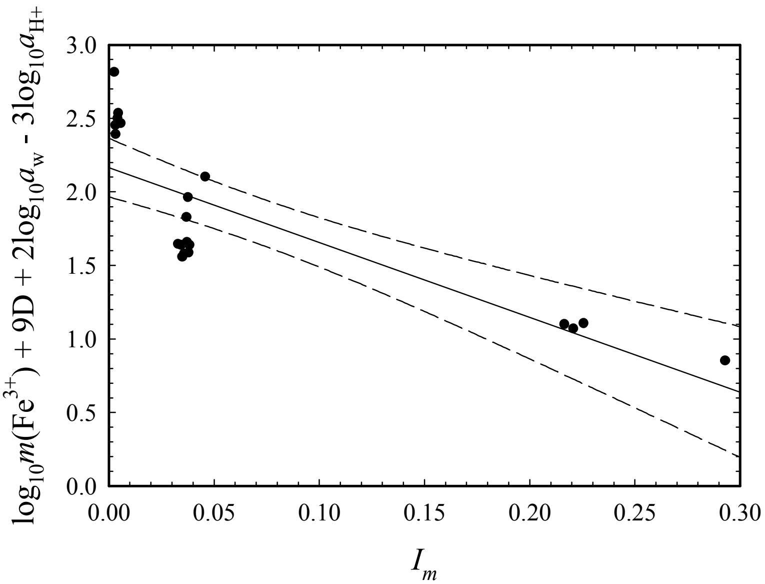
Despite the rather low range of ionic strengths employed, a fairly reasonable SIT plot was obtained as shown in Figure A-34. The resulting value of $\log_{10}\,^{*}K^{\circ}_{s,0}$ is

(2.17 ± 0.10) although $\Delta\varepsilon$ = (5.1 ± 0.9) $kg{\cdot}mol^{-1}$ is unrealistically high. Given a $\log_{10} K^{\circ}_{w}$ for water of − 13.993 at 25 °C, the $\log_{10} K^{\circ}_{s,0}$ for goethite is − (39.81 ± 0.11) which is in the range of the corresponding molar quantities tabulated in this paper, *viz.*, − 39.6 to − 40.83. This is significantly less negative than the value of – (41.83 ± 0.37) derived from thermodynamic data for well-crystallized goethite in the current review (Section VII.2.16).

The interaction coefficient difference is expressed as:

$$\Delta\varepsilon = \varepsilon(\mathrm{Fe^{3+}}, \mathrm{ClO_4^-}) - 3\varepsilon(\mathrm{H^+}, \mathrm{ClO_4^-}) = \varepsilon(\mathrm{Fe^{3+}}, \mathrm{ClO_4^-}) - 3\ (0.14 \pm 0.02).$$

Figure A-34: Plot of $\log_{10} m_{\mathrm{Fe^{3+}}} + 9D + 2\log_{10} a_w - 3\log_{10} a_{\mathrm{H^+}}$ *vs.* I_m for Reaction (A.133) at 25 °C and 1 bar. The solid line is an unweighted linear regression and the dashed curves represent the 95% confidence limits



[1985JAC]

An electrochemical cell of the design described by [1981JAC/ROS], using a Y_2O_3-stabilized ZrO_2 electrolyte, was used to measure the equilibrium potential differences of magnetite-wüstite and magnetite-hematite buffers *vs.* an Fe-wüstite reference.

The following relationships were obtained; the magnetite-hematite data have been incorporated into Figure VII-16:

(magnetite-wüstite *vs*. Fe-wüstite):

E/mV = 19.705 + 1.3458/(T/K) − 0.20514 (T/K)·ln(T/K) ± 1.5 (2σ), based on 108 data at 960.3 to 1602.1 K;

(magnetite-hematite *vs*. Fe-wüstite):

E/mV = – 337.95 + 1.1727(T/K) – 0.19185 (T/K)·ln (T/K) ± 1.8 (2σ), based on 66 data at 1088.9 to 1592.9 K.

[1985MAJ/AWA]

The water activities in the sulfate system were measured at (298.15 ± 0.10) K using a glass isopiestic apparatus containing eleven glass cups, three containing H_2SO_4 and $Fe_2(SO_4)_3$ reference solutions. A transpiration method was used for the corresponding chloride system due to concerns about the volatility of HCl. The temperature for the latter measurements was controlled at (298.15 ± 0.05) K and N_2 was the carrier gas.

The water activities are only represented in small plots which do not allow the individual values to be extracted with any precision or accuracy. The same issues apply to the solute activities derived by the authors and reported in a later paper [1986MAJ/AWA].

[1985SHE/KOE]

The heat capacities of single-crystal specimens (40 to 80 mg) of stoichiometric magnetite, Fe_3O_4, prepared under controlled redox conditions, were measured by relaxation calorimetry. A total of 9 measurements on 3 specimens showed a single, sharp, first-order transition (Verwey transition) at ~121 K with a transition entropy value close to $R\ln 2$ (see [1991SHE/KOE] and references therein for further details of preparation, measurements, and model development). There is a useful tabulation of measurements of the transition temperature and entropy from 15 other sources on samples with varying impurity or dopant levels.

Figures indicate that a large number of C_p measurements were performed at 5 - 340 K, but data are not tabulated. Uncertainty in the C_p measurements was estimated as ± 5% at $T < 30$ K and ±2% at $T > 30$ K. Given the large quantity of high-quality data available from other publications, no attempt was made to obtain original data from this and related studies. The authors state that, except for the Verwey transition region, there was general agreement with other published data (within 5%).

Although zero-point entropy (see [1956AND] and Section VII.2.7.1.3) is not discussed explicitly either here or in [1991SHE/KOE], the authors do provide a plausible explanation for the observed transition enthalpy, which appears to exclude the possibility of a significant a zero-point entropy.

[1985SOL/MON]

Heats of solution were reported for $FeCl_3$(cr) at 25 °C for final salt molalities from 0.02236 m (– 127.38 $kJ\cdot mol^{-1}$) to 0.07578 m (– 134.23 $kJ\cdot mol^{-1}$), and were fitted by the authors to a simple equation: $-((119.5 \pm 0.5) + (167.9 \pm 7.0)\, m^{½})$ $kJ\cdot mol^{-1}$.

At the lower molalities, the results are in reasonable agreement (~ 1.5 $kJ\cdot mol^{-1}$) with the results of Li and Gregory[1952LI/GRE].

[1985VAS/DMI]

The heats of solution of $FeSO_4\cdot 7H_2O$ in water and aqueous perchloric acid solutions at 298.15 K were measured. Equations were reported for the enthalpies of solution as a function of molality in water and 2 M, 3 M and 4 M $HClO_4$. The raw data were not reported except in a figure, and none were shown for the (sixteen) dissolution measurements in water. The value extrapolated to infinite dilution in water, (11.99 ± 0.06) $kJ\cdot mol^{-1}$, is in good agreement with previous work [1968LAR]. However, the heat of dissolution in water is described by an equation that is linear with respect to $m^{½}$, and for solution molalities between 0.005 and 0.05 the slope is consistent neither with the work of Larson [1968LAR] nor with heats of dilution for other 2:2 electrolytes such as $NiSO_4$(sln) or $ZnSO_4$(sln) [1956LAN/MIE]. In the absence of the raw data, ± 0.50 $kJ\cdot mol^{-1}$ is considered to be a more realistic uncertainty estimate.

[1985VAS/DMI2]

Enthalpy of solution measurements for $FeSO_4\cdot 7H_2O$(cr) in 2 M, 3 M and 4 M $HClO_4$ containing H_2O_2(aqueous solution, 1.0 and 1.5 weight-%) were reported. Using the heats of dissolution of Fe(cr) reported previously by Vasil'ev *et al.* [1978VAS/VAS2], and heats of dilution of H_2O_2(sln) and concentrated aqueous sulfuric acid in similar solutions, the enthalpy of formation of $FeSO_4\cdot 7H_2O$(cr) was calculated. As discussed by the authors, in the reaction in 2 M $HClO_4$ there was likely to have been some dissociation of the HSO_4^- product in the final solutions. Although the results calculated assuming deprotonation of 4% of the sulfate in such solutions [1985VAS/DMI2] are consistent with those calculated assuming no deprotonation in the 3 M and 4 M perchloric acid solutions, only the results from measurements in the 3 M and 4 M $HClO_4$ solutions are used in the present review. The average values of the heats of solution of Fe(cr) in the acid solutions containing 1.0 and 1.5 weight-% H_2O_2 were $-(616.59 \pm 0.28)$ and $-(616.47 \pm 0.38)$ $kJ\cdot mol^{-1}$ [1978VAS/VAS2]. The initial weight fractions of the concentrated aqueous solutions of H_2O_2 (0.3473) and H_2SO_4 (0.9428) added to the aqueous perchloric acid solutions were slightly greater than those used in the earlier work. The enthalpy of formation of the concentrated aqueous solution of H_2O_2 was taken from Wagman *et al.* [1982WAG/EVA], as was the value for the enthalpy of formation of the concentrated sulfuric acid solution[1]. With these auxiliary data, the value of $\Delta_f H^o_m$ ($FeSO_4\cdot 7H_2O$, cr, 298.15 K) is – (3015.61 ± 1.54) $kJ\cdot mol^{-1}$.

In the same paper, the authors used their new heats of dilution of concentrated H_2SO_4 into aqueous perchloric acid in a recalculation of the earlier results of Vasil'ev *et al.* [1978VAS/VAS2] to obtain a revised value of – 3918.54 $kJ\cdot mol^{-1}$ for $\Delta_f H^o_m$ ($(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$, cr, 298.15 K). They also reported that a revised value was used for the enthalpy of formation of concentrated H_2SO_4. It is not clear what was done in the recalculation. The latter quantity does not seem to have been modified between [1978VAS/VAS2] and [1985VAS/DMI2]. The values are similarly related to those in the US-NBS tables [1982WAG/EVA]. Also, the acid concentrations in [1978VAS/VAS2] and [1985VAS/DMI2] are different, and thus the heat of dilution values for the H_2SO_4 solutions cannot simply be interchanged.

[1986HOL/NEI]

Solid-state cell-potential measurements were performed on Cu-Cu_2O, Ni-NiO, Co-CoO, and Fe-$Fe_{sat}O$ couples relative to a porous Pt air electrode ($Fe_{sat}O$ represents the equilibrium wüstite composition at given T). Data were subjected to detailed third-law analysis, using optimized heat-capacity equations, and extensive comparison with the literature. The following enthalpy of formation for wustite was obtained:

$$\Delta_f H^o_m (Fe_{0.947}O, \text{cr}, 298.15 \text{ K}) = -266.46 \text{ kJ}\cdot\text{mol}^{-1}$$

The corresponding value for the alternative formulation, $FeO_{1.056}$ is – 281.37 $kJ\cdot mol^{-1}$. This composition was selected because $C^o_{p,m}(T)$ and $H(T)$ data are available [1951TOD/BON], [1951COU/KIN]. The actual boundary composition was evaluated to be nearly constant at $Fe_{0.953}O$ ($FeO_{1.049}$) over the entire stability range. Gibbs energy values are presented in the form of overall linear regressions and segmented curvilinear regressions. The most precise expressions for $Fe_{sat}O$ take the form:

$$\Delta_f G^o_m (Fe_{sat}O, \text{cr}, T_{min} < T < T_{max})/\text{J}\cdot\text{mol}^{-1} = \text{A} + \text{B}(T/\text{K}) + \text{C}(T/\text{K})\cdot\ln(T/\text{K}) + \text{D}(T/\text{K})^2 \pm \text{E}$$

with the parameters shown in Table A-42.

Table A-42: Parameters defining the Gibbs energy of formation of the iron-rich limiting composition of wüstite, $Fe_{sat}O$, at 837 – 1644 K.

T_{min}/K	T_{max} /K	A	B	C	D	E
837	1042	-303097	683.498	-91.3978	0.05180	1
1042	1184	-259869	29.852	4.4638	0	4
1184	1644	-275770	134.841	-8.4742	0	1

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[1] See 2nd footnote in the Appendix A entry for [1963ADA/KEL].

The parameter E represents the precision of the fit, and the claimed accuracy of Gibbs energy values is ±200 J·mol^{-1}, based on the overall consistency of measurements, including measured potentials between solid couples. Agreement with the "best" gas-solid equilibrium measurements [1933EMM/SHU], [1945DAR/GUR], [1972RAU] is within 1 kJ·mol^{-1}. More recent, apparently more accurate measurements at the same laboratory led to slightly different expressions [1988NEI]. Supplementary material (including cell-potential data) is provided in NAPS document No. 04428.

[1986HSI/CHA]

This paper describes another set of experiments using an electrochemical cell to study oxygen chemical potentials in the Fe-S-O system at temperatures from 718.9 to 989.6 K at a total pressure of "~ 1 atm". The study was similar to that of Skeaff and Espelund [1973SKE/ESP], but using an yttria-stabilized zirconia electrolyte. The results are generally consistent with those in other studies, but suggest that the invariant temperature (p_{SO_2} = 1 bar) for the equilibrium between Fe_2O_3, $FeSO_4$ and $Fe_2(SO_4)_3$ is lower by ~ 20 K than that reported previously by Skeaff and Espelund [1973SKE/ESP].

[1986JAC/IYE]

Jacob and Iyengar measured potentials of the cell

Pt, (96.42vol-% Ar, 2.05vol-% SO_2, 1.53vol-% O_2)(g) | Na_2SO_4(I) | Fe_2O_3(cr), $Fe_2(SO_4)_3$, Pt

for temperatures between 800 and 1000 K (Na_2SO_4(I) is the high-temperature crystalline form of Na_2SO_4). The gas composition reflects the inlet composition though, of course, SO_3(g) was formed at the temperatures of the experiment. The authors fit a straight line to their results, and reported

$$\Delta_r G^o_m / \text{J·mol}^{-1} = -576895 + 546.1\,(T/\text{K})$$

for

$$Fe_2O_3(cr) + 3\,SO_3(g) \rightleftharpoons Fe_2(SO_4)_3(cr).$$

Based on this equation, reference data for SO_3(g) and Fe_2O_3(cr), and the thermal functions from Pankratz and Weller [1969PAN/WEL], $\Delta_f H^o_m$ ($Fe_2(SO_4)_3$, cr, 298.15 K) = −2614 $\text{kJ·mol}^{-1}$and S^o_m ($Fe_2(SO_4)_3$, cr, 298.15 K) = 272 $\text{J·K}^{-1}\text{·mol}^{-1}$. A third-law analysis based on $\Delta_r G$ (900 K), using the estimated entropy (283 $\text{J·K}^{-1}\text{·mol}^{-1}$) from Pankratz and Weller [1969PAN/WEL] gives −2604 kJ·mol^{-1} for $\Delta_f H^o_m$ ($Fe_2(SO_4)_3$, cr, 298.15 K). However, a third-law analysis using the entropy value (305.6 $\text{J·K}^{-1}\text{·mol}^{-1}$) from Majzlan *et al.* [2005MAJ/NAV], which properly incorporates the magnetic contribution, gives − 2683.6 kJ·mol^{-1} for $\Delta_f H^o_m$ ($Fe_2(SO_4)_3$, cr, 298.15 K) based on $\Delta_r G$ (900 K) and − 2686.5 kJ·mol^{-1} based on $\Delta_r G$ (800 K). The authors used thermodynamic quantities for SO_3(g) and SO_2(g) based on the assessed values of $\Delta_f H^o_m$, S^o_m and $C^o_{p,m}$ from the 1971 JANAF Tables [1971STU/PRO]. These are similar to the values reported by Gurvich *et al.* [1989GUR/VEY], and differences affect the calculated value of $\Delta_f H^o_m$ ($Fe_2(SO_4)_3$, cr, 298.15 K) by < 1 kJ·mol^{-1}.

[1986KHO/BRO]

Potentiometric titrations of Fe(III) solutions at 1 mol·dm^{-3} ionic strength ($NaClO_4$, KNO_3 and KCl) and 25 °C were performed with a glass combination electrode using a $KHCO_3$ titrant to avoid localized high pH conditions. The electrode was calibrated on an empirical molarity scale. A revised MINIQUAD program was used to treat the data which contained a large number of points per titration (*viz.*, 77 to 260) with iron(III) concentrations varying from 2.14 × 10^{-4} to 2.036 × 10^{-2} mol·dm^{-3} in the former medium. Various schemes were tested with the most favorable including the hydrolyzed species: $FeOH^{2+}$, $Fe(OH)_2^+$, $Fe_2(OH)_2^{4+}$ and $Fe_3(OH)_4^{5+}$. The authors explain in considerable detail the acceptance criteria used to determine the most probable combination of species in each medium as documented in Table A-43.

This is the only study to report direct evidence for the possible existence of the (4,3) species, which was previously reported based on unpublished data by Biedermann by Schlyter (Trans. Royal Inst. Technol., Stockholm, 196, 1962).

Table A-43: Molal $\log_{10} {}^*\beta_{n,m}$ values $^{(a)}$ proposed from this study at 25 °C.

salt	n,m	$\log_{10} {}^*\beta_{n,m}$	3σ	$\log_{10} {}^*\beta_{n,m}$ $^{(b)}$	3σ
$NaClO_4$	1,1	– 2.71	0.02		
I = 1.049 m	2,1	– 6.25	0.03		
	2,2	– 3.12	0.01		
KNO_3	1,1	– 2.75	0.04	– 2.98	0.06
I = 1.045 m	2,1	– 6.57	0.11	– 6.41	0.08
	2,2	– 3.14	0.03	– 3.03	0.02
	4,3	– 6.94	0.11		
KCl	1,1	– 3.20	0.07	– 3.44	0.08
I = 1.033 m	2,1	– 6.70	0.09	– 6.56	0.05
	2,2	– 4.03	0.11	– 3.76	0.02
	4,3	– 7.55	0.13		

(a) converted to molal units from the original molar quantities (1985SOH/NOV].

(b) these values were tabulated as an alternative scheme which excludes the (4,3) species.

[1986LIN2]

This article contains a presentation of experimental results and correlations meant to educate power plant chemists and engineers. It includes a hand-written graph of the logarithm of hydrolysis constants ($\beta^{\circ}_{1,1}$, $\beta^{\circ}_{2,1}$ and $\beta^{\circ}_{3,1}$) for Fe^{2+} ion as a function of reciprocal temperature (kelvin) from [1970SWE/BAE], [1980TRE/LEB] and "Westinghouse (1983)". The latter results range from 200 to 350 °C and tend to show much closer agreement with those reported by Tremaine and LeBlanc. No other reference to the Westinghouse (1983) study has been found and there is no other supporting discussion of the origin of the Westinghouse data.

This is an interesting article, but contains no new information that could be examined by this review.

[1986MAJ/AWA]

No new experimental results are presented in this paper. All activity coefficients derived earlier [1985MAJ/AWA] are only shown graphically. Therefore, these results are not considered further by this review.

[1986MAL/PAN]

The potential differences of Fe-"FeO" and Fe-Fe_3O_4 couples were measured *vs.* Cu-Cu_2O at about 720 to 835 K, using an unusual triple-electrode-bielectrolyte cell with Y_2O_3-stabilized ZrO_2 separating the copper oxide couple from air, and a conical Y_2O_3-stabilized ThO_2 electrolyte separating the solid oxide couples.

The potential-difference values obtained in this study, especially for the Fe-Fe_3O_4 couple, show poor agreement with values derived fron O'Neill [1988NEI] and other studies cited in Section VII.2.7.2.2. The reported Fe-wüstite-Fe_3O_4 eutectoid temperature of 791 K is markedly lower than most reported values (see Section VII.2.8.3). Results from [1986MAL/PAN] are therefore not used in the present review.

[1986MEI/GRO]

Adiabatic-shield calorimetry was used to make two series of measurements of the heat capacities of a sample of $FeCl_3\cdot5.70H_2O(cr)$ (291.9 to 310.4 K). From these, the molar enthalpy of fusion of the salt at 310.0 K was determined to be (52.49 ± 0.35) $kJ\cdot mol^{-1}$. The authors used a literature value of 6.6 $J\cdot K^{-1}\cdot mol^{-1}$ for the (assumed temperature-independent) entropy of fusion of 0.30 moles of H_2O to calculate an estimated value of 2.05 $kJ\cdot mol^{-1}$ for the enthalpy of fusion of 0.30 moles of H_2O at 310.0 K (as the Gibbs energy of fusion is zero at the fusion temperature). From this, they reported $\Delta_{fus}H$ ($FeCl_3\cdot6H_2O$, cr, 310.0 K) = (54.5 ± 0.6) $kJ\cdot mol^{-1}$. The uncertainty reported by the original authors corresponds to a combined estimated uncertainty of ± 0.5 $kJ\cdot mol^{-1}$ from the adjustment to a value for the stoichiometric hexahydrate and from possible systematic errors. On the basis of their measurements on $FeCl_3\cdot5.70H_2O(cr)$, the authors estimated $C^{o}_{p,m}$ ($FeCl_3\cdot6.00H_2O$, cr, 298.15 K) = 342 $J\cdot K^{-1}\cdot mol^{-1}$. In the present review the uncertainty in this value is estimated to be ± 4 $J\cdot K^{-1}\cdot mol^{-1}$.

[1986SJO/SEE]

High-precision cell-potential measurements are reported for (Fe + wüstite) *vs.* (Ni + NiO) in a solid-state electrochemical cell with a CaO-stabilized zirconia electrolyte. The (metal + oxide) couples were in the form of packed powders. About 80 potential-difference measurements between 866 and 1340 K are plotted (their Fig. 2), and show a distinct break in slope at the α-γ phase transition for Fe(cr) at 1184 K. The following

Gibbs energy relationships were derived for the reaction, NiO + xFe $\rightleftharpoons$ Ni + Fe_xO. Note that x, the Fe:O ratio of the iron-rich limiting composition of wüstite, varies slightly with temperature (see Figure VII-16, Section VII.2.7.2.3 and references therein, *e.g.*, [1973GID/GOR], [1978SPE/KUB], [1983KNA], [1986HOL/NEI], and [1991SUN]).

$$\Delta_r G^\circ \text{ (866 to 1184 K)} = -17829 - 102.993T + 10.187T\cdot\ln(T)$$

$$\Delta_r G^\circ \text{ (1184 to 1340 K)} = -52597 + 96.526T - 13.858T\cdot\ln(T)$$

The potential-difference values from this study are systematically 1.45 to 3.80 mV higher than those derived from Gibbs energy expressions for NiO and wüstite furnished by Holmes *et al.* [1986HOL/NEI] over the range of overlap between the two studies (866 to 1340 K). The latter study, unlike most earlier work, also provided different expressions for wüstite above and below the Fe(cr) phase transition. The corresponding discrepancies in ΔG, for the reaction given above, are 0.28 to 0.73 $kJ\cdot mol^{-1}$. These discrepancies are greater than the authors' estimated uncertainties of ± 0.25 mV in the measurements for [1986SJO/SEE] and 0.2 $kJ\cdot mol^{-1}$ overall for [1986HOL/NEI]. Systematic discrepancies of this magnitude appear to be the norm for independent, high-quality solid-state cell-potential studies of oxide systems. It is difficult to identify contributions from differences in instrumentation and cell design, electrolyte performance, experimental procedure, and the physico-chemical form of the specimens. A number of relevant factors have been discussed by Steele and Alcock [1965STE/ALC].

[1986VAL/CAR]

A thermodynamic description is proposed for the three structural modifications of wüstite inferred from earlier studies (*e.g.*, [1964VAL/CAR], [1969FEN/RIL], [1984HAZ/JEA]). Note that other studies indicate that these modifications can not be detected by thermodynamic measurements, and that reported non-linear potential-composition relationships are due to experimental artifacts (*e.g.*, [1973GID/GOR], [1974GID/GOR], [1993GRO/STO]). Further discussion is beyond the scope of the current review.

[1986YIS/RUI]

These batch-type solubility measurements on hematite were made at 300 °C and 10 MPa in aqueous $HClO_4$ and KOH solutions with no agitation. The loading (g solid/mL solution) was not given, nor was the pH measurement, which for solutions with pH < 12 were made of filtered, quenched solution samples at 25 °C, described in any detail. This presents a significant problem in that these latter samples were poorly buffered, and the iron(III) speciation will change unless the $Fe(OH)_3(aq)$ species dominates the speciation and the pH at 300 °C must be estimated from a model which incorporates K_w and activity coefficients. The authors did run tests up to 412 hours and concluded that equilibrium was established well within 48 hours which was the typical run time. XRD of the initial and final solids showed no change had occurred.

The solubilities of hematite obtained in the KOH solutions with pH > 12 are listed in Table A-44.

The tabulated solubility results in [1986YIS/RUI] were recalculated to give the corresponding pH_m values at 300 °C using $\mathrm{p}K_\mathrm{w}$ values for water at 25 and 300 °C and saturation vapour pressure of 13.993 and 11.301 MPa, respectively. Activity coefficients for these dilute solutions were ignored where the neutral $\mathrm{Fe(OH)_3(aq)}$ species dominates. The pH values at 25 and 300 °C and the corresponding $\log_{10} m_\mathrm{Fe}$ values are listed in Table A-45.

Table A-44: Solubility of hematite at 300 °C and 10 MPa (p_sat = 8.58 MPa) with significant KOH present to allow the pH to be measured by titration.

m_KOH $\mathrm{mol \cdot kg^{-1}(H_2O)}$	$10^6 m_\mathrm{Fe}$ $\mathrm{mol \cdot kg^{-1}(H_2O)}$	a_w*	m_KOH $\mathrm{mol \cdot kg^{-1}(H_2O)}$	$10^6 m_\mathrm{Fe}$ $\mathrm{mol \cdot kg^{-1}(H_2O)}$	a_w *
0.797	107.7	0.9796	0.387	50.3	0.9897
0.777	101.7	0.9801	0.254	23.8	0.9931
0.576	89.7	0.9850	0.238	31.1	0.9935
0.524	63.3	0.9863	0.106	16.0	0.9969
0.505	41.8	0.9868	0.103	15.3	0.9970
0.499	57.3	0.9869	0.096	19.6	0.9972
0.483	55.1	0.9873	0.088	19.7	0.9974
0.476	55.9	0.9875	0.056	8.8	0.9983
0.462	69.9	0.9878	0.047	12.3	0.9986
0.453	61.0	0.9881	0.0383	5.6	0.9988
0.443	43.9	0.9883	0.0251	2.8	0.9992
0.422	43.4	0.9891	0.0225	4.1	0.9993
0.390	53.5	0.9896			

* The properties of NaCl solutions from [1992ARC] were used in the absence of similar data for KOH solutions.

Table A-45: Solubility of hematite at 300 °C and 10 MPa at pH < 12 where the pH at 300 °C is recalculated from the quenched pH at 25 °C of each sample.

pH 25 °C	pH 300 °C	$-\log_{10} m_\mathrm{Fe}$	pH 25 °C	pH 300 °C	$-\log_{10} m_\mathrm{Fe}$
11.94	9.25	5.74	8.27	5.83	5.82
11.87	9.18	5.89	8.22	5.81	5.96
11.60	8.91	5.54	8.20	5.80	6.10
11.59	8.90	5.85	8.18	5.80	5.96
11.45	8.76	5.80	7.87	5.72	5.92
11.01	8.32	5.96	7.75	5.70	5.85

(Continued on next page)

Table A-45 (continued)

pH 25 °C	pH 300 °C	$-\log_{10}m_{\mathrm{Fe}}$	pH 25 °C	pH 300 °C	$-\log_{10}m_{\mathrm{Fe}}$
10.82	8.13	6.15	7.63	5.69	6.00
10.81	8.12	6.22	7.53	5.68	5.92
10.77	8.08	6.05	6.92	5.65	6.40
10.73	8.04	5.85	6.70	5.64	5.92
10.51	7.82	6.15	6.50	5.62	6.18
10.27	7.58	6.22	6.10	5.58	5.54
9.74	7.05	6.10	5.94	5.54	5.74
9.71	7.02	5.96	5.90	5.53	6.15
9.61	6.92	5.89	5.84	5.51	5.92
9.46	6.77	6.30	5.68	5.45	5.55
8.60	6.00	6.22	5.67	5.45	5.92
8.44	5.91	5.96	5.66	5.45	5.47
8.32	5.85	6.15	5.64	5.44	5.90
8.29	5.84	6.15	5.48	5.35	5.43

From the results in Table A-44, regardless of how these data plotted in Figure A-35 are extrapolated to infinite dilution, the $\log_{10} K_{s,4}$ value for the isocoulombic equilibrium, $\frac{1}{2}\mathrm{Fe_2O_3(cr)} + \mathrm{OH^-} + 1\frac{1}{2}\mathrm{H_2O(l)} \rightleftharpoons \mathrm{Fe(OH)_4^-}$, of $-(3.9 \pm 0.1)$ at 300 °C is obtained. This value is in very good agreement with that obtained from the temperature dependence of $\log_{10} K_{s,4}$ from [1999DIA/SCH] and corresponds to a $\log_{10} {}^*K_{s,4}$ value of $-(15.2 \pm 0.1)$.

As shown in Figure A-36, if one assumes that three Fe(III) species exist in solution over the pH range of *ca.* 5 to 9, *viz.*, $\mathrm{Fe(OH)_2^+}$, $\mathrm{Fe(OH)_3(aq)}$ and $\mathrm{Fe(OH)_4^-}$, by fixing the $\log_{10} {}^*K_{s,4}$ value at -15.2, regression analysis yields values for $\log_{10} {}^*K_{s,2}$ and $\log_{10} {}^*K_{s,3}$ of $-(0.5 \pm 0.1)$ and $-(6.13 \pm 0.09)$, respectively. Perhaps a more conservative approach would be to assume that, given the experimental scatter in these data, only the $\mathrm{Fe(OH)_3(aq)}$ species should be considered, in which case an average value of $-(5.9 \pm 0.5)$ results. Despite the apparent large experimental uncertainties in these values that clouds their interpretation, this study provides one of the few sources of thermodynamic data for the solubility of hematite in near neutral solutions.

Figure A-35: Plot of $\log_{10} K_{s,4}$ *vs.* the molality of KOH as given in Table A-44 at 300 °C and 10 MPa.

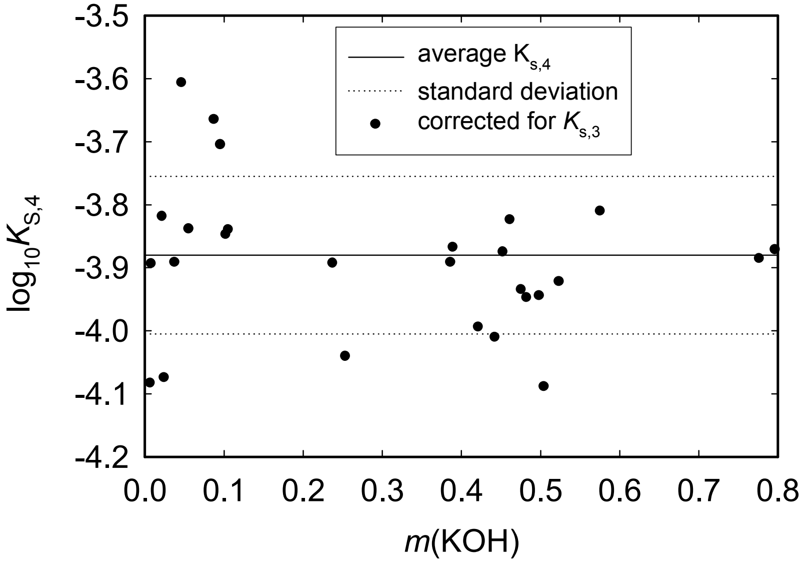
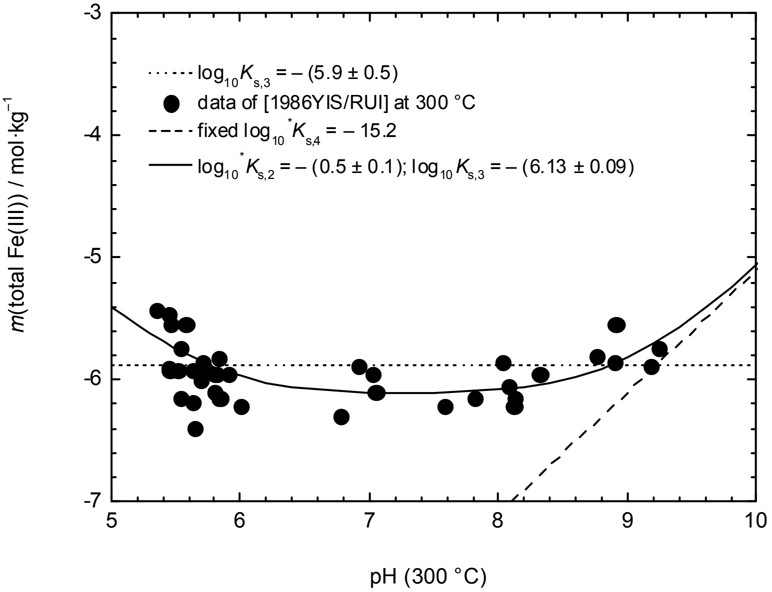


Figure A-36: Plot of $\log_{10} m_{\mathrm{Fe(III)}}$ *vs.* pH(300 °C) as given in Table A-45 at 300 °C and 10 MPa.



[1987MOR/MIL]

The chemistries of the hydrogen sulfide and iron sulfide systems in natural waters were reviewed. The work on the thermodynamics of H_2S in aqueous solutions, solubility of H_2S in water and seawater, ionization of H_2S in water and seawater, formation of polysulfides, and kinetics of oxidation of H_2S in aqueous solution were discussed, and these reviews are of value for reference. General characteristics of the major sedimentary iron sulfide minerals, amorphous FeS, mackinawite, greigite, and pyrite were discussed. For the iron sulfide mineral reactions in aqueous solutions, solubility of iron sulfide minerals, iron sulfide reaction pathways and kinetics, the microbiological formation of iron sulfides, oxidative dissolution of iron sulfides, and trace metal-sulfide association were discussed. On the distribution of hydrogen sulfide and iron sulfide minerals in marine environments, hydrogen sulfides and related compounds, environmental distributions, and iron sulfides in sediments were discussed. In the paper, the solubility constants at $I = 0$ and 298 K, 1 atm were recalculated using the data of Berner [1967BER2] with $\text{p}K_1(H_2S) = 6.98$ and the Davies equation to be $\log_{10}{}^*K = -(2.95 \pm 0.09)$ for $H^+ + \text{FeS(amorphous)} \rightleftharpoons Fe^{2+} + HS^-$, $\log_{10}{}^*K = -(3.55 \pm 0.09)$ for $H^+ + \text{FeS(mackinawite)} \rightleftharpoons Fe^{2+} + HS^-$, and $\log_{10}{}^*K = -(12.85 \pm 0.12)$ for $3\,H^+ + Fe_3S_4\text{(greigite)} \rightleftharpoons 3\,Fe^{2+} + 3\,HS^- + \text{S(rhombic)}$. The reliability of these values is discussed in the Appendix A entry for the original experimental paper [1967BER2].

[1987NEI2]

The authors measured potentials of the solid-state galvanic cells

$$\text{Pt}|\text{Fe}, Fe_2SiO_4, SiO_2\text{(quartz)}|(Y_2O_3)ZrO_2|\text{“FeO”},\text{Fe}|\text{Pt} \qquad \text{(A)}$$

$$\text{Pt}|\text{Fe}, Fe_2SiO_4, SiO_2\text{(quartz)}|(Y_2O_3)ZrO_2|MoO_2,\text{Mo}|\text{Pt} \qquad \text{(B)}$$

at 971 to 1398 K and

$$\text{Pt}|Fe_3O_4, Fe_2SiO_4, SiO_2\text{(quartz)}|(Y_2O_3)ZrO_2|Cu_2O,\text{Cu}|\text{Pt} \qquad \text{(C)}$$

at 1049 to 1311 K to determine the oxygen chemical potentials corresponding to equilibrium.

To calculate $\Delta_f H_m^\circ(Fe_2SiO_4, \alpha, 298.15\text{ K})$, the extensive series of measured potentials for cells (A) and (B) are used, along with consistent auxiliary data for quartz ([1989COX/WAG], [1998CAR/SAL]) and oxygen [1989GUR/VEY], and with the values selected in this review for the heat capacity and entropy of α-Fe_2SiO_4 (Section X.2.1.1.1) and Fe(cr) (Section V.2). Values ranging from -1476.98 to -1476.04 kJ·mol^{-1} are obtained (the average of the 105 values is $-(1476.55 \pm 0.39)\ \text{kJ·mol}^{-1}$, 2σ uncertainty); the values showed a slight drift to more positive values as the temperatures increased above 1150 K. However, the results using the two different reference electrodes (which were also checked against each other) are in good agreement.

The Gibbs energies of reaction as recalculated from the measured potentials for cell (C), when used with TDB auxiliary data, lead to slightly more negative values (by about 1 kJ·mol^{-1}) for $\Delta_f H^\circ_m$ (Fe_2SiO_4, α, 298.15 K) —between −1477.5 and −1478.0 kJ·mol^{-1} (average −(1477.68 ± 0.20) kJ·mol^{-1}, 2σ uncertainty). In general, such cells using magnetite do not seem to be as well behaved as those with Fe, SiO_2 and Fe_2SiO_4 [1987NEI2]. Also, there is the conundrum of deriving values for the thermodynamic quantities for magnetite independently of those for α-Fe_2SiO_4. The values from measurements with magnetite-containing cells are not used in the present review to define $\Delta_f H^\circ_m$ (Fe_2SiO_4, α, 298.15 K).

[1987TAY]

This is a useful general overview of oxides and hydroxides, including those of iron, with emphasis on preparation, morphology, sorption properties, and soil chemistry.

[1987VOG/MCC]

The d → d electronic transitions of Fe(II) complexes in LiCl-DCl-D_2O were studied over the concentration range 1 to 11 m Cl^- at 25 to 82 °C. A first series of solutions contained 0.10 m Fe^{2+} and 1.12 m DCl with addition of 0.00, 3.71, 5.73 and 9.07 m LiCl, and measurements were done at (297.75 ± 0.1), (311.25 ± 0.1), (321.55 ± 0.1), (297.75 ± 0.1), (331.05 ± 0.1) and (344.85 ± 0.2) K. A second series of solutions contained 0.053 m Fe^{2+} and 1.02 m DCl with addition of 0.00, 0.92, 2.02, 3.01, 4.39, 5.49, 6.01, 6.95, 7.95, 9.03 and 9.84 m LiCl, and measurements were done at (297.65 ± 0.1), (322.45 ± 0.2), (344.15 ± 0.2), and (355.55 ± 0.2) K. The authors used a principal factor analysis technique to determine the number of species contributing to the total absorbance of the solutions.

A key result of this study was provided in the authors' Figure 4, where the chloride apparent ligand number is presented as a function of the chloride concentration and of temperature. Below 5 m Cl^- only the octahedral complex $Fe(D_2O)_5Cl^+$ was found at any temperature. At ambient temperature, octahedral complexes that included more than one chloride were observed only above 8 m Cl^-. A maximum of 4 chloride ligands, *i.e.*, corresponding to the species $Fe(D_2O)_2Cl_4^{2-}$, was observed only above ~10 m Cl^- at elevated temperatures, *i.e.*, above ~49 °C. Under such conditions, the anionic tetrachlorido-complex may become dominant.

At or below 4000 cm^{-1}, a spectral region that can only be explored in D_2O, the authors observed a new band with a high molar decadic absorption coefficient. This new band was attributed to tetrahedral complexes $Fe(D_2O)_mCl_n^{2-n}$ with ($m + n = 4$). For the octahedral – tetrahedral equilibrium $Fe(D_2O)_nCl_{6-n}^{n-4} + p\mathrm{Cl}^- \rightleftharpoons Fe(D_2O)_{n-2-p}Cl_{6-n+p}^{n-4-p} + (p+2)D_2O$ the authors estimated an enthalpy of reaction $\Delta_r H$ (298.15 K; I) of 36 to 41 kJ·mol^{-1}, the only "thermodynamic entity" derivable from the study.

It is interesting to note that in 1 m Cl^- the authors found very similar spectra for $Fe(D_2O)_6^{2+}$ and for $Fe(D_2O)_5Cl^+$, and that they failed to determine any stability constants with the help of the program SQUAD [1977LEG]. The authors commented on this by saying that "*Provided that the extinction coefficients are also very similar……, the SQUAD program would have difficulty separating their contributions to the solution spectra, giving unsatisfactory, non-unique fits*". Studies by Heinrich and Seward [1990HEI/SEW] and Zhao and Pan [2001ZHA/PAN] used extended versions of the SQUAD program in their data analyses, but these later authors did not report any such difficulties.

The measurements were performed under nitrogen to avoid oxygen and H_2O contamination, but unfortunately, redox conditions were not actively controlled. From charge-transfer bands in the UV region the authors estimated that 2–3% of the iron was present as Fe(III), but the impact of these impurities was not further discussed in the study.

[1988AZA/SRE]

Azad and Sreedharan carried out measurements of the potential of the cell Pt |Fe, FeF_2 | CaF_2 | NiF_2, Ni | Pt at temperatures from ~ 780 to 1063 K and of the cell Pt | Fe, FeF_2, NaF | β-alumina | NaF, NiF_2, Ni | Pt from 506 to ~ 1054 K. The latter cell was used in an attempt to obtain measurements at lower temperatures than was possible with the simpler cell without NaF and alumina.

The results were not tabulated, though a plot was provided, and the results were reported in the form of a linear equation:

$$E(\text{A.136})/\text{mV} = 244.6 + 0.1378\,(T/\text{K})$$

for

$$\text{NiF}_2(\text{cr}) + \text{Fe}(\text{cr}) \rightleftharpoons \text{FeF}_2(\text{cr}) + \text{Ni}(\text{cr}) \qquad (\text{A.136})$$

with an average uncertainty of ± 3.5 mV. The results from the two electrodes mesh well, but at temperatures above 800 K the potentials (from both cells) are several mV lower than the results from other studies [1966LOF/MCI], [1975CHA/KAR], [1981SCH/GOK]. A third-law analysis of the results was done using auxiliary values from the present review, and thermodynamic quantities for Ni(cr) and NiF_2(cr) from Gamsjäger *et al.* [2005GAM/BUG]. From the equation for the potential, this leads to values of − 709.3 and − 711.0 $\text{kJ}\cdot\text{mol}^{-1}$ for $\Delta_f H_m^\circ$(FeF_2, cr, 298.15 K) at 506 and 1063 K.

[1988DYR]

By using the chemical analogue (Linear Free Energy Relationship) approach with dithizone as a model ligand and stability constants for cadmium, silver and mercury sulfides as reference, the stability constants of metal-sulfide complexes of Cu^+, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Pb^{2+} and Pd^{2+} were estimated. The values for iron sulfides were estimated to be $\log_{10} K = 13.3$ for $Fe^{2+} + S^{2-} \rightleftharpoons FeS(aq)$, $\log_{10} K = 1.4$ for $Fe^{2+} + HS^- \rightleftharpoons Fe(HS)^+$, $\log_{10} K = 8.9$ for $Fe^{2+} + 2\,HS^- \rightleftharpoons Fe(HS)_2(aq)$, and $\log_{10} K_{s1} = -4.7$ for $FeS(am) \rightleftharpoons FeS(aq)$ at $I = 0$ and 298 K, where $\log_{10} {}^*K = 6.88$ for

$H^+ + HS^- \rightleftharpoons H_2S$ and $\log_{10} {}^*K = 14.15$ for $H^+ + S^{2-} \rightleftharpoons HS^-$ were used. Using these values, $\log_{10} {}^*K = 3.03$ is derived for $FeS(am) + 2\,H^+ \rightleftharpoons Fe^{2+} + H_2S(aq)$ in this review. The estimated values depend on the cadmium, silver and mercury values and on whether dithizone is a good analogue for sulfide. As the paper provided no experimental evidence for specific iron sulfide complexes and their stability constants, the results are not taken into consideration in this review.

[1988EGG/SCH]

This is a useful review of the crystallography of iron oxides and hydroxides, and of iron-rich silicate and aluminosilicate minerals. Crystallographic packing and topology of oxyhydroxides are discussed, but in less detail than by Waychunas [1991WAY].

[1988FEN/WAK]

Small variations in the apparent formation constant for $FeCl^{2+}$ as measured spectrophotometrically for pairs of solutions of different ionic strengths (centred on an ionic strength of ~0.4 M perchlorate/chloride media, 20 °C) were used to evaluate the stability of a Fe(III) perchlorato complex and to propose a "true" ("absolute") value for the formation constant for $FeCl^{2+}$. The results ($K_{c,\text{absolute}}(FeCl^{2+}, I_c = 0.4\text{ M}) = 7.6$ and $K_{c,\text{absolute}}(FeClO_4^{2+}, I_c = 0.4\text{ M}) = 2.1$, both at 20 °C) are not used further in the present review, as the analysis in terms of a perchlorato complex, rather than interaction coefficients, is not consistent with the SIT treatment as described in Appendix B.

Similarly, the formation constants $K_{c,\text{conventional}}(FeSO_4^+, I_c = 0.4\text{ M}) = 196\text{ M}^{-1}$ and $K_{c,\text{absolute}}(FeSO_4^+, I_c = 0.4\text{ M}) = 383\text{ M}^{-1}$ at 20 °C were determined at a constant ionic strength of 0.4 M using $HClO_4$-H_2SO_4 mixtures. Again, these values are not used further in the present review, as the detailed results were not supplied, and the authors' analysis in terms of a perchlorato complex, rather than interaction coefficients, is not consistent with the SIT treatment as described in Appendix B.

[1988FOX]

As the title indicates, this is another study of iron(III) colloids in solution using dialysis as the method for separating the soluble iron. A correlation of published solubility data for synthetic precipitates of "colloidal ferric hydroxide" and for Fe concentrations in natural waters, corrected for hydrolysis and ionic strength, presumably at ambient temperature, resulted in the following linear function with respect to pH (1.7 – 6.6):

$$-\log_{10} a_{\text{Fe}^{3+}} = 2.35\text{pH} - 1.17\,.$$

from which the correlation $a_{\text{Fe}^{3+}} \cdot a_{\text{OH}^-}{}^{2.35} = 10^{-31.7}$ was obtained. This correlation does not make sense as a solubility expression for a single iron(III) oxyhydroxide phase with fixed particle size. Moreover, the suggestion of a common solid phase containing 2.35 hydroxide ligands per iron(III) appears to be naïve, as the colloids correlated here were studied in a wide range of synthetic brine concentrations and compositions. However, the discussion of the effect of entrained colloids on solubility measurements performed by previous investigators using filtration to separate the solid phase from the solution is certainly valid. Moreover, the author's claim may be valid that the existence of the correlation given above indicates that most river waters are in equilibrium with colloidal iron(III).

[1988HOV]

This thesis contains unpublished data on the apparent molar heat capacities and volumes for solutions of iron(III) and iron(II) perchlorates from 10 to 55 °C. The measurements were obtained using a flow calorimeter and flow densimeter. The results for Fe(II) solutions were corrected by the author for the presence of small amounts of Fe(III) (< 0.0062 m). All solutions contained aqueous perchloric acid (< 0.1 m for Fe(II) solutions, < 0.2 m for Fe(III) solutions) so that hydrolysis would not be important.

The experimental work and data analysis appear to have been carried out carefully. The following equations were reported for the molar heat capacities:

$$C^{\mathrm{o}}_{p,2,\mathrm{m}}(\mathrm{Fe(ClO_4)_3, sln}, T)/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = 4233.0 - 189440/(T/\mathrm{K} - 190) - 8.9529(T/\mathrm{K})$$

$$C^{\mathrm{o}}_{p,2,\mathrm{m}}(\mathrm{Fe(ClO_4)_2, sln}, T)/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = 2128.1 - 96384/(T/\mathrm{K} - 190) - 4.4089(T/\mathrm{K})$$

The original analysis by Hovey [1988HOV] used a value of -25.2 J·K^{-1}·mol^{-1} for the partial molar heat capacity of $\mathrm{HClO_4(sln)}$. Reanalysis and comparison of the apparent molar heat capacity data of $\mathrm{HClO_4}$ is not within the scope of the present review. However, using the partial molar heat capacity of $\mathrm{ClO_4^-}$ at 298.15 K from the measurements of Oakes and Rai [2001OAK/RAI], -26.3 J·K^{-1}·mol^{-1}, the value of $C^{\mathrm{o}}_{p,2,\mathrm{m}}(\mathrm{Fe^{2+}}$, 298.15 K) is $-(25.0 \pm 10.0)$ J·K^{-1}·mol^{-1} and $C^{\mathrm{o}}_{p,2,\mathrm{m}}(\mathrm{Fe^{3+}}$, 298.15 K) is $-(108.1 \pm 20.0)$ J·K^{-1}·mol^{-1}. Then, based on the value of the partial molar heat capacities of $\mathrm{Fe^{2+}}$ and $\mathrm{Cl^-}$ (-123.2 J·K^{-1}·mol^{-1} [2002PAT/WOO]) at 25 °C, the value of $C^{\mathrm{o}}_{p,2,\mathrm{m}}(\mathrm{FeCl_2}$, sln, 298.15 K) is $-(271 \pm 20)$ J·K^{-1}·mol^{-1}. The uncertainties are estimated in this review.

The thesis also provides equations for the ionic strength dependence of the heat capacities for total ionic strengths below 1.8 mol·kg^{-1}.

[1988KHO/ROB]

The paper reports on a potentiometric study of the complexation of sulfate ions with iron(III) in aqueous $\mathrm{NaNO_3}$ solution (1.0 M) at 25 °C. Solutions with Fe(III) molarities ranging from 0.2×10^{-3} to 19.77×10^{-3} and total sulfate molarities from 0.2×10^{-3} to 20.0×10^{-3}, and relatively low initial acid concentrations (< 0.017 M [H$^+$]) were titrated with aqueous $\mathrm{NaHCO_3}$ solutions. Measurements were done using a pH meter with a combination (glass) electrode. As in an earlier hydrolysis study done by the same group [1986KHO/BRO], the electrode was calibrated on an empirical molarity scale, and a revised MINIQUAD program was used to treat the titration data (12 solutions and 127 to 214 measurements per solution). At the end of the titrations the hydrogen ion molarities were between 0.00056 and 0.0043 M.

Several fitting schemes were tested by the authors, and the following values were found to give the most satisfactory results.

Table A-46: Formation constants$^{(a)}$ proposed in Khoe and Robins [1988KHO/ROB] (1.034 mol·kg^{-1} $NaNO_3$ at 25 °C). The authors' calculation scheme used fixed (molar) values of -13.75 for $\log_{10} K_w$ and -1.104 for $\log_{10} K^{-1}_{c1,1(HSO_4^-)}$, (the deprotonation constant of HSO_4^-).

	q, m, r	$\log_{10} {}^*\beta_{q,m,r}$	$\log_{10} {}^*\beta_{q,m,r}$ (molal)	2σ $^{(b)}$
$FeOH^{2+}$	1,1,0	-3.01	-3.00	0.02
$Fe_2(OH)_2^{4+}$	2,2,0	-3.09	-3.08	0.01
$Fe_3(OH)_4^{5+}$	4,3,0	-6.92	-6.89	0.06
$FeSO_4^+$	0,1,1	1.51[1]	1.50	0.02
$Fe_3(OH)_4SO_4^{2+}$	4,3,1	-4.34	-4.32	0.04

(a) ${}^*\beta_{q,m,r}$ is the equilibrium constant for $m\mathrm{Fe}^{3+} + q\mathrm{H_2O} + r\,\mathrm{SO_4^{2-}} = \mathrm{Fe}_m(\mathrm{OH})_q(\mathrm{SO_4})_r^{3m-q-2r} + q\mathrm{H}^+$.

(b) Uncertainty from the fitting, not including experimental or systematic uncertainties.

The authors found no evidence for several other species including $Fe(OH)_2^+$, $FeOHSO_4(aq)$, $FeHSO_4^{2+}$, $Fe(SO_4)_2^-$, $Fe(HSO_4)SO_4(aq)$ or $Fe(OH)_2SO_4^{2+}$. The value for the formation constant for $FeSO_4^+$ is markedly smaller than found in most studies at the same temperature in perchlorate medium. This suggests that the results might have been affected by Fe(III)-nitrate interactions [1952SYK]. It is also possible that the kinetics of some of the reactions involving hydrolytic species are slow, and equilibrium was not attained.

[1988KUB/MOC]

Conductivity measurements were made for 10^{-4} to 10^{-3} mol·dm^{-3} aqueous Fe(II)sulfate solutions at temperatures from 10 to 35 °C. Care was taken to prevent oxidation of the iron(II) solutions by saturating the water with nitrogen before each conductance series, and then maintaining a nitrogen atmosphere over the solutions during the experiments. A Hawes-Kay device [1965HAW/KAY] was used to add the samples of $FeSO_4(cr)$.

The conductivity data were claimed to have been analyzed using the Quint and Viallard conductivity equation for symmetrical electrolytes [1978QUI/VIA] with the form

$$\Lambda = \gamma[\Lambda_0 - S\sqrt{(c\,\gamma)} + E c\,\gamma \log_{10}(c\,\gamma) + J_1 c\,\gamma - J_2\sqrt{(c\,\gamma)^3}].$$

---

[1] There is a minor discrepancy in the authors' reported value for the formation constant for $FeSO_4^+$. From the values in the abstract and Table 4, the value of $\log_{10}\{[FeSO_4^+]/([Fe^{3+}][SO_4^{2-}])\}$ would be 1.51, whereas the value given in Table 6 is 1.53.

Then, the degree of dissociation γ, and the association constant for $FeSO_4(aq)$ was calculated with

$$K_A = (1 - \gamma)/c\,\gamma^2 f_{\pm}^2$$

and

$$-\log_{10} f_{\pm} = A\sqrt{(c\,\gamma)}/(1 + B\text{å}\sqrt{(c\,\gamma)})$$

as the expression for the mean activity coefficients, based on Robinson and Stokes ([1965ROB/STO]; p.229, Eq. 9-7). However, these appear to be the equations for a 1:1 electrolyte. Both the Quint and Viallard equation [1978QUI/VIA] and the referenced Robinson and Stokes equation include terms in ionic strength I, not the molar concentration, c. Hence, it is not clear whether the authors applied the incorrect formulae, or if this is merely a set of typographical errors. Therefore, the value of the reported formation constant, β_1^o ($FeSO_4$, aq, 25 °C) = (247 ± 2), must be treated with caution. The total ionic strength range is not directly specified, but the concentrations of the salt ($FeSO_4$) are low, ranging from 5×10^{-4} to 4.5×10^{-2} $mol \cdot dm^{-3}$. The data set itself seems very reliable and a thorough re-evaluation of the conductivity measurements is clearly indicated.

For the purposes of internal consistency in the present review, the data have been reanalysed (Table A-47) using the series form [1980PET/TAB][1] of the Lee-Wheaton equation, modified so that the activity-coefficient equation matches the SIT equation usually used in the TDB project (Appendix B). For each temperature this meant keeping the Bjerrum critical distance fixed (at ~ 1.4 nm).

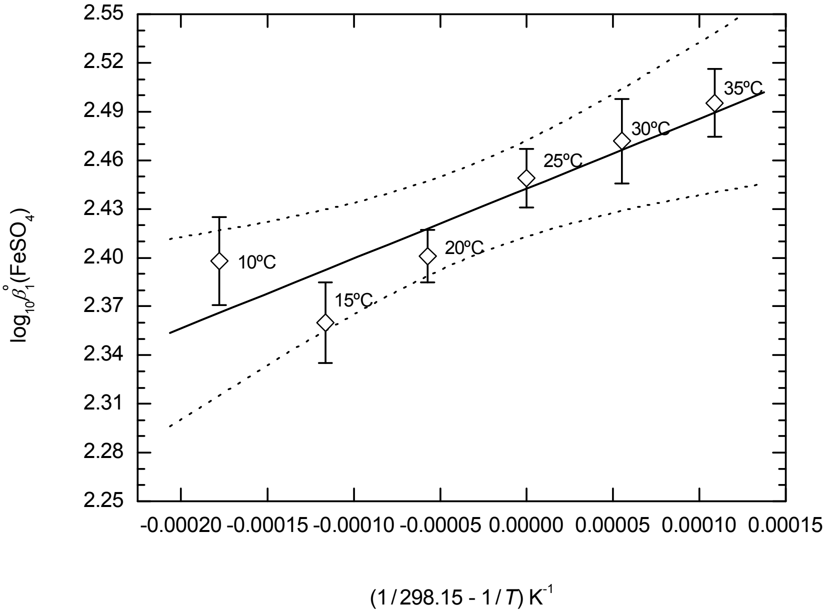
Table A-47: Comparison of the Quint and Viallard analysis of data from [1988KUB/MOC] with values recalculated in the present review using a modification of the Lee-Wheaton equation.

T / °C	$\frac{1}{2}\Lambda_0 / S \cdot cm^2 \cdot mol^{-1}$		β_1^o	
	[1988KUB/MOC]	recalculated	[1988KUB/MOC]	recalculated
10	93.1	95.8	201	250.0 ± 15.5
15	105.0	106.7	215	229.1 ± 13.0
20	119.4	121.7	231	251.7 ± 9.4
25	133.8	137.2	247	281.2 ± 11.6
30	150.4	153.8	264	296.2 ± 17.7
35	167.1	170.8	281	312.8 ± 15.0

---

[1] In 1979, Dr. A.D. Pethybridge kindly provided one of us (RJL) with a version of the computer program that has been used here (with modifications) for the analysis of conductance data.

Figure A-37: Regression of $\log_{10} \beta_1^{\circ}$ (FeSO$_4$, T) data *vs.* a function of inverse temperature ($T_0 = 298.15$ K). The error bars correspond to the σ-values obtained from the regression according to Bevington [1969BEV]. The (2σ) uncertainties are obtained by multiplying by the student-t factor (5%,4) of 2.7765.



The regression of $\log_{10} \beta_1^{\circ}$ *vs.* ($1/T_0 - 1/T$) (Figure A-37) is straightforward, with $R^2 = 0.82$ and produces

$$\log_{10} \beta_1^{\circ}\,(\mathrm{FeSO_4, aq, 25\ ^\circ C}) = (2.44 \pm 0.03)\ (2\sigma)$$

and

$$\Delta_r H_m^{\circ}\,(\mathrm{Fe^{2+} + SO_4^{2-} \rightleftharpoons FeSO_4(aq)}) = (8.4 \pm 6.2)\ \mathrm{kJ \cdot mol^{-1}}\ (2\sigma),$$

leading to

$$\Delta_r S_m^{\circ}\,(\mathrm{Fe^{2+} + SO_4^{2-} \rightleftharpoons FeSO_4(aq)}) = (75 \pm 21)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}\ (2\sigma).$$

The regression is sensitive to the number of data points selected to evaluate values of $\log_{10} \beta_1^{\circ}$ (FeSO$_4$, aq) at each temperature, and is also sensitive to the magnitudes assigned to the calculated uncertainties. A sensitivity analysis was performed by varying the number of data points (actually the concentration range) selected to evaluate individual K values. From this sensitivity analysis and from fits evaluated without using the 10 °C point it is concluded that the 10 °C measurement most likely is an outlier. If this 10 °C measurement is omitted in the evaluation, the fit produces $\log_{10} \beta_1^\circ$ = (2.44 ± 0.04) and $\Delta_r H_m^\circ$ = (11.9 ± 9.8) kJ·mol^{-1} with a coefficient of determination R^2 = 0.97. However, the present review does not have sufficient evidence to exclude any of the individual points and, hence, results evaluated by regression on all points are selected.

[1988NEI]

The main aim was to calibrate certain metal–oxide and oxide-oxide couples *vs*. air in order to maximize the accuracy of solid-state cell-potential studies. This work is, in part, a refinement of previous measurements of Fe-"FeO" and Cu-Cu_2O potentials at the same laboratory [1986HOL/NEI], and also complements the same author's study of equilibria in the Fe-Si-O system [1987NEI2].

A Y-doped ThO_2 electrode was developed as the air sensor. This eliminated the problem of sluggish and unstable performance of platinum-black electrodes below 900 K, and thus permitted direct measurement of the Fe(cr)-Fe_3O_4(cr) potential from the wüstite eutectoid (here estimated as 833 K; see Section VII.2.8.3) down to about 750 K. Use of a static, high-purity Ar cover gas in the solid electrode compartment(s) helped assure solid-gas equilibrium and hence accurate potential-difference measurements for couples such as Cu-Cu_2O and Fe_3O_4-Fe_2O_3 with significant equilibrium O_2 partial pressures.

Oxygen chemical potential measurements *vs*. air are tabulated for the following couples: Fe-"FeO" (N = 91 at 850.1 ≤ T/K ≤ 1405.7, his Tables 2 and 3), Fe-Fe_3O_4 (N = 21 at 750.7 ≤ T/K ≤ 832.4, his Table 3) and Cu-Cu_2O couples (N = 71 at 749.6 ≤ T/K ≤ 1332.2, his Table 1). Additional data are presented for Fe-"FeO" *vs*. Cu-Cu_2O (N = 133 at 850 ≤ T/K ≤ 1331, his Tables 4 and 5), "FeO"-Fe_3O_4 *vs*. Fe-"FeO" (N = 85 at 838 ≤ T/K ≤ 1270, his Table 6), "FeO"-Fe_3O_4 *vs*. Ni-NiO (N = 36 at 928 ≤ T/K ≤ 1248, his Table 6), Fe_3O_4-Fe_2O_3 *vs*. Cu-Cu_2O (N = 49 at 1013 ≤ T/K ≤ 1322, his Table 7), Fe_3O_4-Fe_2O_3 *vs*. Ni-NiO (N = 23 at 1019 ≤ T/K ≤ 1268, his Table 7), and Cu_2O-CuO *vs*. Cu-Cu_2O (N = 55 at 804 ≤ T/K ≤ 1269, his Table 8).

The following expressions for $\mu_{O_2}(T)/\text{J·mol}^{-1}$ with a reference pressure of 10^5 Pa were obtained.

For Cu + Cu_2O: $\mu_{O_2}(T) = \{-347705 + 246.096T - 12.9053T\cdot\ln T\} \pm 62$ $(750 \le T/\text{K} \le 1330)$.

For Fe + "FeO": $\mu_{O_2}(T) = \{-605812 + 1366.718T - 182.7955T\cdot\ln T + 0.10359T^2\} \pm 100$ $(833 \le T/\text{K} \le 1042)$.

$\mu_{O_2}(T) = \{-519357 + 59.427T + 8.9276T\cdot\ln T\} \pm 100$ $(1042 \le T/\text{K} \le 1184)$.

$\mu_{O_2}(T) = \{-551159 + 269.404T - 16.9484T\cdot\ln T\} \pm 100$ $(1184 \le T/\text{K} \le 1450)$.

For "FeO" + Fe_3O_4: $\mu_{O_2}(T) = \{-581927 - 65.618T + 38.7410T\cdot\ln T\} \pm 306$ $(833 \leq T/\mathrm{K} \leq 1270)$.

For Fe + Fe_3O_4: $\mu_{O_2}(T) = \{-607673 + 1060.994T - 132.3909T\cdot\ln T + 0.06657T^2\} \pm 107$ $(750 \leq T/\mathrm{K} \leq 833)$.

For Cu_2O + CuO: $\mu_{O_2}(T) = \{-292245 + 377.012T - 23.1976T\cdot\ln T\} \pm 117$ $(800 \leq T/\mathrm{K} \leq 1300)$.

A corresponding equation for the Fe_3O_4 + Fe_2O_3 equilibrium is not presented, because the measurements were less certain than for the other equilibria (see discussion below and Section VII.2.2.1).

A value of $\Delta_f H_m^\circ$ (Fe_3O_4, cr, 298.15 K) = $-(1115.4 \pm 0.2)$ kJ·mol^{-1} was derived, but the uncertainty reflects only the accuracy of the high-temperature potential-difference measurements and not that of the calorimetric data used to obtain this value.

This work appears to have been performed with extreme care to identify and minimize all potential sources of inaccuracy. For example, whereas most publications on potential-difference measurements *vs.* an air electrode assume a constant oxygen chemical potential for air, this author made corrections for variations in atmospheric pressure and humidity, and adjusted barometric measurements for the absolute value of gravity at the laboratory site. In this way, the total error in μ_{O_2}(air) was reduced to ± 40 J·mol^{-1}. Comparable care was applied to electrode design, temperature control and measurement, correction for thermoelectric effects, achievement of equilibrium, and assurance of internal consistency among the data sets. Respective precisions of ± 50 J·mol^{-1} and ± 40 J·mol^{-1} were estimated for the temperature and potential-difference measurements, for an overall precision of ± 75 J·mol^{-1}, corresponding to ± 0.003 in $\log_{10} f_{O_2}$ at 1200 K. The author went to great lengths to eliminate sources of systematic error and support claims that the accuracy is comparable to this precision. It seems reasonable to accept that the data presented are the most accurate available for the equilibria examined, with the possible exception of Fe_3O_4-Fe_2O_3, and they are treated as such in Section VII.2.7.2.3.

Difficulties with the Fe_3O_4-Fe_2O_3 system arise from sluggish reaction below ~ 1000 K and deviation from exact Fe_3O_4 stoichiometry by the equilibrium magnetite composition above about 1150 K. Results suggest that the Fe_3O_4-Fe_2O_3 couple is somewhat more reducing (by about 1 kJ·mol^{-1} Fe_2O_3) than indicated by most previous studies. Since the data from this study deviate in the sense expected from the change in magnetite stoichiometry (and hence Fe_3O_4 activity), it seems likely that the author succeeded where others had narrowly failed in achieving true equilibrium between magnetite and hematite. Though the author is quite diffident in his discussion of these results, Hemingway [1990HEM] argued that O'Neill is most likely correct, and adjusted his recommended value for $\Delta_f H_m^\circ$ (Fe_2O_3, α, 298.15 K) accordingly. The treatment of hematite in Section VII.2.2.1 is largely consistent with Hemingway's conclusion.

[1988SAD/LIN]

A maghemite-rich sample (92-96% Fe_2O_3) was extracted by repeated magnetic separation from a sandy loam soil collected in Colorado, U.S.A. Specimens of various particle sizes (based on mesh separation, not crystallite size) were suspended in 0.01 M $Ca(NO_3)_2$ (0.5 g solid in 125 cm^3 aqueous solution) and analysed at intervals up to a total of 15 days for pH, pe (defined by the authors as Eh(mV)/59.2), and total dissolved Fe. The Fe^{3+} activity and hence the solubility product, $a_{Fe^{3+}} a^3_{OH^-}$, were derived from these measurements, based on equilibration between aqueous Fe^{2+}, $FeOH^+$, Fe^{3+}, $FeOH^{2+}$, and $Fe(OH)_2^+$, using the Davies equation to calculate ionic activity coefficients. The 5- and 15-day data on triplicate samples of the three size fractions yielded a mean $-\log_{10} K_s$ value of (40.36 ± 0.07).

While this value is plausible, and it agrees quite well with directly determined thermodynamic data (see further discussion in Section VII.2.4.2), it is not included in the final assessment, in part because of the relatively low purity and unknown crystallite size of the specimen. The accuracy of the Eh measurements and the apparent major role of Fe(II) in the speciation are also difficult to evaluate. In addition there is a major typesetting error in the main data table, with identical data being given for two of the size fractions. Diakonov [1998DIA] estimated $-\log_{10} K_s$ = (40.06 ± 0.16) from a selected subset of data (criteria for selection unstated) from this paper but considered this only to be an estimate, because of uncertainty that reversible equilibrium (*i.e.*, maghemite saturation) was achieved.

[1988SER/SUL]

The reviewer could only trace an abstract of this work, but it appears to be based on the same experimental data presented in their later paper, [1999SER/SUL] and therefore this older reference was not pursued further.

[1988SHA/BAR]

Differential-scanning calorimetry (DSC), thermogravimetry and evolved gas-analysis results are reported for the iron(II) chloride hydrates for temperatures from 300 to 478 K. The heating rate of 0.27 $K \cdot s^{-1}$ was quite rapid. No information is given on how samples of the lower hydrates were handled when removed from the DSC apparatus for weighing. No X-ray diffraction or wet analysis information is provided for the samples after dehydration (or partial dehydration). DSC dehydration maxima from closed-pan experiments were found at 330, 410, and 461 K (with dehydration of the tetrahydrate to the dihydrate and $H_2O(l)$ occurring at 330 K). The DSC dehydration maximum for conversion of the tetrahydrate to the dihydrate and $H_2O(g)$ (from open pan experiments) was found to occur near 347 K. The tabulated enthalpies of dehydration are much more endothermic than those determined by Schäfer [1949SCH] (by approximately a factor of four), and essentially no information is provided on how the enthalpies were calculated. The authors' Figure 3 shows that separation of the enthalpies of the last two hydration steps by DSC is unlikely to be successful. The enthalpy of dehydration values from this paper are not credited in the present review.

[1989BRU/PET]

This paper deals with the stability constant of $FeCl^{2+}$ over the temperature range 298 to 398 K. A spectrophotometry technique was used at various temperatures with a cell that was resistant to corrosion and large volume changes, and which permitted the solution compositions to be maintained at the higher temperatures.

For I_m = 1.05 m (1 M $HClO_4$(sln)) and 25 °C $K_{1m} = (5.18 \pm 0.22)$ was found. However, as this K_1 value is greater than many of the other literature values, the estimated uncertainty has been increased to $\pm$ 1.00 $mol^{-1}\cdot kg$ in the present review.

The variation of K_1 with temperature as analyzed by the authors using the van't Hoff equation gave $\Delta_r H_c = (24.3 \pm 0.8_4)$ $kJ\cdot mol^{-1}$. This value lies in the upper range of literature values, and was calculated assuming that $\Delta_r C_p = 0$. Recalculations taking as the value for K_{1c} the unweighted average of the three constant values at a constant temperature as given by the authors led to $\Delta_r H^\circ_m = (18.1 \pm 2.1)$ $kJ\cdot mol^{-1}$. However the function $\ln K^\circ_m$ as a function of $1/T$ is not linear. That means that $\Delta_r H^\circ_m$ is not constant and $\Delta_r C^\circ_{p,m}$ is different from zero within the temperature range of the study. This confirms the results of previous [1967VAS/LOB2] investigations. We did not use this value in determining the recommended value of $\Delta_r H^\circ_m$, but the value of K_1 was included in the set of literature values used for the determination of K°_1 and $\varepsilon(FeCl^{2+}, ClO_4^-)$ at 298.15 K.

[1989COR/GIO]

This paper presents a review of iron(III) solid phases and their interconversion.

Contrary to the suggested content of this review based on its title, there is no discussion of hydrolysis constants.

[1989EFI/EVD]

See the discussion of [1989EVD/EFI2].

[1989EVD/EFI2]

Efimov and Evdokimova [1989EFI/EVD] measured the heats of solution of bromine, Fe(cr), $FeBr_2$(cr), and $FeBr_3$(cr) into aqueous solutions with H_2O:KBr:Br_2:HBr molar ratios of 50.78:1.00:0.43:0.12. The rapid bromine oxidation of Fe(cr) avoids possible problems with hydrogen gas evolution, which might occur when the metal is dissolved in acid alone. A minimum of five measurements was carried out for each reaction. From appropriate cycles it was found that $\Delta_f H^\circ_m$ ($FeBr_2$, cr, 298.15 K) = $-(244.73 \pm 0.22)$ $kJ\cdot mol^{-1}$ and $\Delta_f H^\circ_m$ ($FeBr_3$, cr, 298.15 K) = $-(262.63 \pm 0.20)$ $kJ\cdot mol^{-1}$. The uncertainties are the statistical 95% confidence limits. Similar solutions [1989EVD/EFI2] were used to determine the heats of dissolution of $FeCl_2$(cr), $FeCl_3$(cr), KCl(cr) and KBr(cr). Using the values selected [2005GAM/BUG] for

$\Delta_f H^o_m$ (KBr, cr, 298.15 K) and $\Delta_f H^o_m$ (KCl, cr, 298.15 K), the values $\Delta_f H^o_m$ ($FeCl_2$, cr, 298.15 K) = $-(341.04 \pm 0.53)$ $kJ \cdot mol^{-1}$ and $\Delta_f H^o_m$ ($FeCl_3$, cr, 298.15 K) = $-(395.57 \pm 0.74)$ $kJ \cdot mol^{-1}$ are calculated. This appears to be an excellent set of experimental results. Samples were properly prepared and analyzed and handled with appropriate precautions. The uncertainties are greater for the enthalpies of formation of the iron chlorides than for the bromides primarily because of the relative uncertainties in the values for the potassium halide solids.

[1989JAC/KAL]

The authors measured potentials of the solid-state galvanic cells

$$\text{Pt}|\text{Fe}, Fe_2SiO_4, SiO_2(\text{quartz})|(Y_2O_3)ZrO_2|\text{“FeO”},\text{Fe}|\text{Pt} \qquad (A)$$

at 900 to 1400 K and

$$\text{Pt}|Fe_3O_4, Fe_2SiO_4, SiO_2(\text{quartz})|(Y_2O_3)ZrO_2|\text{NiO},\text{Ni}|\text{Pt} \qquad (B)$$

at 1080 to 1340 K to determine the oxygen chemical potentials corresponding to equilibrium.

The measured potentials for cell (A) (recovered from the authors' Figure 2) are in good agreement with, for example, those obtained by O'Neill [1987NEI2] for a similar cell. Jacob *et al.* used a set of measurements from Steele [1968STE] to convert their measured potentials to values of Gibbs energies of reaction. When, instead, the corresponding reference electrode values from O'Neill are used, along with consistent auxiliary data for quartz ([1989COX/WAG], [1998CAR/SAL]) and oxygen [1989GUR/VEY], and with the values selected in this review for the heat capacity and entropy of α-Fe_2SiO_4 (Section X.2.1.1.1) and Fe(cr) (Section V.2), values of − 1477.53 to − 1476.90 $kJ \cdot mol^{-1}$ were obtained for $\Delta_f H^o_m$ (Fe_2SiO_4, α, 298.15 K) (average, $-(1477.25 \pm 0.46)$ $kJ \cdot mol^{-1}$), 2σ uncertainty). The thirteen values showed a very slight drift to more positive values as the temperatures increased from 905 to 1400 K.

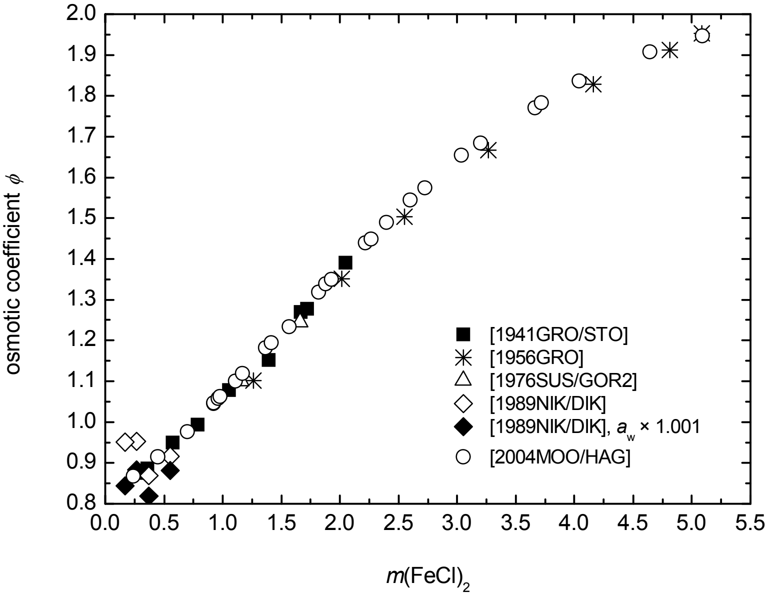
The Gibbs energies of reaction, as recalculated from the measured potentials for cell (B), do not correspond as well with those of O'Neill [1987NEI2] (differences are 2 to 3 $kJ \cdot mol^{-1}$). In general, such cells using magnetite do not seem to be as well behaved as those with metal/metal oxide reference electrodes (including Fe/"FeO") [1987NEI2], and the values from measurements with magnetite-containing cells are not used in the present review to define $\Delta_f H^o_m$ (Fe_2SiO_4, α, 298.15 K).

[1989NIK/DIK]

Iron(II) sulfate (hydrate) crystals were prepared from analytical iron(II) sulfate solutions at 50 °C in the presence of iron powder after filtration. No iron(III) was detected when these crystals were dissolved in dilute H_2SO_4. Iron(II) chloride crystals, $FeCl_2 \cdot 4H_2O$, were prepared in an analogous manner. The solutions of both crystals were analyzed potentiometrically for iron(II) using potassium dichromate with the indicator, phenylaminesulfonic acid. Isopiestic measurements were performed using four vacuum desiccators at 298.15 K maintained at ±0.1 K, which is at least an order of magnitude less stable than is usually required for such measurements. The cups within the desiccators could be capped *in situ* thereby minimizing contact with air upon opening. Sodium chloride solutions were utilized as the standard, but the reference to their activities was not provided. Only two to three days were allowed for equilibration which is very short especially for the low concentrations investigated. The reviewer's experience would suggest that at least one to two weeks is required for equilibration even when the solutions are agitated and the inner walls of the cups are lined with gauze to enhance the exposed surface area of the solutions.

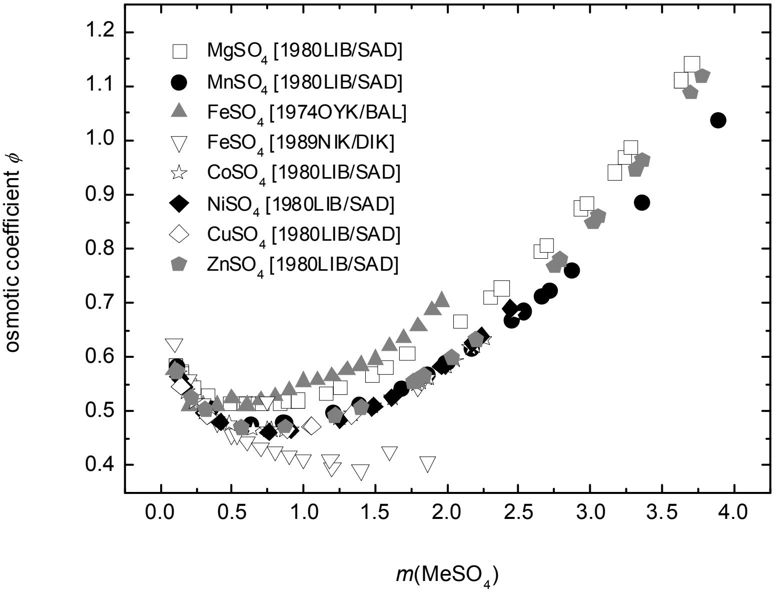
For the end-member solutions of pure $FeCl_2$ the following water activities are tabulated: 0.9730, 0.9826, 0.9862 and 0.9912 at molalities of 0.553, 0.374, 0.270 and 0.172, respectively. The water activities can be converted to osmotic coefficients of 0.9158, 0.8684, 0.9522 and 0.9508, which are plotted in Figure A-38. It can be seen that the last two molalities are lower than any of the other values. Moreover, for example, an increase of 0.1% in the measured water activity results in lowering of the osmotic coefficient by 3.65, 5.69, 7.19 and 11.31%, respectively.

Figure A-38: Plot of the osmotic coefficient values for aqueous $FeCl_2$(sln) at 298.15 K *vs*. molality.



In their Table 1 the authors provided osmotic coefficients of $FeSO_4$-solutions as a function of the molality. These data are plotted in Figure A-39 (open triangles) together with osmotic coefficient data for many other divalent transition metal sulfate solutions. The four data points for the pure $FeSO_4$ end-member solutions provided in their Table 2 are also plotted in Figure A-39 (large open triangles).

Figure A-39: Osmotic coefficients from [1980LIB/SAD] ($MgSO_4$, $MnSO_4$, $CoSO_4$, $NiSO_4$, $CuSO_4$, $ZnSO_4$), [1974OYK/BAL] ($FeSO_4$, filled diamonds), and from this study [1989NIK/DIK] ($FeSO_4$, open inverted triangles).



Due to the experimental shortcomings, the lack of knowledge of the water activities of the standard NaCl solution and to the low molalities of $FeCl_2$ investigated, these results were not included in the overall fit of osmotic coefficient data.

As shown in Figure A-39, the osmotic coefficients for $FeSO_4$(sln) given in the authors' Table 1 do not agree well with the data from Oykova and Balarew [1974OYK/BAL], and neither set is particularly consistent with results for other Me(II) sulfates. Additionally, two of the data points from Table 2 of Nikolaev *et al.* [1989NIK/DIK] are inconsistent with the rest of their data (the points at m = 0.744 and 1.867 m). Again, it is not clear what values were used by Nikolaev *et al.* for the water activities of the NaCl standards. Because of the inconsistencies, these $FeSO_4$(sln) osmotic data cannot be included in the review to determine the formation constant of $FeSO_4(aq)$.

However, there have been considerably fewer osmotic measurements for $FeSO_4$ solutions than for $FeCl_2$ solutions. Therefore, a refit of the Pitzer equation for 2:2 electrolytes to the data from Nikolaev *et al.* was done, similar to that outlined in the Appendix A entry for Oykova and Balarew [1974OYK/BAL]. With the value of $\beta^{(2)}$ fixed as -42 and an unconstrained value of $\gamma_{\pm}$ for the 0.1 m solution, values of -0.1189, 4.4354 and 0.16527 for $\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ} are obtained from the fitting. At saturation this results in ϕ, $\gamma_{\pm}$, and a_w values of 0.513, 0.0366 and 0.960, and hence 13.76 $kJ\cdot mol^{-1}$ for $\Delta_r G^o_m$ (A.137).

$$FeSO_4.7H_2O(cr) \rightleftharpoons FeSO_4(sln) + 4\,H_2O(l) \qquad (A.137)$$

As discussed above, there is considerable scatter in the results at the higher molalities, and the uncertainty in $\Delta_r G^o_m$ (A.137) is estimated here as ± 1.00 $kJ\cdot mol^{-1}$.

[1989RIC]

Initial precipitate formation from the reaction between aqueous Fe(II) salts and dissolved sulfide at ambient temperature (18 ± 2) °C and $pH < 9$ was investigated by the T-tube method. The T-tube was constructed from thick-walled glass tubing with a 1.8 mm inner diameter. The mixing chamber at the junction of the T had parallel inlets and a perpendicular outflow. Solutions of iron(II) ammonium sulfate and Na_2S were pumped with a peristaltic pump. Silver-silver sulfide electrodes, used to measure the total dissolved sulfide concentration, were situated at the distances corresponding to the reaction times 0.26, 0.40, 0.53, 0.60 and 0.81 s. The experiments were conducted with 10^{-4} to 10^{-3} M total dissolved sulfide and total dissolved Fe(II). A typical plot of dissolved sulfide *vs*. time involved two major reaction regimes. Regime 1 consisted of a rapid initial reaction which typically resulted in the removal of up to 99 % of total dissolved sulfide from solution. Regime 2 involved an initial increase in dissolved sulfide concentration followed by a slow, steady decrease in dissolved sulfide concentration. A final steady-state dissolved sulfide concentration was not observed in the experiment. The rate of formation of the initial precipitate could be approximated by a pseudo-first-order reaction, directly dependent on total sulfide concentration and with an apparent pseudo-first-order rate constant of (48 ± 9) s^{-1}. The dissolved Fe concentration did not appear to be rate limiting. This precipitate was considered to be a highly disordered gel approaching the composition of $Fe(HS)_2$ on a water-free basis. The solubility of this phase was variable but estimated to be consistently one to two orders of magnitude greater than the measured solubilities for amorphous FeS. After ~ 0.4 s, this precipitate seemed to lose sulfide and amorphous FeS began to appear. The observations in this paper are informative but rather qualitative. This review takes the result only as supplementary information.

[1989STU/TOG]

Stubina and Toguri [1989STU/TOG] monitored the equilibrium decomposition pressure of $FeCO_3$(cr) between 567 and 679 K, and reported values for $\Delta_r S^\circ_m$ (A.138) and $\Delta_r H^\circ_m$ (A.138)

$$3\,FeCO_3(cr) \rightleftharpoons Fe_3O_4(cr) + CO(g) + 2\,CO_2(g). \qquad (A.138)$$

The gas mixture was not monitored, and it is not clear that the oxygen partial pressure was buffered [2004KOZ]. The results for $\Delta_r H^\circ_m$ (A.138) lead to a value of $\Delta_f H^\circ_m$ ($FeCO_3$, cr, 298.15 K) ~ − 749 kJ·mol^{-1}, that is in marginal agreement with values from other sources. However, $\Delta_r S^\circ_m$ (A.138) from the same analysis leads to a value for S°_m ($FeCO_3$, cr, 298.15 K) of ~ 127 J·K^{-1}·mol^{-1}, more than 25% greater than determined by calorimetry results. If the entropy of reaction is fixed at a value consistent with the work of Robie *et al.* [1984ROB/HAS], an average value of ~ − 770 kJ·mol^{-1} is obtained for $\Delta_f H^\circ_m$ ($FeCO_3$, cr, 298.15 K), and there is a clear temperature dependence.

[1989WAL/THO]

A reanalysis of the magnetite solubility data from [1970SWE/BAE] and [1980TRE/LEB] is presented concisely. No new experimental solubility results are presented. The reanalysis involved using the isocoulombic form of the solubility equilibria where possible and, in the case of Sweeton and Baes' results, these authors introduced a simple Debye-Hückel term to account for the ionic activity coefficients. They also constrained the ΔS° (298.15 K) value from an undisclosed literature source for the equilibrium,

$$\tfrac{1}{3}\,Fe_3O_4(cr) + 2\,H^+ + \tfrac{1}{3}\,H_2(g) \rightleftharpoons Fe^{2+} + \tfrac{4}{3}\,H_2O(l)$$

where the authors omitted the $\tfrac{1}{3}$ factor for Fe_3O_4(cr), as they also did for all the equilibria cited in their paper. Moreover, they did not attempt to reconcile the two sets of thermodynamic parameters for the iron(II) and (III) species from these two primary sources, and simply reported the two sets independently.

No useful information can be obtained from this treatment of existing results.

[1989ZEN/AI]

The solubility of a mixture of crystalline magnetite and hematite was measured in a batch-type gold-bag apparatus at 300 °C and 500 bars in 0.10, 1.00 and 3.00 mol·kg^{-1} NaCl solutions. The initial hematite charge was partially reduced to 56 wt% magnetite at 1450 °C as confirmed by XRD. The iron content of the *in situ* filtered solution samples was determined spectrophotometrically and the pH of the quenched samples was measured with a "glass" electrode at room temperature, although the calibration procedure was not mentioned. However, the initial pH of the starting solutions was used to calculate the pH at the experimental temperature, except for solutions of pH > 12 where a titration technique was employed which would necessitate then using a molality-based pH scale. The following aqueous iron-bearing species were considered in the modelling of these data, *viz*., Fe^{2+}, $FeOH^{+}$, $Fe(OH)_2$(aq), $Fe(OH)_3^-$, $Fe(OH)_3$(aq), $Fe(OH)_4^-$, $FeCl^+$, and $FeCl_2$(aq). A fully speciated model was employed (*i.e.*, one taking into account all ion pairs in solution such as those of NaCl, HCl and NaOH) that was based on previous Russian work, Bryzgalin, O.V., Geochimiya, 8, 1187-1195 (1985). The activity coefficients were taken from the Helgeson-Kirkham-Flowers model.

The experimental condition of 300 °C and 500 bars combined with the complexity of the solution compositions cause these results to be inapplicable to the current NEA database.

[1990EFI/EVD]

Efimov and Evdokimova [1990EFI/EVD] measured the heats of solution of iodine and of FeI_2(cr) into aqueous solutions with H_2O:KBr:Br_2:HBr molar ratios of 51:1.00:0.4:0.12. With the value of the heat of solution of Fe(cr) from their earlier study [1989EFI/EVD], $\Delta_f H_m^o$ (FeI_2, cr, 298.15 K) = – (118.08 ± 0.27) kJ·mol^{-1} is calculated. From the heat of dissolution of KI(cr) in the same mixture, a second cycle (similar to that used to determine $\Delta_f H_m^o$ ($FeCl_2$, cr, 298.15 K) [1989EVD/EFI2]) was used to obtain $\Delta_f H_m^o$ (FeI_2, cr, 298.15 K) = – (118.05 ± 0.54) kJ·mol^{-1} (as recalculated in the present review with the value selected in [2005GAM/BUG] for $\Delta_f H_m^o$ (KI, cr, 298.15 K)). The two cycles have two measurements in common, and the greater uncertainty from the second cycle is primarily the consequence of the uncertainties in the values for the enthalpies of formation of KBr(cr) and KI(cr). The reported analysis of the sample of FeI_2(cr) suggests that the solid might have been very slightly substoichiometric with respect to iodine (but less so than the samples described by Oetting [1960OET]), or might have contained a minor (~ 0.5 weight-%) impurity. Nevertheless, these appear to be careful, useful measurements.

[1990HEI/SEW]

The formation of iron(II) chlorido complexes was studied by Heinrich and Seward at various temperatures (25, 50, 100, 150 and 200 °C) in HCl solutions up to 3.3 mol·kg^{-1} by means of UV-spectrophotometry.

At each temperature the absorbance data at various HCl concentrations were evaluated with a modified and extended version of the SQUAD code ([1975LEG/BRY], [1977LEG], [1984SEW]). Within the program, activity coefficient corrections were performed with an extended Debye-Hückel model. From this evaluation the authors simultaneously obtained the cumulative equilibrium formation constants for iron(II) chloride complexes as well as molar decadic absorption coefficients of the species involved (Fe^{2+}, $FeCl^+$, $FeCl_2$(aq)) at the experimental temperature and at I = 0. Below 150 °C and for HCl concentrations ≤ 3.3 mol·kg^{-1} the authors did not detect the neutral complex $FeCl_2$(aq). Corresponding formation constants are given in Table A-48.

For the present review it would be useful to know the formation constants as a function of the ionic strength at the given temperature in order to derive the corresponding interaction coefficients, but formation constants and molar decadic absorption coefficients are available explicitly for zero ionic strength only. However, in their Appendix I the authors provided normalized raw absorbance data together with the chemical system composition, and these enable the reconstruction of formation constant values as a function of the ionic strength. The corresponding procedure is outlined below.

Table A-48: Formation constants for iron(II) chlorido complexes at the given temperature of the system (saturated vapour pressure), expressed for $I = 0$. The neutral complex $FeCl_2(aq)$ was not found at $t < 150$ °C.

t/°C	$\log_{10}\beta_1(FeCl^+)$	Range	$\log_{10}\beta_2(FeCl_2, aq)$	Range
25	−0.16	−0.30…+1.3	-	
50	−0.02	−0.34…+0.10	-	
100	0.21	+0.09…+0.38	-	
150	0.66	+0.55…+0.72		(≤ −0.8)
200	1.10	+0.93…+1.36	−0.11	−0.77…+ 0.30

The absorptivity spectra plotted in [1990HEI/SEW] (Fig. 3) were digitized and sampled at desired wavelengths with the help of spline procedures using commercial software (MATLAB®, [2007MAE/NEU], http://www.mathworks.com). Ten years later Zhao and Pan [2001ZHA/PAN] (Fig. 9) presented an identical spectrum for the molar decadic absorption of Fe^{2+} and a nearly identical spectrum for the complex $FeCl^+$ at 25 °C[1]. Hence, there is independent evidence for the reliability of the molar decadic absorption coefficients provided by the authors. The molar decadic absorption coefficients extracted from both reports are provided in Table A-49 and the spectra for $FeCl^+$ are plotted in Figure A-40.

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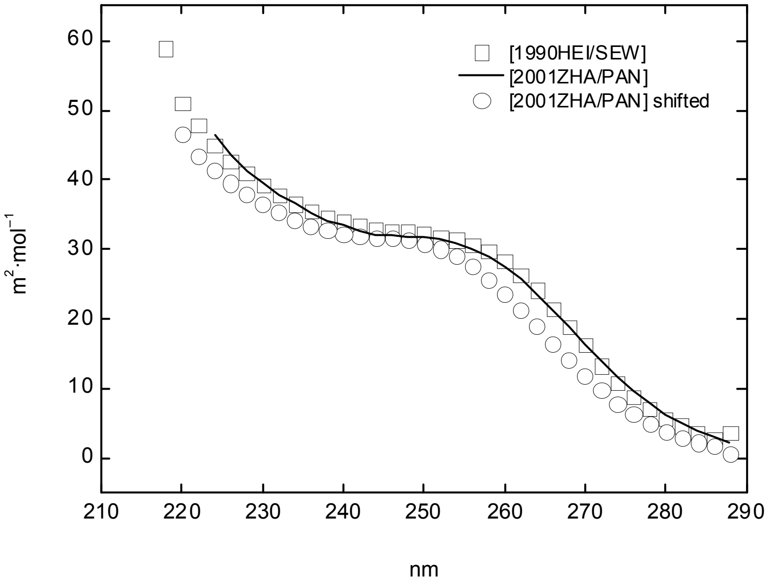
[1] Here, "nearly identical" means that the spectrum obtained from [2001ZHA/PAN, Fig. 9] has to be shifted towards higher wavelengths by 4 nm to become congruent with the [1990HEI/SEW; Fig. 3]-spectrum (see Figure A-40).

Table A-49: 25 °C molar decadic absorption coefficients extracted from [1990HEI/SEW] (Fig. 3) and from [2001ZHA/PAN] (Fig. 9). The [2001ZHA/PAN] spectrum for $FeCl^+$ is shifted towards higher wavelengths by 4 nm (see Figure A-40). Equally spaced values were obtained from processing digitized data with spline procedures using commercial software (MATLAB).

Wavelength/nm	$\varepsilon_{(Fe^{2+})}$ /m^2·mol^{-1} [1990HEI/SEW]	$\varepsilon_{(Fe^{2+})}$ /m^2·mol^{-1} [2001ZHA/PAN]	$\varepsilon_{(FeCl^{+})}$ /m^2·mol^{-1} [1990HEI/SEW]	$\varepsilon_{(FeCl^{+})}$ /m^2·mol^{-1} [2001ZHA/PAN]
220	22.73	22.12	51.11	
222	21.71	21.58	47.87	
224	21.02	20.94	45.01	46.55
226	20.28	20.28	42.79	43.49
228	19.59	19.75	40.93	41.30
230	18.93	19.52	39.25	39.53
232	18.44	19.08	37.82	37.88
234	18.10	18.89	36.50	36.56
236	17.69	18.66	35.54	35.31
238	17.50	18.38	34.55	34.18
240	17.49	18.30	33.88	33.40
242	17.33	18.14	33.38	32.71
244	17.07	17.76	32.93	32.12
246	16.90	17.38	32.69	31.95
248	16.48	16.79	32.49	31.71
250	16.05	16.01	32.20	31.63
252	15.28	15.02	31.82	31.41
254	14.35	13.87	31.32	30.88
256	13.05	12.54	30.68	30.06
258	11.65	10.97	29.67	29.03
260	10.23	9.55	28.26	27.58
262	8.80	8.15	26.28	25.66
264	7.30	6.85	24.18	23.51
266	6.02	5.51	21.53	21.19
268	5.04	4.51	18.90	18.92
270	4.03	3.68	16.32	16.38
272	3.18	2.86	13.24	13.98
274	2.43	2.27	10.72	11.76
276	1.75	1.70	8.84	9.71
278	1.23	1.30	7.15	7.92
280	0.81	1.04	5.67	6.34
282	0.36	0.79	4.62	4.94
284	0.16	0.60	3.55	3.80
286				2.96
288				2.21

Figure A-40: Molar decadic absorption coefficients ($m^2 \cdot mol^{-1}$) for $FeCl^+$ reported by [1990HEI/SEW] (Fig. 3) and [2001ZHA/PAN]. Both spectra were retrieved from published spectra using digitizing and spline sampling procedures (commercial software). The solid line corresponds to the [2001ZHA/PAN] (Fig. 9a) spectrum, shifted towards higher wavelengths by 4 nm.



According to Beer's law, the absorbance A_λ at each wavelength λ is a linear function of the (amount-of-substance) concentrations of the species in solution:

$$A_\lambda = \left(\frac{l}{\text{m}}\right)\left[\left(\frac{\varepsilon_{\lambda(\text{Fe}^{2+})}}{\text{m}^2\cdot\text{mol}^{-1}}\right)\left(\frac{c_{\text{Fe}^{2+}}}{\text{mol}\cdot\text{m}^{-3}}\right)+\left(\frac{\varepsilon_{\lambda(\text{FeCl}^{+})}}{\text{m}^2\cdot\text{mol}^{-1}}\right)\left(\frac{c_{\text{FeCl}^{+}}}{\text{mol}\cdot\text{m}^{-3}}\right)\right]. \qquad (\text{A.139})$$

Note that here, the ε_λ values (units of $m^2 \cdot mol^{-1}$) denote molar decadic absorption coefficients (not to be confused with the interaction coefficients $\varepsilon(j,k)$ used in the SIT formalism), l is the path length (in metres) and all concentrations c_x have units of $mol \cdot m^{-3}$.

Together with the mass balance for the total iron in solution, *i.e.* $c_{\text{Fe}_{\text{tot}}} = c_{\text{Fe}^{2+}} + c_{\text{FeCl}^+}$, one obtains

$$A_\lambda - \left(\frac{l}{\text{m}}\right)\left(\frac{\varepsilon_{\lambda(\text{Fe}^{2+})}}{\text{m}^2\cdot\text{mol}^{-1}}\right)\left(\frac{c_{\text{Fe}_\text{tot}}}{\text{mol}\cdot\text{m}^{-3}}\right) = \\ \text{k} + \left(\frac{l}{\text{m}}\right)\left(\frac{c_{\text{FeCl}^+}}{\text{mol}\cdot\text{m}^{-3}}\right)\left[\left(\frac{\varepsilon_{\lambda(\text{FeCl}^+)}}{\text{m}^2\cdot\text{mol}^{-1}}\right) - \left(\frac{\varepsilon_{\lambda(\text{Fe}^{2+})}}{\text{m}^2\cdot\text{mol}^{-1}}\right)\right]. \qquad \text{(A.140)}$$

A linear regression of this equation with $(\varepsilon_{\lambda(\text{FeCl}^+)} - \varepsilon_{\lambda(\text{Fe}^{2+})})$ as the running variable will produce the slope $lc_{(\text{FeCl}^+)}$ as well as k, an intercept that should statistically not deviate from zero. The analysis indicated that k is small ($< 1.2 \times 10^{-2}$).

Since Beer's law operates on the molar scale it was necessary to first convert $c_{\text{Fe}_\text{total}}$ to moles per litre (using the density of the solution) and to convert back the resulting c_{FeCl^+} to molality.

Parameters and results are provided in the first part of Table A-50.

From the SIT evaluation (Figure VIII-1, Section VIII.2.2.1), for

$$\text{Fe}^{2+} + \text{Cl}^- \rightleftharpoons \text{FeCl}^+ \qquad \text{(A.141)}$$

using only the data for solutions in which the free Fe^{2+} concentration contributed less than 30% to the ionic strength (systems with $I_m > 0.1\ \text{mol}\cdot\text{kg}^{-1}$)

$$\log_{10} \beta_1^\circ\ ((\text{A.141}), 298.15\ \text{K}) = -(0.111 \pm 0.027)$$

and

$$\varepsilon(\text{FeCl}^+,\text{Cl}^-) - \varepsilon(\text{Fe}^{2+},\text{Cl}^-) - \varepsilon(\text{H}^+,\text{Cl}^-) = -(0.075 \pm 0.013)\ \text{kg}\cdot\text{mol}^{-1}.$$

Table A-50-a: Concentration quotient $\log_{10} \beta_1$ for the reaction $\text{Fe}^{2+} + \text{Cl}^- \rightleftharpoons \text{FeCl}^+$ at 25 °C in HCl solutions. FeCl^+ was evaluated using Eq. (A.140).

Ident.	$[\text{FeCl}^+]$, molal	$[\text{Fe}^{2+}]$, molal	$[\text{Cl}^-]$, molal	$\log_{10}\beta_1$	I_m
25.A2	$(1.521.14) \times 10^{-4}$	5.25×10^{-3}	2.50×10^{-2}	0.062 ± 0.326	0.030
25.A1	$(3.31 \pm 1.32) \times 10^{-4}$	1.04×10^{-2}	2.49×10^{-2}	0.109 ± 0.173	0.035
25.B1	$(2.93 \pm 1.30) \times 10^{-4}$	1.11×10^{-2}	5.01×10^{-2}	-0.279 ± 0.193	0.061
25.C2	$(2.29 \pm 1.64) \times 10^{-4}$	1.04×10^{-2}	9.43×10^{-2}	-0.630 ± 0.311	0.105
25.C1	$(8.33 \pm 2.27) \times 10^{-4}$	2.04×10^{-2}	9.37×10^{-2}	-0.360 ± 0.119	0.114
25.D2	$(5.01 \pm 1.68) \times 10^{-4}$	9.90×10^{-3}	2.52×10^{-1}	-0.697 ± 0.145	0.262
25.D1	$(1.37 \pm 0.20) \times 10^{-3}$	1.94×10^{-2}	2.51×10^{-1}	-0.551 ± 0.065	0.271
25.E1	$(1.27 \pm 0.37) \times 10^{-3}$	9.03×10^{-3}	5.07×10^{-1}	-0.556 ± 0.126	0.516
25.F1	$(1.30 \pm 0.06) \times 10^{-3}$	9.60×10^{-3}	9.59×10^{-1}	-0.849 ± 0.022	0.968
25.H1	$(1.74 \pm 0.11) \times 10^{-3}$	9.06×10^{-3}	1.62	-0.927 ± 0.028	1.626
25.I1	$(2.72 \pm 0.20) \times 10^{-3}$	8.58×10^{-3}	2.64	-0.919 ± 0.035	2.644
25.G1	$(3.25 \pm 0.36) \times 10^{-3}$	8.35×10^{-3}	3.33	-0.933 ± 0.052	3.343
25.G2	$(8.43 \pm 0.52) \times 10^{-3}$	1.50×10^{-2}	3.33	-0.771 ± 0.032	3.345

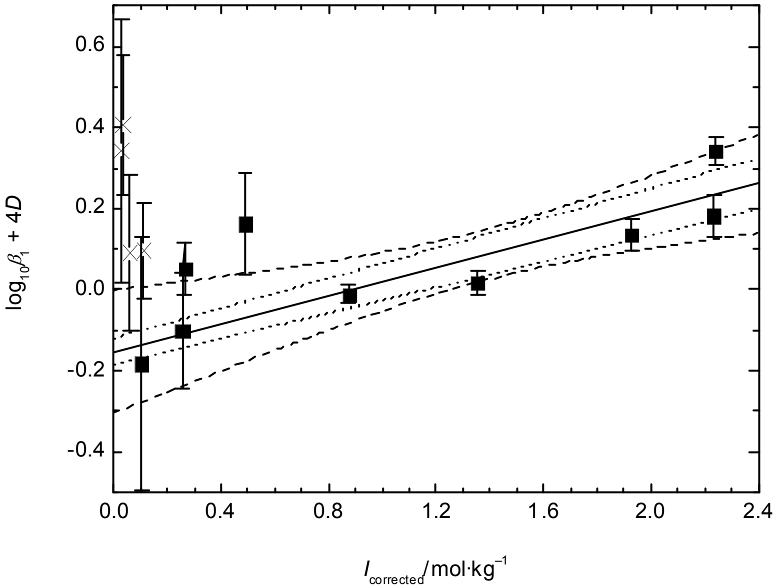
Table A-50-b: Data used to perform the SIT evaluation. The uncertainties of ($\log_{10}\beta_1$ + $4D$) are the same as those for $\log_{10}\beta_1$. Column 4 indicates, how much the free Fe^{2+} concentration contributes to total ionic strength.

	I_m	$\log_{10}\beta_1 + 4D$	Contribution of Fe^{2+} to I_m	$\log_{10}\beta_1$
25.A2	0.030	0.3431	34.6%	0.062 ± 0.326
25.A1	0.035	0.407	58.9%	0.109 ± 0.173
25.B1	0.061	0.0885	36.3%	−0.279 ± 0.193
25.C2	0.105	−0.1862	19.8%	−0.630 ± 0.311
25.C1	0.114	0.0968	35.7%	−0.360 ± 0.119
25.D2	0.262	−0.1076	7.6%	−0.697 ± 0.145
25.D1	0.271	0.0443	14.3%	−0.551 ± 0.065
25.E1	0.516	0.1485	3.5%	−0.556 ± 0.126
25.F1	0.968	−0.0393	2.0%	−0.849 ± 0.022
25.H1	1.626	−0.0350	1.1%	−0.927 ± 0.028
25.I1	2.644	0.0436	0.6%	−0.919 ± 0.035
25.G1	3.343	0.0622	0.5%	−0.933 ± 0.052
25.G2	3.345	0.2235	0.9%	−0.771 ± 0.032

It is interesting to note that Ruaya and Seward [1987RUA/SEW] used a different model that included the formation of aqueous HCl ion pairs, particularly at elevated temperatures and at higher concentrations. At ambient temperature the dissociation (of HCl) was concluded to be very strong. Based on a Pitzer treatment of the available data, Ruaya and Seward [1987RUA/SEW] gave a dissociation constant for HCl(aq) $\log_{10} K^{\circ}_{d}$ (298.15 K) = (0.71 ± 0.07) (1σ). Conversely, a strong dissociation is equivalent to a weak association. However, the key question concerned the impact of this "weak" association on the ionic strength of the solution. Obviously, the ionic strength would decrease when the solution includes un-dissociated HCl. Using an (HCl) association constant $\log_{10} K^{\circ}_{a}$ (298.15 K) = −0.71 and $\varepsilon(H^+,Cl^-)$ = 0.12 kg·mol^{-1} the amount of resultant un-dissociated HCl(aq) for the systems could be calculated to be as much as 1 m and a significant impact on ionic strength would appear above $m_{HCl_{total}}$ ~ 0.25 m.

A weighted linear regression of $\log_{10}\beta_1 + 4D$ *vs*. the *corrected ionic strength* produces $\log_{10}\beta^{\circ}_1 = -(0.153 \pm 0.033)$ and $\Delta\varepsilon = -(0.173 \pm 0.022)$ kg·mol^{-1} (Figure A-41). Again the calculation was restricted to data for solutions in which the free Fe^{2+} concentration contributed less than 30% to the ionic strength (systems with $I_m > 0.1$ mol·kg^{-1}).

Figure A-41: Weighted linear regression of ($\log_{10}\beta_1$ + 4D) data. This alternate analysis was based on the model for HCl association [1987RUA/SEW] that was used by Heinrich and Seward [1990HEI/SEW]. Data points marked with a cross were not used in the calculation because of the large contribution of Fe^{2+} to the ionic strength. Dashed line pairs delimit the uncertainty band and thin solid line pairs define the confidence band.



Discussion:

For the equilibrium $Fe^{2+} + Cl^- \rightleftharpoons FeCl^+$ in HCl solution the formally correct SIT expression would read

$$\log_{10}\beta_1 - \Delta z^2\cdot D = \log_{10}\beta_1^\circ + \varepsilon(\mathrm{H^+,Cl^-})\,m_{\mathrm{H^+}} - \varepsilon(\mathrm{FeCl^+,Cl^-})\cdot(m_{\mathrm{Cl^-}} - m_{\mathrm{FeCl^+}})$$
$$+\,\varepsilon(\mathrm{Fe^{2+},Cl^-})\cdot(m_{\mathrm{Cl^-}} + m_{\mathrm{Fe^{2+}}}).$$

However, if the approximation with $\Delta\varepsilon = \varepsilon(\mathrm{FeCl^+,Cl^-}) - \varepsilon(\mathrm{Fe^{2+},Cl^-}) - \varepsilon(\mathrm{H^+,Cl^-})$ is used

$$\log_{10}\beta_1\ (I_m) - \Delta z^2\cdot D = \log_{10}\beta_1^\circ - \Delta\varepsilon\cdot I_m, \qquad \text{(A.142)}$$

This approximation is certainly not fulfilled when Fe^{2+} contributes more than 30% to the ionic strength as this is the case for experiments 25.A1, 25.A2, 25.B1, 25.C1; therefore these experiments were excluded from the fit (labeled with an asterisk in Figure A-41).

From the slope $\Delta\varepsilon$ the difference $\varepsilon(\mathrm{FeCl^+,Cl^-}) - \varepsilon(\mathrm{Fe^{2+},Cl^-}) - \varepsilon(\mathrm{H^+,Cl^-})$ = – (0.075 ± 0.022) kg·mol^{-1} is derived. Using $\varepsilon(\mathrm{H^+,Cl^-})$ = (0.12 ± 0.01) kg·mol^{-1} one obtains

$$\varepsilon(\mathrm{FeCl^+,Cl^-}) - \varepsilon(\mathrm{Fe^{2+},Cl^-}) = (0.05 \pm 0.03)\ \mathrm{kg \cdot mol^{-1}}.$$

This difference is a key result from this paper, but unfortunately it cannot be resolved without further assumptions/data.

As was the case for 25 °C, the authors also provided data for 50 °C and 100 °C that do not indicate any formation of $\mathrm{FeCl_2(aq)}$. However, the authors' values for $\log_{10}\beta_1^{\circ}$ at these higher temperatures were used here without further recalculation.

The $\Delta_r H_m^{\circ}$ value presented in the paper is 5.6 kJ·mol^{-1}, which was derived from the given parameterized $\ln\beta_1^{\circ}(T)$ function:

$$\ln\beta_1^{\circ}(T) = 56.08 + 4.96\times10^{-2}(T/\mathrm{K}) - 12.50\ln(T/\mathrm{K}).$$

This $\ln\beta_1^{\circ}(T)$-function implies that $\Delta_r H_m^{\circ}(T)$ has the form $\Delta_r H_m^{\circ}(T)$/kJ·mol^{-1} = $\mathrm{B}(T/\mathrm{K})^2 + \mathrm{C}(T/\mathrm{K})$, but such an equation cannot be justified on the basis of just 5 measured points (see also the Appendix A discussion of Palmer and Hyde [1993PAL/HYD]). The simplest approximation that can be made is that the heat-capacity change for the reaction is zero over this temperature range. This calls for a simple $1/T$-regression of the $\log_{10}\beta_1^{\circ}(T)$ values. With the present values this leads to $\Delta_r H_m^{\circ}$ = (10.7 ± 7.9) kJ·mol^{-1} for the range 25 to 100 °C (Figure A-42, solid line).

Inspection of all data of the authors (*i.e.*, also including the data for 150 and 200 °C) clearly reveals that $\Delta_r H_m^{\circ}$ for the upper temperature range is much larger (Figure A-42). For the three high-temperature points $\Delta_r H_m^{\circ}$ = (28.9 ± 8.9) kJ·mol^{-1} was evaluated (note that extrapolation of the high-temperature data to t = 25 °C would produce $\log_{10}\beta_1^{\circ}$ = –(0.8 ± 0.4)). Comparison with the data from Palmer and Hyde [1993PAL/HYD] measured between 125 and 300 °C ($\Delta_r H_m^{\circ}$ = (29.1 ± 2.5) kJ·mol^{-1}) shows nearly identical $\Delta_r H_m$ values from both studies in the upper temperature range, though at different ionic strengths.

If a regression of all points from this work is done against $1/T$ (Figure A-43), one obtains an approximately linear relationship with a value of (18.6 ± 3.7) kJ·mol^{-1} for $\Delta_r H_m^{\circ}$ ($\mathrm{FeCl^+}$, 298.15 K, I = 0) and –(0.30 ± 0.17) for $\log_{10}\beta_1^{\circ}$ ($\mathrm{FeCl^+}$).

Figure A-42: All $\log_{10}\beta_1^{\circ}(T)$ data in the range 25 to 200 °C. It is evident that slopes in the upper and lower temperature ranges are different.

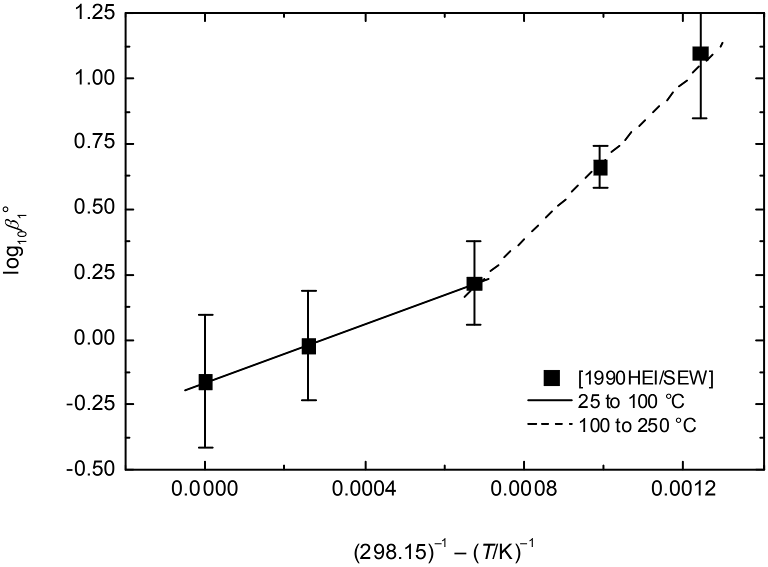
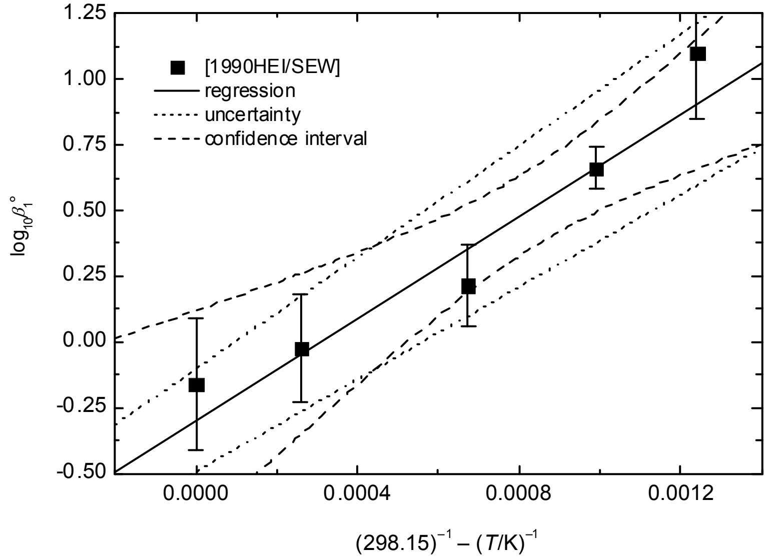


Figure A-43: Regression of all $\log_{10}\beta_1^{\circ}(T)$ data in the range 25 to 200 °C. The dashed lines represent the uncertainty band, the solid lines the confidence band.



[1990HEM]

A total of 138 $C^{\circ}_{p,\mathrm{m}}$ measurements (by DSC) between 338.9 and 997.0 K, including 68 measurements in the Curie transition region between 804.9 and 871.0 K, are reported for a 38.244 mg sample of the synthetic magnetite prepared and studied by Bartel *et al.* [1976BAR/WES]. Hemingway's conclusion that this material contained as much as 13% Fe_2O_3 impurity, even after removal of hematite particles by hand-picking, has been refuted, and the associated corrections questioned by Grønvold *et al.* [1993GRO/STO]. Eight additional measurements are reported for two other synthetic, stoichiometric Fe_3O_4 specimens at 338.9 to 499.0 K. These data are included in the evaluation of $C^{\circ}_{p,\mathrm{m}}$ (Fe_3O_4, cr, T) in Section VII.2.7.1

The following C_p expressions were obtained by Hemingway from a pooled data set including values from [1969WES/GRO], [1976BAR/WES], and [1951COU/KIN] as well as this paper; the stated average deviation for the resulting $C^{\circ}_{p,\mathrm{m}}$ values was ±0.34%.

$$\begin{aligned}[C^{\circ}_{p,\mathrm{m}}]^{800\mathrm{K}}_{290\mathrm{K}}(\mathrm{Fe_3O_4, cr}, T)/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = {} & 2659.108 - 2.52153(T/\mathrm{K}) \\ & + 1.36769\times10^{-3}(T/\mathrm{K})^2 \\ & - 3.645541\times10^{4}(T/\mathrm{K})^{-0.5} \\ & + 2.07344\times10^{7}(T/\mathrm{K})^{-2}\end{aligned}$$

$$\begin{aligned}[C^{\circ}_{p,\mathrm{m}}]^{845.5\mathrm{K}}_{800\mathrm{K}}(\mathrm{Fe_3O_4, cr}, T)/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = {} & -3.483016217\times10^{6} + 944.389435(T/\mathrm{K}) \\ & + 8.866012817\times10^{7}(T/\mathrm{K})^{-0.5} \\ & - 2.603798463\times10^{11}(T/\mathrm{K})^{-2}\end{aligned}$$

$$\begin{aligned}[C^{\circ}_{p,\mathrm{m}}]^{1800\mathrm{K}}_{900\mathrm{K}}(\mathrm{Fe_3O_4, cr}, T)/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = {} & 11761.609 - 3.8316705(T/\mathrm{K}) \\ & + 6.391782\times10^{-4}(T/\mathrm{K})^2 \\ & - 2.9975290\times10^{5}(T/\mathrm{K})^{-0.5} \\ & + 1.115308\times10^{9}(T/\mathrm{K})^{-2}\end{aligned}$$

Hand integration was necessary to obtain thermodynamic quantities between 845.5 and 900 K *(i.e.*, on the steeply descending portion of the C_p anomaly at the Curie transition). Evidently Hemingway encountered similar fitting problems to those described in Sections VII.2.2.2 and VII.2.7.1.5 (note the unusually large coefficients and correspondingly large number of significant figures in the second equation).

The paper includes a re-evaluation of $\Delta_f H^{\circ}_{\mathrm{m}}$ (Fe_2O_3, α, 298.15 K) in the light of O'Neill's high-precision solid-state potential-difference measurements on magnetite-hematite equilibrium [1988NEI]. Recommended thermodynamic quantities are tabulated for both Fe_3O_4 and α-Fe_2O_3 at 298.15 to 1800 K.

[1990SAL/VAS]

These authors employed a glass electrode in conjunction with a perchlorate (ISE) at (25.00 ± 0.02) °C to monitor the hydrolysis of Fe^{3+} (2×10^{-4} to 1×10^{-2} $\mathrm{mol\cdot kg^{-1}}$) in $NaClO_4$ solutions (0.513, 1.05, 2.21, and 3.5 $\mathrm{mol\cdot kg^{-1}}$). The resulting hydrolysis constants were fitted with the SIT and the interaction coefficients were found to be functions of ionic strength. The raw experimental data were not provided.

This appears to be a careful study and one of the few to generate $\log_{10}{}^*\beta_{2,1}$ values. Their SIT treatment yielded $\log_{10}{}^*\beta^{\circ}_{1,1} = -(1.98 \pm 0.02)$, $\log_{10}{}^*\beta^{\circ}_{2,1} = -1.65$ to -4.4, and $\log_{10}{}^*\beta^{\circ}_{2,2} = -(2.86 \pm 0.02)$ (all uncertainties are given as 3σ). Note that these authors used only the data at $I_m > 1$, where the $\Delta\varepsilon$ for the first hydrolysis equilibrium was shown to be constant to derive their $\log_{10}{}^*\beta^{\circ}_{1,1}$ value such that use of a second term to account for the apparent ionic strength dependence of $\Delta\varepsilon$ at $I_m < 1$ would lead to a lower $\log_{10}{}^*\beta^{\circ}_{1,1}$ value.

Table A-51: Reported overall hydrolysis constants for Fe^{3+} at 25 °C as a function of molal ionic strength ($NaClO_4$), where the uncertainties are 3σ.

	0.513	1.05	2.21	3.50
$\log_{10}{}^*\beta_{1,1}$	-2.70 ± 0.02	-2.80 ± 0.02	-2.91 ± 0.02	-2.98 ± 0.02
$\log_{10}{}^*\beta_{2,1}$	≤ -5.70	-5.8 ± 0.1	-6.0 ± 0.1	-6.2 ± 0.1
$\log_{10}{}^*\beta_{2,2}$	-2.84 ± 0.02	-2.83 ± 0.02	-2.79 ± 0.02	-2.84 ± 0.02

[1990STI]

This paper contains a literature review of the stability constants of Fe(III) and Fe(II) sulfato and hydroxido complexes and Fe(III)/Fe(II) oxidation potentials. The constants were introduced in a geochemical model for acidic waters from mines to calculate the solution compositions and the oxidation potential. The results were compared with the measured pe and pH of real or simulated acid-mine waters containing iron.

To get the formation constants of the complexes at zero ionic strength, activity coefficients were calculated using three equations —Debye-Hückel [1974HEL/KIR], Davies [1981STU/MOR] and the ion-association method described by Truesdell and Jones [1974TRU/JON]— all are useful for the rather low ionic strength solutions of acidic mine water.

For $I_m = 0$, at 25 °C the calculations and the literature yielded:

$$a_{HSO_4^-} /(a_{H^+}\ a_{SO_4^{2-}}) = 10^{(1.99\pm0.01)}$$

$$a_{KSO_4^-} /(a_{K^+}\ a_{SO_4^{2-}}) = 10^{(0.85\pm0.05)}$$

$$a_{FeSO_4^+} /(a_{Fe^{3+}}\ a_{SO_4^{2-}}) = 10^{(4.04\pm0.10)}$$

$$a_{Fe(SO_4)_2^-} /(a_{Fe^{3+}}\ (a_{SO_4^{2-}})^2) = 10^{(5.38\pm1.00)}$$

$$a_{HFeSO_4^{2+}} /(a_{Fe^{3+}}\ a_{HSO_4^-}) = 10^{2.48}$$

$$a_{FeOHSO_4(aq)} /(a_{FeOH^{2+}}\ a_{SO_4^{2-}}) = 10^{2.3}$$

$$a_{\mathrm{Fe(OH)_2SO_4^-}} / (a_{\mathrm{Fe(OH)_2^+}}\ a_{\mathrm{SO_4^{2-}}}) = 10^{0.8}$$

$$a_{\mathrm{FeClO_4^{2+}}} / (a_{\mathrm{Fe^{3+}}}\ a_{\mathrm{ClO_4^-}}) = 10^{1.15}$$

A set of stability constant values for the corresponding Fe^{2+} complexes was also gathered and analysed with respect to their usefulness for geochemical models.

Calculated values of pe were in fair agreement with measured values. The straight line obtained by plotting the calculated pe as a function of measured pe has a slope of 0.97 at the 95% confidence limit.

The causes of uncertainties were evaluated and compared; it is the value of the formation constant of $\mathrm{FeSO_4^+}$ which introduces the highest uncertainty.

In spite of a good general agreement between measured and calculated pe values, some of the formation constants are questionable.

The perchlorate complexes of Fe(III) have been investigated by several workers, generally without success (but also see [1988KHO/ROB]), so the value noted by the author was not recommended for geochemical modelling.

Values for the formation constants of soluble mixed hydroxidosulfato complexes were evaluated by introducing them into the model. Their influence was found to be weak, so the existence of these species can not be justified by this work, and the author did not recommend adding them in the geochemical models.

The recommended formation constants for the complexes $\mathrm{FeHSO_4^{2+}}$ (Fe(III)) and $\mathrm{FeHSO_4^+}$ (Fe(II)) are probably erroneously inverted, as the value for the weaker associated iron(II) species, $\mathrm{FeHSO_4^+}$, is recommended although the value for the iron(III) species is not.

Many of the papers quoted in this review were used to determine the recommended thermodynamic values of iron(III) species for geochemical modelling; but the numbers given were not considered as a primary source of information and were not selected for the application of the SIT formalism.

[1991BRA]

The solubility of $FeCO_3$ was measured in phthalate and phosphate buffers at temperatures from 30 to 80 °C. The measured solubilities are lower than found by other researchers, especially at higher temperatures [1981REI/JOH], [1992GRE/TOM]. This is especially puzzling, as the authors make special mention of the small size of the $FeCO_3(s)$ particles. Only the measurements in the pH 7 buffer were used to determine the reported solubility products. The temperature dependence of the solubility products suggests a value of $\sim -50\ \mathrm{kJ \cdot mol^{-1}}$ for $\Delta_r H$ for

$$\mathrm{FeCO_3(cr) + 2\,H^+ \rightleftharpoons Fe^{2+} + H_2O(l) + CO_2(g)},$$

a much more negative value than suggested by other solubility [1992GRE/TOM] or enthalpy of formation [1994CHA/NAV] measurements.

The solid does not appear to have been characterized either before or after the measurements. Although the effect of possible phosphate complexation was discussed, no attempt seems to have been made to ensure that phosphate was not incorporated in the solid, nor was possible conversion of the siderite to an iron oxide considered. The partial pressure of CO_2(g) was not measured, and because of the sampling technique the equilibrium between the solution and the gas phase (primarily purified nitrogen) was re-established after each (~ weekly) measurement. No attempt to determine the presence of iron(III) in the solution or solid is reported.

Because of the lack of characterization of the solid, the results of this study are not credited in the present review.

[1991DAV]

A critical evaluation of literature values for the solubility products, $K_s^{\mathrm{NBS}} = c_{\mathrm{Fe}^{2+}} c_{\mathrm{HS}^-} \gamma_{\mathrm{Fe}^{2+}} \gamma_{\mathrm{HS}^-} a_{\mathrm{H}^+}(\mathrm{NBS})^{-1}$ of various iron sulfide phases was carried out, where $a_{\mathrm{H}^+}(\mathrm{NBS})$ represents the approximate activity of H^+ measured on the NBS scale. The reliability of the reported values was judged by the agreement with other reported values and the adherence to the expected relationship between $\log_{10} c_{\mathrm{Fe}^{2+}}$ and pH. The proposed best estimates were pK_S = (2.95 ± 0.1) for amorphous iron(II) sulfide, (3.6 ± 0.2) for mackinawite (tetragonal $Fe_{1+x}S$), (4.4 ± 0.1) for greigite (spinel Fe_3S_4), (5.1 ± 0.1) for pyrrhotite (monoclinic and two modifications of hexagonal iron sulfide compounds with a range of composition between Fe_7S_8 and FeS), (5.25 ± 0.2) for troilite (a compound with a close structural relationship to pyrrhotite, $FeS_{1.00}$) and (16.4 ± 1.2) for pyrite (FeS_2). To judge the reliability of these data, the original papers should be consulted especially with respect to the characterization of the solid phase and the attainment of the equilibrium or the steady state.

[1991SCH/COR]

See entry of 2nd edition [2000SCH/COR].

[1991SHE/KOE]

This is a systematic study of the C_p of magnetite, expressed as $Fe_{3(1-\delta)}O_4$, as a function of the stoichiometric deviation δ, at temperatures from 5 to 200 K, with particular attention to the Verwey transition. Single crystal specimens were prepared by skull melting followed by subsolidus annealing in controlled CO/CO_2 mixtures to attain the desired compositions. Measurements were made on cut and polished specimens approximately $5 \times 5 \times 0.7$ mm (40 - 80 mg), using a relaxation calorimeter. Individual C_p measurements are not tabulated, therefore results in general could not be used in the current assessment, but several observations are relevant to the discussion in Section VII.2.7.1.

A critical value $\delta_c \approx 0.004$ was found, below which the Verwey transition is a sharp 1st-order process with $\Delta_{\text{trs}}S_{\text{m}}^{\text{o}} = R\ln 2$ and above which it is a continuous 2nd-order process, occurring primarily within 5 - 30 K below the nominal transition temperature, T_v, but extending in principle down to 0 K, with $\Delta_{\text{trs}}H_{\text{m}}^{\text{o}} = 2R\ln 2$. The transition was not detected for $\delta > 0.012$.

Nine measurements on essentially stoichiometric Fe_3O_4 (reproduced from [1985SHE/KOE]) gave experimental $\Delta_{\text{trs}}S_{\text{m}}^{\text{o}}$ values from 5.63 to 6.09 $J{\cdot}K^{-1}{\cdot}mol^{-1}$, with an average value of (5.91 ± 0.06) $J{\cdot}K^{-1}{\cdot}mol^{-1}$ plus ~0.25 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ for pre- and postmonitory effects within a few degrees of T_v. This is close to the calculated 1st-order transition enthalpy of $R\ln 2 = 5.763$ $J{\cdot}K^{-1}{\cdot}mol^{-1}$. The value of T_v declined from ~ 121 K for near-stoichiometric material to ~ 110 K for $\delta = 0.0035$, with a discontinuous change from ~ 109 to ~ 101 K at δ_c and a further decline to ~ 81 K at $\delta = 0.012$.

No additional C_p anomalies were detected below T_v, in agreement with most other studies.

[1991SUN]

This is a Calphad-type thermodynamic assessment of wüstite, magnetite, hematite, and liquid Fe–O. Fundamental differences from the current review preclude useful comparisons, *e.g.*, a zero-point entropy of $2R\ln 2$ is applied to magnetite and relatively old $\Delta_{\text{f}}H_{\text{m}}^{\text{o}}$ values were selected for magnetite and hematite.

[1992BRU/STU]

This paper reported measurements of the solubility of 50 nm spherules of hematite (Fe_2O_3) in aqueous solutions in contact with a gas phase containing CO_2. The solubilities were investigated at two partial pressures of CO_2 (98 and 30 kPa) for aqueous pH values between 5.25 and 8.25. The pH was increased by additions of 0.2 M $NaHCO_3$; however, constant ionic strength was not maintained [2000BRU/DUR].

The first contact time with hematite lasted one week. After that, the $NaHCO_3$ additions were done every day or two. The stability of the pH value was used as the criterion of equilibrium. The iron analyses were carried out using the spectrophotometric ferrozine method after filtration of the supernatant solution through a 0.05 µm pore filter.

The solubility of hematite in aqueous solutions at the same pH, in the presence of $CO_2(g)$ at a pressure of 98 kPa, is orders of magnitude greater than in the absence of CO_2. The shape of the curve in a plot of $\log_{10} c_{\text{Fe(III)}_{\text{total}}}$ *vs*. $(\text{pH} + 2\log_{10} p_{CO_2})$ suggests the formation of two soluble species—$FeCO_3OH$ at pH values from 5 to 6 and $Fe(CO_3)_2^-$ at higher pH values. The discussion and the data analysis contained substantial errors, and the principal author later [2000BRU/DUR] provided corrections and a reinterpretation of the data.

[1992BRU/WER]

The solubility of $FeCO_3(cr)$ in acidic solutions was measured under different partial pressures of $CO_2(g)$ (~ 5.1 kPa, 1.0 kPa) in H_2/CO_2 mixtures (the H_2 was used to prevent oxidation of Fe(II)), at 25 °C in I = 1 $mol{\cdot}dm^{-3}$ ($NaClO_4(sln)$) for "pH" (actually $-\log_{10} c_{H^+}$ values) between 6.0 and 9.0. Values for the solubility product ($c_{Fe^{2+}} c_{CO_3^{2-}}$), $10^{-(9.45 \pm 0.05)}$ ($10^{-(10.8 \pm 0.2)}$ corrected to I = 0), and formation constants for $FeCO_3(aq)$ and $Fe(CO_3)_2^{2-}$ were reported.

The siderite, hydrothermally produced under CO_2 pressure at 100 °C, was analysed with XRD, TEM and Kr-BET. Redox conditions were controlled (kept at low Eh) with a coulometrically prepared Pd-electrode. Fe(II) was determined spectrophotometrically using ferrozine.

The experiments seem to have been performed very carefully and, though equilibration times were rather short (72h/24h) [2002JEN/BOD], they appear to have been sufficient to allow equilibrium to be reached. At equilibrium, the electrode potential was stable within ± 0.1 mV, allowing determination of c_{H^+} to better than 1%.

This paper is the only known work that provides a traceable determination of the formation constant for $FeCO_3(aq)$. It is based on the thesis of Wersin [1990WER] and uses exactly the same data as given there.

The reported iron concentration and p_{CO_2} values for the solutions with the six highest hydrogen ion concentrations (runs 25 to 30) were reanalysed using CODATA values for $CO_2(g)$, $CO_2(aq)$, HCO_3^-, CO_3^{2-} and $H_2O(l)$ at 298.15 K. The original molar concentration values given by the authors were converted to molal values for 1 M $NaClO_4$ solutions (the conversion factor is 1.0515 $dm^3{\cdot}kg^{-1}$ based on a density of 1.07345 $kg{\cdot}dm^{-3}$ [1985SOH/NOV]). The solubility product values were corrected to I = 0 using the standard TDB SIT procedure (Appendix B, $\varepsilon(Fe^{2+}, ClO_4^-)$ = 0.37 $kg{\cdot}mol^{-1}$). The average value for $\log_{10}{}^{*}K_{s,0}$ (A.143) at 298.15 K is (7.30 ± 0.05) (this uncertainty represents the 95% confidence limit, not including uncertainties in the auxiliary data).

$$FeCO_3(cr) + 2\,H^+ \rightleftharpoons Fe^{2+} + CO_2(g) + H_2O(l) \qquad (A.143)$$

This value is less than the value of ~7.4 from the recalculation in the paper of Preis and Gamsjäger [2002PRE/GAM] (their Figure 4). The difference is traceable to their use of the Davies equation for a solution with an ionic strength of 1.05 $mol{\cdot}kg^{-1}$ ($NaClO_4(sln)$), well beyond the normal range of applicability of the equation.

From twelve measurements in the pH range 7.2 to 7.9 (runs 12 to 23) the authors derived

$$\log_{10} K(A.144)(FeCO_3, aq, 25\ °C, 1\ M\ NaClO_4) = -(5.28 \pm 0.05)$$

(molar units) for the reaction

$$FeCO_3(cr) \rightleftharpoons FeCO_3(aq) \qquad (A.144)$$

Based on the shape of the solubility curve as a function of hydrogen-ion concentration and partial pressure of $CO_2(g)$, the authors assumed the formation of a dicarbonato complex in more basic solutions

$$\mathrm{FeCO_3(cr) + H_2O(l) + CO_2(g) \rightleftharpoons Fe(CO_3)_2^{2-} + 2\,H^+} \qquad \text{(A.145)}$$

Then, from the series of runs in the more basic pH range from 8.3 to 8.9 (runs 1 to 11), and assuming that only the complexes $FeCO_3(aq)$ and $Fe(CO_3)_2^{2-}$ were formed, total Fe(II) in solution could be expressed as

$$[\mathrm{Fe(II)}] = K(\mathrm{A.144}) + {}^{*}K(\mathrm{A.145})\, p_{\mathrm{CO_2}} / m_{\mathrm{H^+}}^2 \qquad \text{(A.146)}$$

From a least-squares plot the authors obtained $\log_{10} K(\mathrm{A.144}) = -(5.36 \pm 0.05)$ and $\log_{10} {}^{*}K(\mathrm{A.145}) = -(20.88 \pm 0.12)$ (these constants were designated by the authors as $\log_{10} K_{s1}$ and $\log_{10} K_{s2}$).

The calculations have been repeated in the present review, but using molalities rather than molarities and using the 0.1 MPa standard state for pressure. Using equal weighting for the solubilities from the results of runs 12 to 23, this led to a value of $\log_{10} K(\mathrm{A.144}) = -(5.26 \pm 0.18)$ (2σ uncertainty).

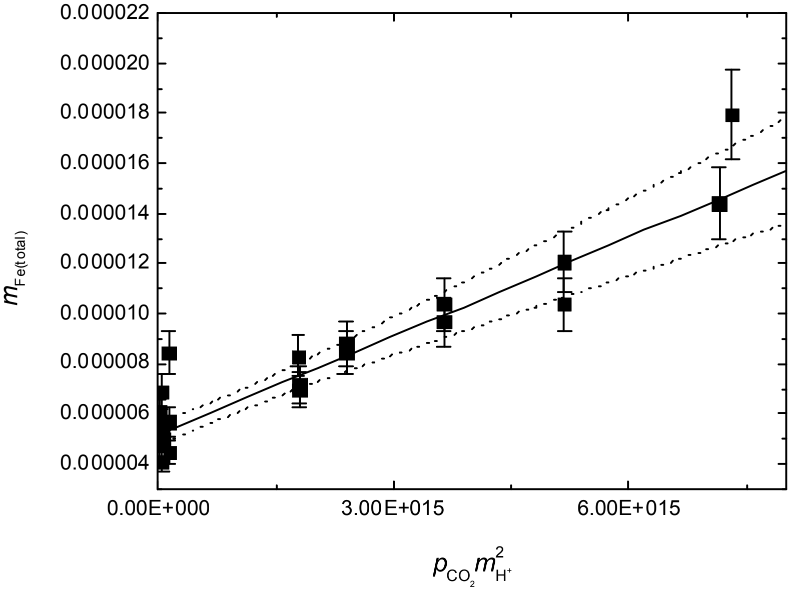
If Equation (A.146) is used for the data from all runs from 1 to 23, the plot shown in Figure A-44 leads to values of $\log_{10} K(\mathrm{A.144}) = -(5.29 \pm 0.01)$ and $\log_{10} {}^{*}K(\mathrm{A.145}) = -(20.88 \pm 0.03)$. However, based on these constants more than 15% of the total iron in several of runs 12 to 23 should actually have been Fe^{2+}, rather than $FeCO_3(aq)$. Therefore, the equation:

$$[\mathrm{Fe}]_{\mathrm{total}} = {}^{*}K_{p,\mathrm{s},0}\,(\mathrm{A.143})\; m_{\mathrm{H^+}}^2 / p_{\mathrm{CO_2}} + K(\mathrm{A.144}) + {}^{*}K\,(\mathrm{A.145})\, p_{\mathrm{CO_2}} / m_{\mathrm{H^+}}^2 \qquad \text{(A.147)}$$

was fitted to the experimental data. Two different weightings were attempted. First the data were equally weighted by assuming that the uncertainties in the reported iron molalities for all measurements were equal (0.1×10^{-6} m). From this analysis, values of (7.638 ± 0.004), – (5.39 ± 0.18) and – (20.85 ± 0.19) were obtained for $\log_{10} {}^{*}K_{p,\mathrm{s},0}$, $\log_{10} K(\mathrm{A.144})$, and $\log_{10} {}^{*}K(\mathrm{A.145})$, respectively. Then the calculation was repeated by weighting the data assuming a 10% uncertainty in each of the reported values for the total iron concentraion at equilibrium. From this analysis, values of (7.52 ± 0.05), –(5.41 ± 0.04) and –(20.82 ± 0.06) were obtained for $\log_{10} {}^{*}K_{p,\mathrm{s},0}$, $\log_{10} K(\mathrm{A.144})$, and $\log_{10} {}^{*}K(\mathrm{A.145})$, respectively. The 10% assigned uncertainty is a reasonable reflection of the spread in the reported iron concentrations (as shown in the Figure), but is much greater than would be expected from the analysis method alone [1970STO], [1994BAL/NOR].

The main difference in the constants from the two fits lies in the values of $\log_{10} {}^{*}K_{p,\mathrm{s},0}$. The value obtained assuming a constant uncertainty in the iron molality heavily weights the analysis in favour of the measurements from the more acidic solutions. Therefore the value of $\log_{10} {}^{*}K_{p,\mathrm{s},0}$ is essentially the same value as recalculated above from runs 25-30 only. The lower value from the fit assuming an equal percentage uncertainty in the final iron molalities suggests that the nature of the surface of the solid or the rate of equilibration might have been a function of pH. In the present review the result from this second weighting scheme is accepted, and leads to (7.19 ± 0.05) for $\log_{10}{}^{*}K_{s,0}$ (A.143) at 298.15 K. Because there was no confirmation that the nature of the solid did not change as a function of the hydrogen ion concentration, and because of the rather large effects introduced by reasonable changes in the weightings of the data, the uncertainty in $\log_{10}{}^{*}K_{s,0}$ (A.143) for the authors' sample of $FeCO_3(s)$ is more realistically estimated as ± 0.15.

Figure A-44: The solubility of $FeCO_3(s)$ in 1.0515 m $NaClO_4$ at 25 °C in the pH range 7.2 to 8.9 according to [1992BRU/WER]. The linear fit of Eq. (A.143) is based on the assumption that $FeCO_3(aq)$ and $Fe(CO_3)_2^{2-}$ are the dominant (and only) Fe(II) species in solution. Error bars correspond to an uncertainty of 10% in the determination of total dissolved iron(II).



From the fitted values of K(A.144) and ${}^{*}K$(A.145), (30.88 ± 0.04) kJ·mol^{-1} is calculated for $\Delta_r G^o_m$ ((A.144), 298.15 K, 1.05 m $NaClO_4$) and (118.84 ± 0.24) kJ·mol^{-1} for $\Delta_r G^o_m$ ((A.145), 298.15 K, 1.05 m $NaClO_4$). As Reaction (A.144) only involves creation of a neutral aqueous species, the same value as that for the 1.05 m $NaClO_4$ solution, can be used as a good approximation for $\Delta_r G^o_m$ ((A.144), 298.15 K):

$$\Delta_r G^o_m\text{((A.144), 298.15 K)} = (30.88 \pm 0.90)\ \text{kJ·mol}^{-1}.$$

Here, the estimated uncertainty has been increased slightly to allow for uncertainty in the consistency in the nature of the solid.

The interaction coefficient $\varepsilon(\mathrm{Na^+}, \mathrm{Fe(CO_3)_2^{2-}})$ is not known, but an "analogy" estimate based on $\varepsilon(\mathrm{Na^+}, \mathrm{CO_3^{2-}}) = -(0.08 \pm 0.03)$ kg·mol^{-1} and $\varepsilon(\mathrm{Na^+}, \mathrm{UO_2(CO_3)_2^{2-}}) = -(0.02 \pm 0.09)$ kg·mol^{-1} [2005GAM/BUG] leads to $\varepsilon(\mathrm{Na^+}, \mathrm{Fe(CO_3)_2^{2-}}) \approx -(0.05 \pm 0.05)$ kg·mol^{-1}. Using this estimate, 0.966 for the activity of water and (0.14 ± 0.02) kg·mol^{-1} for $\varepsilon(\mathrm{H^+}, \mathrm{ClO_4^-})$ (Appendix B), the value of $\log_{10}{}^*K$(A.145) is $-(21.80 \pm 0.12)$ and, again with a small increase in the estimated uncertainty,

$$\Delta_r G_m^\circ \text{((A.145), 298.15 K) is } (124.4 \pm 0.9) \text{ kJ·mol}^{-1}.$$

[1992GRE/TOM]

$FeCO_3$ was synthesized from iron(II) ammonium sulfate and sodium hydrogen carbonate in water purged with CO_2(g) and with CO_2 cover gas. The solubility was measured as a function of temperature (298 to 367 K), as well as the precipitation rate (300 to 349 K). A single pressure of CO_2(g) was used at each temperature (305 kPa at 298 K decreasing to 251 kPa at 367 K). There were no reported measurements of the H^+ molality.

The reported iron concentrations and $p_{\mathrm{CO_2(g)}}$ values were reanalysed using CODATA values for CO_2(g), CO_2(aq), $\mathrm{HCO_3^-}$, $\mathrm{CO_3^{2-}}$ and H_2O(l) at 298.15 K and the temperature dependence of the carbonate equilibria and ion product of water from the equations of Nordstrom *et al.* [1990NOR/PLU]. Because the final solutions all had ionic strengths of less than 0.1 mol·kg^{-1}, essentially no additional uncertainty is introduced by correction of these values to $I = 0$ using the standard TDB procedure, but neglecting interaction coefficients. The values for $\log_{10}{}^* K_{s,0}$ (A.148) are (7.59 ± 0.05) at 298.15 K, (7.37 ± 0.05) at 316.15 K, (7.33 ± 0.05) at 335.15 K, (7.24 ± 0.05) at 356.15 K, (7.16 ± 0.05) at 367.15 K, (the uncertainties are estimates, and do not include uncertainties in the auxiliary data)

$$\mathrm{FeCO_3(cr)} + 2\,\mathrm{H^+} \rightleftharpoons \mathrm{Fe^{2+}} + \mathrm{CO_2(g)} + \mathrm{H_2O(l)}. \qquad \text{(A.148)}$$

These are essentially the same as the values reported from recalculations in the paper of Preis and Gamsjäger [2002PRE/GAM].

The equilibrium constants in this paper, with good temperature functions for the carbonate equilibria [1990NOR/PLU], can be used to estimate a value of $-(9.4 \pm 3.1)$ kJ·mol^{-1} for $\Delta_r H$ (A.148).

[1992HER/NEI]

These authors used the first-order difference method of neutron diffraction to study the coordination of Fe^{3+} in three concentrated D_2O solutions, *i.e.*, 1.48 to 1.96 mol·dm^{-3}. The anion:Fe^{3+} concentration ratio is reported to vary from 3.58 to 3.96 such that the excess acid (HNO_3 or $HClO_4$) could be assumed to be in the range 1 to 1.9 mol·dm^{-3}. In the former case this was sufficient to minimize hydrolysis, except for a second HNO_3

solution which was heated to 90 °C causing irreversible hydrolysis. The octahedral symmetry of the un-hydrolyzed Fe^{3+} ion in nitrate solution was confirmed. In the case of perchlorate solutions, the authors speculated that dimeric Fe(III) species existed separated by an oxygen or two hydroxide bridging groups. In all solutions, a well-defined hydration structure was identified with nearest neighbour Fe^{3+}…O and Fe^{3+}…D correlations of (2.01 ± 0.02) and (2.68 ± 0.03) Å, respectively.

The structural information contained in this work is perhaps preliminary but insightful.

[1992HER/NEI2]

In a companion study to [1992HER/NEI], neutron diffraction was used to interrogate the structure of a 1 molal iron(II) chloride D_2O solution (the molality of DCl was greater than 1). The octahedral hydration shell of Fe^{2+} was identified with nearest neighbour Fe^{2+}…O and Fe^{2+}…D distances of (2.12 ± 0.02) and (2.75 ± 0.05) Å, respectively.

This simple system was studied by neutron diffraction and confirmed the octahedral hexaaquo hydration symmetry.

[1992KUM/NAK]

The authors measured the rate constants and solubilities of colloidal hydrous iron(III) oxide (aged for one week after precipitation from natural seawater) over the pH range 5.5 to 8.1 at 20 °C using dialysis to achieve phase separation. In the pH range 6.8 to 8.1, the first-order rate constant was independent of pH with a value reported at $(6.3 \pm 0.8) \times 10^{-4}\ \mathrm{h}^{-1}$ where a solubility minimum of $(1.05 \pm 0.05) \times 10^{-8}\ \mathrm{mol \cdot dm^{-3}}$ was also believed to have been found. No description of the pH measurements or pH electrode calibration was given. As with previous papers that have addressed these same issues of an ultra-fine, unstable solid phase, no thermodynamic data can be extracted from this study, except possibly for the hydrolysis constant involving $\mathrm{Fe(OH)_2^+}$, because the authors claim to have observed the correct pH dependence of the logarithm of the solubility in terms of this species and the product, $Fe(OH)_3$(aq). However, regression of the limited data set of eight data points required weighting the two highest pH values heavily to reproduce the pH dependence shown in Figure 4 of [1992KUM/NAK]. Ignoring for the moment that this assumption appears to be unjustified yielded a $\log_{10}{}^{*}K_{s,3}$ value of – (6.6 ± 0.2) (20 °C, salinity 33.6%, density = $1.024\ \mathrm{g \cdot cm^{-3}}$). The step-wise hydrolysis constant, ${}^{*}K_{3}$, corresponds to an isocoulombic equilibrium such that the extrapolation to infinite dilution would at least involve a relatively minor ionic strength correction.

Given the nature of these experiments where colloids are involved, no thermodynamic data can be extracted and even the value of $\log_{10}{}^{*}K_{s,3} = -(6.6 \pm 0.2)$ (20 °C, salinity 33.6%, density = $1.024\ \mathrm{g \cdot cm^{-3}}$) cannot be considered as being useful.

[1992PRZ/WIS]

See the discussion under the entry for [1993PRZ/WIS].

[1992PTA]

Solubilities of $FeCO_3$(s) were measured in salt solutions (NaCl, Na_2SO_4, $FeSO_4$) at 25.0 °C. Several methods for preparing the siderite were described, however only samples prepared from washed, precipitated $FeCO_3$(s), heated at 160 to 170 °C under ~ 1 bar of CO_2(g), were used for the measurements. The author noted that unheated precipitated samples were fine-grained and intergrown, and did not ripen substantially over several months. However, there seems to have been no attempt to reanalyze the solids at the end of the solubility experiments except by visual inspection.

All solubility experiments were carried out in an anaerobic chamber in sealed flasks, and had a duration of at least two months. The siderite samples were contacted by solutions of aqueous NaCl (0 to 6.05 mol·kg^{-1}), Na_2SO_4 (0 to 2.25 mol·kg^{-1}) or $FeSO_4$ (1.7×10^{-4} to 1.73 mol·kg^{-1}), with and without added $NaHCO_3$. The partial pressure of CO_2 was established by equilibration of the carbonate solution with the gas space above it. Therefore, the final solutions were primarily solutions with pH values > 7.0.

The final equilibrium molalities of iron, total carbonate, "alkalinity", "pH", and p_{CO_2} were measured. The latter was determined not from a sample of the gas-space solid, but by re-equilibrating samples of the solution with helium gas. Corrections to the measured p_{CO_2} were then applied for the differences in pH, water vapour pressure and total carbon concentration in these solutions. The reported "pH" values were from measurements against "standard" buffer solutions, and were not measurements of acid molality.

No attempt was made to ensure charge balance in the original calculations. The author used the values of the iron and total carbonate molalities and p_{CO_2} in the chloride solutions to calculate comparison values of the alkalinity and hydrogen ion activity. The values are reasonable, although there are minor inconsistencies in the analyzed values of the total carbon in solution and the alkalinities, especially for those solutions with little or no added $NaHCO_3$. Therefore, the author used only the data for her chloride runs 1 and 2 (maximum NaCl concentration 4.0 mol·kg^{-1}), which initially had 1 to 4 millimolar $NaHCO_3$, citing experimental and modelling uncertainties. A mixture of Pitzer-equation interaction-parameters and estimated formation constant values for $FeCO_3$(aq) and $FeHCO_3^+$ [1990NOR/PLU] (from [1979LAN], [1984FOU/CRI]) were used to obtain $-(11.06 \pm 0.13)$ (95% confidence limit) for the value of $\log_{10} {}^*K_s^\circ$.

These results are less reliable than those carried out in other studies at higher (and/or constant) partial pressures of CO_2. Recalculations were done using data from experiments in the author's series 1 and 2 with pH < 7.4 and $I < 3.5$ mol·kg^{-1}, *i.e.*, experiments for which the SIT is suitable, and in which complexation of carbonate species with iron(II) should be less important. If formation of $FeCO_3(aq)$ is neglected, a somewhat less negative value of $\log_{10}{}^{*}K_{s}^{\circ}$, -10.88 ($\log_{10}{}^{*}K_{p,s,0}^{\circ} = 7.27$, *i.e.*, for Eq. (X.8)) is obtained. The value is in fair agreement with results from other studies on well-characterized, heat-treated $FeCO_3(cr)$. However, in all of Ptacek's experiments the formation of $FeCO_3(aq)$ ($K_{A}^{\circ} = a_{FeCO_3(aq)}/(a_{Fe^{2+}}a_{CO_3^{2-}})$) probably cannot be neglected, and the data are not sufficiently reliable to evaluate useful values of both $\log_{10}{}^{*}K_{s}^{\circ}$ and $\log_{10} K_{A}^{\circ}$. For reasonable values of the formation constant of $\log_{10}{}^{*}K_{s}^{\circ}$ the calculated value of the $FeCO_3(aq)$ formation constant is of the order of 10^{5}.

The results from the measurements in Na_2SO_4 and $FeSO_4$ solutions would need to include allowance for formation of the complex $FeSO_4(aq)$, and also are not used further in the present review.

[1992PTA/REA]

See the discussion of the original thesis [1992PTA] on which this paper was based.

[1993DIN/ISH]

In this solubility study at 423 K of the solubility of a commercially "pure", coarse-grained magnetite, which was only characterized before the experiments by ICP and XRD, three experiments were conducted. The first two were carried out in "pure" water from which no reliable thermodynamic data can be obtained, while the third contained traces of HCl, namely, $(2.2 - 3.0) \times 10^{-5}$ mol·kg^{-1} with a *ca.* 3.3×10^{-6} mol·kg^{-1} impurity of F^{-}. The scatter in the iron analyses for the last experiment, $(7.67 \pm 0.34) \times 10^{-6}$ mol·kg^{-1} precluded any trend with pH to be discerned over this very narrow pH range. Finally, the solutions were apparently kept under an Ar atmosphere so that there was no knowledge of the partial pressure of H_2, other than the statement by the authors that the oxygen content of the solution was eventually exhausted allowing for thermodynamic equilibrium to be established.

Considering all the experimental uncertainties, or lack of experimental constraints including the true purity of the magnetite, no valuable information can be gleaned from this study.

[1993GRO/STO]

The main focus of this detailed and important paper is the heat capacity and derived thermodynamic properties of two synthetic wüstite specimens with the compositions $Fe_{0.9379}O$ and $Fe_{0.9254}O$, which are near the eutectoid composition (C_E), plus a small number of measurements on a specimen of composition $Fe_{0.9427}O$. Measurements were performed on quenched, metastable specimens up to ~350 K, decomposing specimens below the eutectoid temperature (T_E), and reconstituted wüstite above T_E. Bridging $C_{p,m}^{\circ}$ expressions were obtained for intermediate temperatures where decomposition of wüstite is too rapid for measurements to be made.

Key derived values include:

$[\Delta_{0\,\mathrm{K}}^{298.15\,\mathrm{K}} S_{\mathrm{m}}^{\circ}]((1/1.9379)\mathrm{Fe}_{0.9379}\mathrm{O, cr}) = 29.46\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$;

$[\Delta_{0\,\mathrm{K}}^{298.15\,\mathrm{K}} S_{\mathrm{m}}^{\circ}]((1/1.9254)\mathrm{Fe}_{0.9254}\mathrm{O, cr}) = 29.21\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$;

$[\Delta_{\mathrm{r}} H_{\mathrm{m}}^{\circ}](0.1817\mathrm{Fe(cr)} + \frac{1}{4}\mathrm{Fe_3O_4(cr)}) = \mathrm{Fe}_{0.9317}\mathrm{O(cr, 298.15\ K)} = (9.04 \pm 0.25)\ \mathrm{kJ \cdot mol^{-1}}$;

evaluated $C_E = \mathrm{Fe}_{0.932\pm0.004}\mathrm{O}$; evaluated $T_E = (847 \pm 7)$ K.

Combined with an extensive literature review and evaluation of published enthalpy-titration and oxygen-chemical-potential data, these measurements make this paper the most definitive study to date on the thermal properties of wüstite. Thermodynamic properties are estimated for the fictive compositions $\mathrm{Fe}_{0.90}\mathrm{O}$ and FeO. Lattice constants for wüstite of various compositions are also reviewed. An appendix presents an important re-evaluation of thermal data for magnetite.

Discussion of this study (Section VII.2.8) is constrained by the scope of the current review.

[1993KUM/SUZ]

The equilibrium (noting that this is a metastable state) and kinetics of dissolution of colloidal lepidocrocite (γ-FeOOH) in natural seawater were studied at 20 °C over the pH range 5.5 to 8.2 using a ^{59}Fe tracer technique. A dialysis method was used to determine the soluble iron(III) content of the solution. The collected seawater was allowed to age for one week while the iron(II) species present were oxidized and partially crystalline, colloidal γ-FeOOH precipitated. A minimum solubility at pH ≥ 7.5 was reported to be $1.4 \times 10^{-9}\ \mathrm{mol \cdot L^{-1}}$ where the rate constant of dissolution normalized for the calculated surface area is $2 \times 10^{-4}\ \mathrm{h^{-1}}$.

The colloidal nature of the solid and fact that seawater was employed render these results outside the scope of this review.

[1993LUT/FER]

Square-wave voltammetry at mercury electrodes (scan range − 0.1 to − 0.8 V, 100 Hz frequency, 50 mV pulse height) was applied to monitor the reaction, $\mathrm{HS^-} + \mathrm{Hg(l)} \rightarrow \mathrm{HgS(s)} + \mathrm{H^+} + 2\mathrm{e^-}$, in the titration of field samples (marine waters and porewaters) with NaOH/HCl and in the titration of sulfide with Fe(II) in seawater. The peak potential E_p was considered to shift to more negative values with an increase in the concentration of electroactive species and to more positive values with protonation or complexation of sulfide. From the plots of E_p *vs*. pH, the iron sulfide species was concluded to be $\mathrm{Fe(SH)^+}$ and $\mathrm{Fe_2(SH)^{3+}}$. In the plots of E_p *vs*. $\log_{10} c_{\mathrm{Fe(II)}_{\mathrm{total}}}$, the function, $F_0(\mathrm{X}) = 1 + \beta_1[\mathrm{X}] + \beta_2[\mathrm{X}]^2 + \ldots + \beta_n[\mathrm{X}]^n$ where [X] is the analytical concentration of the metal ion, was related to the peak potential (E_p) and peak current (I_p) by $F_0(\mathrm{X}) = \mathrm{antilog}\{[0.434nF/RT][(E_\mathrm{p})_\mathrm{s} - (E_p)_\mathrm{c}] + [\log(I_\mathrm{p})_\mathrm{s}/(I_\mathrm{p})_\mathrm{c}]\}$, where $n = -2$, and c indicates complexed sulfide and s indicates free or uncomplexed sulfide. Leden's method of successive extrapolations was applied, that is, $F_0(\mathrm{X})$, $F_1(\mathrm{X}) = [F_0(\mathrm{X}) - 1]/[\mathrm{X}]$, $F_2(\mathrm{X}) = [F_1(\mathrm{X}) - \beta_1]/[\mathrm{X}]$, … , and $F_n(\mathrm{X}) = [F_{n-1}(\mathrm{X}) - \beta_{n-1}]/[\mathrm{X}]$ were calculated to determine β_n values. For Fe(II), the values obtained for $\log_{10}\beta_n$ were (5.50 ± 0.24) ($FeSH^+$) and (11.08 ± 0.25) ($Fe_2(SH)^{3+}$) in seawater. Activity corrections were not carried out. All the species such as HS^-, H_2S(aq) and sulfides complexed with metal ion were assumed to be similarly electroactive and labile, and to behave similarly on and near the mercury electrode; the difference in the speciation changes the peak potential. However, the relation of the electrode reaction or E_p to the equilibrium concentrations of the sulfide species, such as HS^-, H_2S(aq) and sulfides complexed with metal ion in the solution is uncertain. Also in the data processing, the differences between the analytical concentrations and the equilibrium concentrations were not properly considered. In the application of the proposed successive-extrapolation method, the propagation of the errors in the peak potentials and current and in [X] to the uncertainty in β_n must be carefully evaluated. This method could be used only when the concentration range of [X] is taken appropriately for the target values of β_n. As a whole, this review does not accept the results in this paper.

[1993PAL/HYD]

Palmer and Hyde studied the formation of iron(II) chlorido complexes in the temperature range 125 °C to 295 °C in 1 molal aqueous trifluoromethanesulfonate solutions. A high-temperature hydrogen-electrode concentration cell was used to perform the measurements.

This work was a very careful experimental study producing reliable results. Unfortunately, the temperature range of 125 to 295 °C is outside the temperature range considered in this review. Hence, the values presented in this study are used only in an indirect way.

Inspection of the formation data (the molal formation quotients, Table A-52, column 2) as given reveals two facts:

1) a very close to linear $1/T$ dependency of $\log_{10}\beta_1$, and

2) very optimistic single-value uncertainties.

A weighted regression (using the authors' uncertainty values) produces rather strange behaviour because the few points with low uncertainties fix the regression curve. The resulting coefficient of determination is only 0.74. An unweighted regression produces a much better fit (the coefficient of determination is 0.94, Figure A-45). The unweighted extrapolation to 25 °C gives

3) $\log_{10}\beta_1$ ($FeCl^+$, 1 m, 25 °C) = −(1.71 ± 0.31), and $\Delta_r H_m$ ($FeCl^+$, 1 m) = (28.7 ± 4.5) $\mathrm{kJ\cdot mol^{-1}}$.

Table A-52: Individual and re-evaluated logarithm (base 10) of the molal formation quotients for the reaction $Fe^{2+} + Cl^{-} \rightleftharpoons FeCl^{+}$ at various, elevated temperatures. Fits of these data against $1/T_0 - 1/T$ are shown in Figure A-45 and Figure A-46.

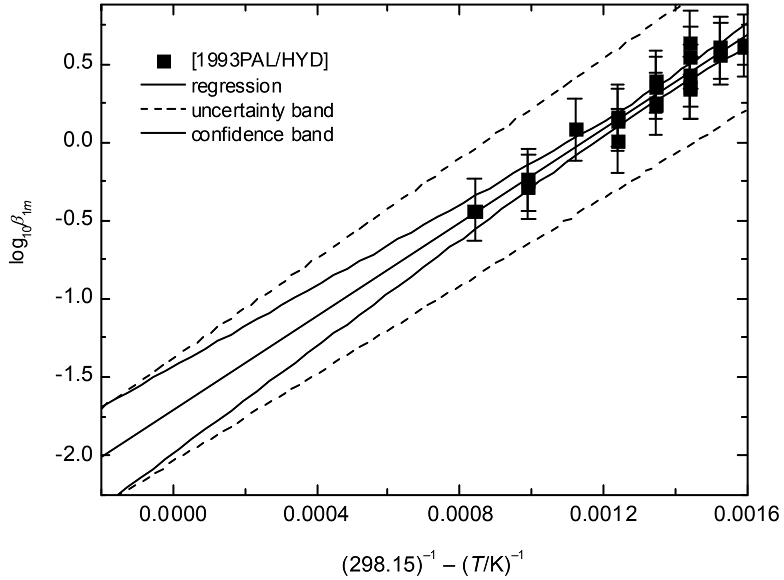
t/°C	Reported $\log_{10} \beta_{1m}(T)$	weighted average $\log_{10} \beta_{1m}(T)$ *
294.9	0.619 ± 0.009	0.619 ± 0.134
273.8	0.606 ± 0.011	
273.8	0.566 ± 0.023	0.586 ± 0.055
249.8	0.350 ± 0.015	
249.8	0.353 ± 0.010	
249.8	0.544 ± 0.078	
249.8	0.636 ± 0.002	
249.8	0.428 ± 0.043	0.462 ± 0.245
224.8	0.248 ± 0.002	
224.8	0.352 ± 0.008	
224.8	0.389 ± 0.027	0.330 ± 0.143
199.8	0.009 ± 0.020	
199.8	0.143 ± 0.060	
199.8	0.166 ± 0.016	0.106 ± 0.166
174.8	0.083 ± 0.012	0.083 ± 0.134
149.8	− 0.285 ± 0.040	
149.8	− 0.241 ± 0.038	− 0.263 ± 0.061
124.8	− 0.436 ± 0.062	− 0.436 ± 0.134

* The uncertainties listed for measurements at those temperatures at which single measurements were reported are estimates. The estimate (±0.134) is the average of the uncertainties determined for the measurements at all the other temperatures.

At several temperatures multiple measurements are available. To carry out an improved weighted fit, the assigned uncertainties should somehow reflect the variability of the individual measurements at such temperatures.

Finally, a coefficient of determination of 0.99 is obtained when the re-evaluated measurements from column 3 are fitted with a $1/T$ model and the resulting parameters are $\log_{10} \beta_1$ ($FeCl^{+}$, 1 m, 25 °C) = $-(1.74 \pm 0.17)$, and $\Delta_r H$ ($FeCl^{+}$, 1 m) = (29.1 ± 2.5) $kJ \cdot mol^{-1}$.

Figure A-45: Linear regression of measurements provided in Table A-52, using equal weights (an arbitrary value of ±0.2). This demonstrates excellent linearity of the data with 1/*T*.



This improved fit is shown in Figure A-46. Note that the extrapolated $\Delta_r H_m$ ($FeCl^+$, 1 m, 25 °C) value of (29.1 ± 2.5) (1σ) $kJ\cdot mol^{-1}$ agrees well with the (28.7 ± 8.9) (1σ) $kJ\cdot mol^{-1}$ extrapolation from the high-temperature data (200, 150, 100 °C) of Heinrich and Seward [1990HEI/SEW].

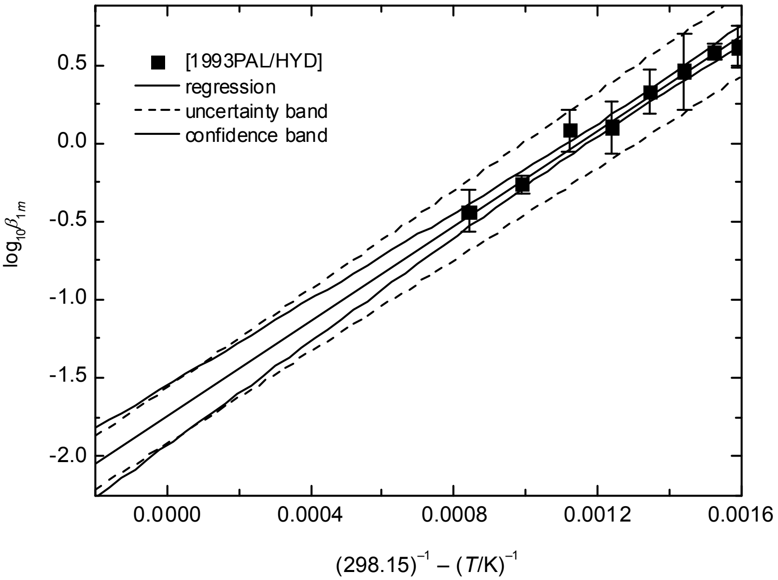
Palmer and Hyde used an empirical approach to extrapolate their $\log_{10} Q_1$ values to the standard state conditions of infinite dilution. This approach included the assumption that the activity coefficient ratio $\gamma_{FeCl^+} / \gamma_{Cl^-}$ is equal to the ratio $\gamma_{FeAc^+} / \gamma_{Ac^-}$ determined under the same conditions. With this reasonable assumption they were able to express the resulting $\log_{10} \beta_1 (T)$ values with the equation

$$\log_{10} \beta_1^o(T) = -7.1783 + 911.13\,(T/K)^{-1} + 0.013407(T/K). \qquad (A.149)$$

This equation produces results similar to those from the equation provided by [1990HEI/SEW] (see Figure A-47):

$$\log_{10} \beta_1^o(T) = 24.355 + 0.0215\,(T/K) - 5.429 \ln (T/K). \qquad (A.150)$$

Figure A-46: Weighted linear regression of measurements provided in Table A-52, using re-evaluated measurements and weights. The values at individual temperatures represent weighted averages [1999WAN/OST] (Table A-52, column 3). The resulting coefficient of determiantion is 0.99.



It should, however, be noted that the derivation of (A.149) was performed *including* the points formerly measured by Heinrich and Seward [1990HEI/SEW]. The good agreement between the two equations is thus not unexpected.

However, (A.149) means that $\Delta_r H^\circ_m$ ($FeCl^+$, T) is expressed as

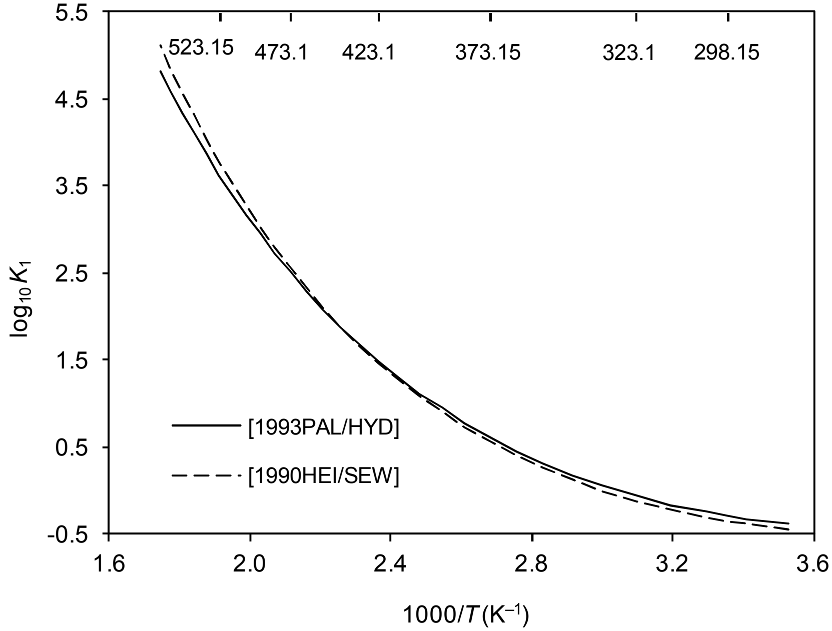
$$\Delta_r H^\circ (\mathrm{FeCl}^+, T)/\mathrm{J \cdot mol^{-1}} = \mathrm{A} + \mathrm{B}\,(T/\mathrm{K})^2$$

(in this particular case: A = – 17433.46 $\mathrm{J \cdot mol^{-1}}$ and B = 0.2567 $\mathrm{J \cdot mol^{-1} \cdot K^{-2}}$) whereas, (A.150) produces the relation

$$\Delta_r H^\circ (\mathrm{FeCl}^+, T)/\mathrm{J \cdot mol^{-1}} = \mathrm{B}\,(T/\mathrm{K})^2 + \mathrm{C}\,(T/\mathrm{K}),$$

with B = 0.4116 $\mathrm{J \cdot mol^{-1} \cdot K^{-2}}$ and C = – 103.94 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$.

Figure A-47: Graphical representation of Eqs. (A.149) and (A.150). The difference between the two curves is less than the uncertainty of individual measurements (not shown).



Both studies in principle use more or less arbitrarily functions of T to represent $\log_{10} \beta_1 = \mathrm{f}(T)$. More chemically meaningful approximations are given in TDB-2.2 [2000GRE/WAN], particularly for those cases where good heat-capacity functions are missing:

For the case when the heat capacity of reaction is taken as zero, the equation for $\log_{10} \beta_1$ has the form

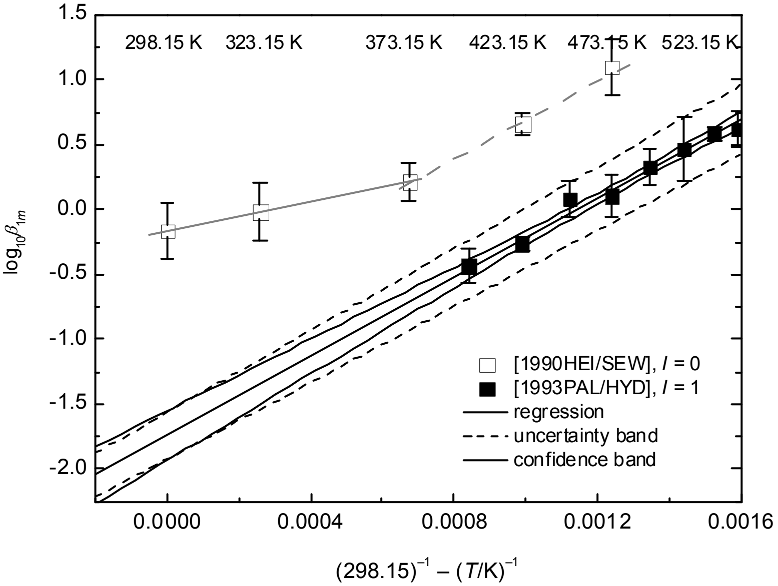
$$\log_{10} \beta_1 (T) = \mathrm{A'} + \mathrm{C'}(T/\mathrm{K})^{-1}, \text{ with } \Delta_r H / \mathrm{J \cdot mol^{-1}} = \text{constant},$$

whereas the equation

$$\log_{10} \beta_1 (T) = \mathrm{A'} + \mathrm{C'}(T/\mathrm{K})^{-1} + \mathrm{D'} \log_{10}(T/\mathrm{K}), \text{ with } \Delta_r H / \mathrm{J \cdot mol^{-1}} = \mathrm{A''} + \mathrm{B''}(T/\mathrm{K}),$$

should be used when a constant heat capacity of reaction is assumed. Obviously, the models also are substantially modified by the procedures used to extrapolate to standard state conditions of infinite dilution.

Figure A-48: Comparison of [1993PAL/HYD] and [1990HEI/SEW] data. Both data sets are consistent with the assumption of a constant $\Delta_{\mathrm{r}}H_{\mathrm{m}}$ value in the temperature range ~ 100 to 300 °C, the slopes being nearly identical. As discussed in the Appendix A entry for [1990HEI/SEW], the low-temperature data set of [1990HEI/SEW] exhibits a different value for $\Delta_{\mathrm{r}}H_{\mathrm{m}}$.



In conclusion, the high-temperature data of [1993PAL/HYD] cannot directly be used to derive 25 °C values of $\log_{10}\beta_1^\circ$ and $\Delta_{\mathrm{r}}H_{\mathrm{m}}^\circ$ for the reaction $\mathrm{Fe}^{2+} + \mathrm{Cl}^- \rightleftharpoons \mathrm{FeCl}^+$, though the results of this study are used for comparison purposes.

[1993PRZ/WIS]

Przepiera *et al.* reported the heats of solution of $\mathrm{FeSO_4 \cdot 7H_2O(cr)}$ (and $\mathrm{MnSO_4 \cdot H_2O(cr)}$ and $\mathrm{NiSO_4 \cdot 7H_2O(cr)}$) into water and into aqueous solutions of sulfuric acid (0.0256 to 2.0901 m). In each case, the constant mass ratio "of salt to water in solution was 5×10^{-4}". This corresponds to a final solution concentration of $\mathrm{FeSO_4}$ of 1.80×10^{-3} m (during the preparation of the present review, this molality value was confirmed by the first author [2006PRZ]). The value reported for dissolution in water at 298.15 K (to obtain 1.80×10^{-3} m $\mathrm{FeSO_4(sln)}$) was 13.808 $\mathrm{kJ \cdot mol^{-1}}$, based on extrapolation of the results at non-zero $\mathrm{H_2SO_4}$ concentrations [2006PRZ], and 13.65 $\mathrm{kJ \cdot mol^{-1}}$ on further extrapolation to $I = 0$. This value is incompatible with the results provided in an earlier paper [1992PRZ/WIS] for the heat of solution of $\mathrm{FeSO_4 \cdot 7H_2O(cr)}$ in water as a function of final molality (the authors later suspected problems caused by hydrolysis of iron(II)

[2006PRZ]). The values in [1992PRZ/WIS] do not extrapolate smoothly to their reported value of 11.67 kJ·mol^{-1} for $\Delta_{\mathrm{sln}}H_{\mathrm{m}}^{\mathrm{o}}$, nor do they agree well with the values of $\Delta_{\mathrm{sln}}H_{\mathrm{m}}$ from Larson [1968LAR]. Furthermore, the molar integral heats of dilution of other 2-2-valent salts extrapolate to I = 0 following a line with a much sharper slope [1959LAN], especially for molalities below the experimental molalities used in the experiments of Przepiera *et al.* [1992PRZ/WIS]. The results in these two papers are roughly compatible with those from other studies, but cannot be used to obtain a useful value for the enthalpy of solution of $\mathrm{FeSO_4{\cdot}7H_2O(cr)}$ in water at infinite dilution.

[1993REF/GEN]

Chloride-containing green rust 1 was prepared by precipitation from mixing of aqueous solutions of NaOH (0.40 M effective final molality if precipitation had not occurred) and $\mathrm{FeCl_2{\cdot}4H_2O(cr)}$ (a molar excess such that the initial ratio of $\mathrm{Fe^{2+}}$ to $\mathrm{OH^-}$ was 0.513 to 0.875). The electrode potential (platinum electrode with a calomel reference electrode) of each solution ((25.0 ± 0.5) °C) was measured during the oxidation to form green rusts.

The reported potentials and pH values for the solutions with initial ratios of $\mathrm{Fe^{2+}}$ to $\mathrm{OH^-}$ from 0.513 to 0.875 are used to calculate E^{o} values for the overall reaction written as

$$4\mathrm{Fe(OH)_2(s)} + \mathrm{Cl^-} + m\,\mathrm{H_2O(l)} \rightleftharpoons \mathrm{(Fe^{III})(Fe^{II})_3(OH)_8Cl{\cdot}}m\mathrm{H_2O(s)} + \mathrm{e^-} \qquad \text{(A.151)}$$

In these recalculations, SIT activity coefficients (Appendix B) for correction to zero ionic strength have been used. An average value of −(0.552 ± 0.012) V *vs.* the standard hydrogen electrode is obtained (2σ uncertainty). Within the experimental uncertainties, this E^{o} value is the same as the value reported by the authors. The number of waters of hydration is not well defined, and the green rust is probably better formulated as $\mathrm{(Fe^{III})(Fe^{II})_3(OH)_8Cl{\cdot}}n\mathrm{H_2O}$ ($\Delta_{\mathrm{r}}G_{\mathrm{m}}^{\mathrm{o}}$(A.151) = −53.3 kJ·mol^{-1}). The procedure used to calibrate the pH electrode was not described, and this introduces an additional uncertainty in the measurements. The total (2σ) uncertainty is estimated here as ±2.0 kJ·mol^{-1}.

[1994BAG/CAR]

The apparent ($^*K_{\mathrm{s}}$') and $^*K_{\mathrm{s}}$(NBS) solubility products of amorphous iron sulfide (FeS) for the reaction $\mathrm{FeS(am) + H^+ \rightleftharpoons Fe^{2+} + HS^-}$, were determined experimentally, *in situ*, in the Baltic Sea. The apparent solubility product is defined as $^*K_{\mathrm{s}}' = c_{\mathrm{Fe^{2+}}}c_{\mathrm{HS^-}}/c_{\mathrm{H^+}}$ here complex formation of Fe(II) with $\mathrm{OH^-}$, $\mathrm{Cl^-}$ and $\mathrm{SO_4^{2-}}$ in the sea water was neglected and pH = $-\log_{10} a_{\mathrm{H^+}}$ where pH was measured on the National Institute for Standards and Technology pH scale. The $^*K_{\mathrm{s}}$(NBS) was defined as $^*K_{\mathrm{s}}'y_{\mathrm{Fe2+}}y_{\mathrm{HS-}}$ where the activity coefficients, y, were estimated with the Davies equation. The *in situ* experiments were conducted at 10 m water depth in closed sediment-water systems consisting of Plexiglas boxes with a salinity of 4.83‰. The boxes, with the bottom open, were gently pressed down into the sediment and were closed at the start of the experiment. One transparent and two opaque boxes were used. The water samples were filtered through 0.45 µm Millipore filters and the concentrations of iron and sulfide were obtained spectrophotometrically. The total concentration of iron was considered to be equal to the concentration of Fe^{2+} and the concentration of HS^- was calculated from total sulfide using the apparent first dissociation constant of hydrogen sulfide, $-\log_{10} K_1' = 2.525 - 0.169Cl^{1/3} + 1359.96/T$ where Cl stands for chlorinity (chlorine equivalent of the total halide concentration in $g\cdot(kg\ seawater)^{-1}$ and T for temperature in kelvin. Over the first days, there was a rapid increase in c_{H^+}, by approximately a factor of 10, in all three boxes. As a result of oxidation of organic matter $CO_2(g)$ produced in the box could not leave the closed system. Subsequent to that, the pH stabilized at around 7, indicating that the sulfate-sulfide system controlled the pH. Assuming that the Fe^{2+} and HS^- in the solution were in equilibrium with amorphous FeS, the $-\log_{10} {}^*K_s'$ and $-\log_{10} {}^*K_s(NBS)$ values were found to be 2.6 and 3.15, respectively, at a mean experimental temperature of 15.8 °C. The temperature dependence of the apparent equilibrium constant (within the range 12.8 to 18.8 °C) was described by $-\log_{10} {}^*K_s' = -0.068t + 3.70$, where t denotes the temperature in Celsius. Calculations by the reviewer indicated that the deviations (2σ) for the parameters were $-(0.068 \pm 0.022)$ and (3.70 ± 0.19). From the relationship between $c_{Fe^{2+}}$ and c_{HS^-} in the solution, the composition of the amorphous precipitate was estimated to be $FeS_{0.86}$. Although the solubility-controlling solid is believed to be amorphous FeS, there may be other metal ions which also form insoluble sulfides and the ageing state of FeS may affect the equilibrium. Moreover, it is not certain that the concentrations of total iron and total sulfide are controlled by the reaction $FeS(am) + H^+ \rightleftharpoons Fe^{2+} + HS^-$ at a rather higher pH of 7. This review does not use the result of this paper.

[1994CHA/NAV]

Chai and Navrotsky used a drop-calorimetry method to determine the enthalpy of formation of $FeCO_3(cr)$. Samples initially at 298.15 K were oxidized and decomposed to hematite and $CO_2(g)$ using Calvet-type calorimeters at 978 K ((19.31 ± 0.23) $kJ\cdot mol^{-1}$, 14 measurements) and 1075 K ((30.66 ± 0.76) $kJ\cdot mol^{-1}$, 8 measurements). These recalculated uncertainties are 95% confidence limits.

The enthalpy increments for hematite from 298.15 to 978 K and 1075 K, based on the equation for $C_p(T)$ selected in the present review (Section VII.2.2.2), are 96.98 $kJ\cdot mol^{-1}$ and 111.19 $kJ\cdot mol^{-1}$, respectively. However, the authors reported (95.83 ± 0.62) $kJ\cdot mol^{-1}$ and (95.92 ± 0.85) $kJ\cdot mol^{-1}$ based on 7 measurements and 9 measurements from (298 to 978 K) on material from two separate syntheses, and (109.19 ± 0.64) $kJ\cdot mol^{-1}$, based on 10 measurements (298 to 1075 K). Later Laberty and Navrotsky [1998LAB/NAV] and Majzlan *et al.* [2003MAJ/GRE] reported enthalpy differences for hematite of (100.0 ± 1.1) $kJ\cdot mol^{-1}$ (298 to 979 K) and (96.86 ± 0.45) $kJ\cdot mol^{-1}$ (298 to 975 K). These become (99.8 ± 1.1) $kJ\cdot mol^{-1}$ and (97.33 ± 0.45) $kJ\cdot mol^{-1}$ when adjusted to the temperature change from 298 to 978 K. Strangely enough, the later papers do not comment on the differences (nor do they even cite the previous results)!

The results in [2003MAJ/GRE] were apparently adjusted using measurements for Al_2O_3(cr) from an unstated source, and their reported value for hematite is reasonably consistent with the value from the integrated heat-capacity function. The spread in the values for hematite suggests that the uncertainties in the drop-calorimetry results for $FeCO_3$(cr) [1994CHA/NAV] should be increased to ~ 2.0 kJ·mol^{-1}, and that in the calculations the integrated heat-capacity function should probably be used to determine the enthalpy change for hematite as a function of temperature.

The enthalpy increments for O_2(g) and CO_2(g) are based on the CODATA assessment [1989COX/WAG], and introduce additional uncertainties to the calculation of $\Delta_f H^\circ$ ($FeCO_3$, cr, 298.15 K) of < 0.01 kJ·mol^{-1}.

On this basis, the values from the experiments at 978 K and 1075 K were used to calculate − 56.04 and − 56.25 kJ·mol^{-1} for $\Delta_r H$ ((A.152), 298.15 K)

$$FeCO_3(cr) + \tfrac{1}{4} O_2(g) \rightleftharpoons \tfrac{1}{2} \alpha\text{-}Fe_2O_3 + CO_2(g). \qquad (A.152)$$

The average value, − 56.14 kJ·mol^{-1}, initially with an uncertainty of ± 2.3 kJ·mol^{-1}, was used in the calculations to optimize the chemical thermodynamics quantities for iron (Chapter XI).

Using the selected value for $\Delta_f H^\circ_m$ (Fe_2O_3, α, 298.15 K) (Section VII.2.2.1), the average value for $\Delta_f H^\circ_m$ ($FeCO_3$, cr, 298.15 K) is − (750.5 ± 2.7) kJ·mol^{-1} (estimated uncertainty).

The authors used their results to calculate the invariant curve for the reaction between siderite and hematite to form magnetite and carbon dioxide, and rather poor agreement with literature results (differences of 70 to 100 K) was found.[1]

[1994DAN/RIG]

Potentiometric measurements using a glass electrode and a calomel reference electrode were made at (25.0 ± 0.1) °C of iron(III) nitrate, (0.3 - 12.0) × 10^{-3} M, in KNO_3 solutions, I_c = 0.02 to 1.0 M, to pH values ≤ 3.8. No experimental titration data were provided. The calibration of their electrochemical cell was not mentioned, although liquid-junction potentials were calculated using a computer program apparently developed earlier by these authors. Moreover, only averaged hydrolysis constants are provided at each average ionic strength for the formation of $FeOH^{2+}$ and $Fe_{12}(OH)^{2+}_{34}$, and their data analysis involved fixing values of $\log_{10} {}^*\beta^\circ_{2,1}$ at − 5.7 and $\log_{10} {}^*\beta^\circ_{2,2}$ = − 2.91 (on a molar scale) based on a compilation of earlier data in the literature. The

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[1] The heat-capacity equation for $FeCO_3$(cr) attributed to T. Holland "(a = 0.1722, b = 0.0477, c = 95.389, d = − 1.5731 for C_p = a + bT + c/T^2 + d/$T^{½}$)" appears to contain a typographical error. If the units for heat capacity are assumed to be in J·K^{-1}·mol^{-1} and temperature in kelvin, the equation generates values for $C^\circ_{p,m}$ ($FeCO_3$, cr) that are ~ 70 J·K^{-1}·mol^{-1} smaller than the experimental values.

following $\log_{10} {}^*\beta^{\circ}_{1,1}$ values are tabulated: $-(2.50 \pm 0.03)$, $-(2.56 \pm 0.02)$, $-(2.59 \pm 0.02)$ and $-(2.52 \pm 0.04)$ at 0.05, 0.1, 0.5 and 1.0 M, respectively.

There are assumptions made in the data treatment that either are not transparent to the reader (*e.g.*, pH calibration, liquid-junction potential values, averaging of titration results, *etc.*) or that are dubious (*e.g.*, the fixing of two hydrolysis constants at $I = 0$). Furthermore, consideration of the formation of $\mathrm{Fe_{12}(OH)_{34}^{2+}}$, which other studies would indicate as a multi-nuclear Fe(III) species is slow to form, if at all, is difficult to accept without more detailed information being made available. Therefore, the results from this paper are not considered further.

[1994DIA/KHO]

This paper presents an evaluation of the thermodynamic properties of goethite, α-FeOOH, with particular attention to the surface-area-dependent heat-of-dissolution studies of [1934FRI/ACK], [1935FRI/KLE], and [1966FER]. A "best" value of $\Delta_r H^{\circ}_m = (13.7 \pm 2.4)\ \mathrm{kJ \cdot mol^{-1}}$ was obtained from data of [1966FER] for the reaction:

$$2\,\alpha\text{-FeOOH} \rightleftharpoons \alpha\text{-Fe}_2\text{O}_3 + \text{H}_2\text{O(l)},$$

and a similar value with a larger uncertainty, $(13.6 \pm 3.5)\ \mathrm{kJ \cdot mol^{-1}}$, was derived from critical evaluation of available data for the corresponding, more problematic transformation involving H_2O(g). Also based on [1966FER], surface-enthalpy values were recalculated as 1550 $\mathrm{mJ \cdot m^{-2}}$ for goethite and 1100 $\mathrm{mJ \cdot m^{-2}}$ for hematite. Unfortunately, the value of all these painstaking evaluations is diminished by the more recent, detailed experimental study of Mazeina *et al.* [2005MAZ/NAV].

Eight $C^{\circ}_{p,m}$ values for goethite at 309 to 490 K are reproduced from Korobeinikova (Ph.D. Thesis, Moscow State University, 1975). The specimen was initially dried at 470 K, after the onset of thermal decomposition to hematite was observed at 490 K.

[1994HAN/BOR]

Aqueous solutions containing mixtures of iron(II) and iron(III) sulfates (~0.025 M in H_2SO_4) under argon were prepared, and solids were precipitated by titration with NaOH(sln) at (23 ± 1) °C. The solubility product was calculated using Fe^{3+} activities derived from the formulation of Fox [1988FOX] for ferrihydrite. As discussed by Refait *et al.* [1999REF/BON] the reported value of $-(4380 \pm 4)\ \mathrm{kJ \cdot mol^{-1}}$ for the Gibbs energy of formation of $\mathrm{(Fe^{III})_2(Fe^{II})_4(OH)_{12}SO_4 \cdot 3H_2O(s)}$ at ~298 K is much too positive to be compatible with the results of electrochemical studies [1998GEN/BOU], [1999REF/BON]. Refait *et al.* noted that a considerable portion of the difference was related to use of the US-NBS values for Fe^{2+} and Fe^{3+} in the solubility product calculations. Use of values for the iron species as selected in the present review lower the discrepancy from 120 $\mathrm{kJ \cdot mol^{-1}}$ to ~30 $\mathrm{kJ \cdot mol^{-1}}$, a difference still sufficiently large to suggest that either some problem remains with the calculated iron(III) activities in solutions in contact with both the green rust and ferrihydrite or that the stoichiometry of the authors "green rust" was not the assumed stoichiometry.

[1994TAK/AKI]

The heat capacity of stoichiometric magnetite was measured at 13 - 300 K, and the Verwey transition was observed as a single, sharp anomaly at the relatively high temperature of 123.82 K (*cf.* [1985SHE/KOE], [1991SHE/KOE]), with tail portions extending from ~80 to ~230 K. The values $\Delta_{\mathrm{trs}}H^{\circ}_{\mathrm{m}}$ = 980.8 J·mol^{-1} and $\Delta_{\mathrm{trs}}S^{\circ}_{\mathrm{m}}$ = 7.67 J·K^{-1}·mol^{-1} (including tail contributions of 218.3 J·mol^{-1} and 1.50 J·K^{-1}·mol^{-1}, respectively) were obtained. The specimen consisted of melt-grown single crystals obtained under a CO/CO_2 atmosphere, cooled rapidly to ambient temperature, then annealed at 973 K for 10 days to remove residual stress. "Typical" $C^{\circ}_{p,\mathrm{m}}$ measurements are tabulated, comprising 203 closely spaced values between 13.56 and 299.94 K, including 42 values in the immediate Verwey transition region between 116.09 and 127.17 K. These high-quality data are included in the evaluation of $C^{\circ}_{p,\mathrm{m}}$ (Fe_3O_4, cr, T) in Section VII.2.7.1.

[1995DRI/REF]

Carbonate-containing green rust 1 was prepared by precipitation from mixing of aqueous solutions of NaOH (0.30 M, probably the effective final concentration if precipitation had not occurred) and $FeSO_4\cdot 7H_2O$ (a slight molar excess such that the initial ratio of Fe^{2+} to OH^- was 0.52 to 0.61). Solutions of Na_2CO_3 then were added so that the final carbonate molarity was 0.03 M or 0.18 M. The electrode potential (platinum electrode with a calomel reference electrode) of each solution ((25.0 ± 0.5) °C) was measured during the oxidation to form green rusts. At the lower carbonate concentration mixtures of sulfate and carbonate green rusts were formed. At the higher carbonate concentration ($I \approx 1$ m) only the carbonate-containing green rust was formed.

The reported potentials and pH values for the solutions with initial ratios of Fe^{2+} to OH^- from 0.52 to 0.61 and 0.18 M Na_2CO_3(sln) were used to calculate E° values for the overall reaction written as

$$6\,\mathrm{Fe(OH)_2(s)} + \mathrm{CO_3^{2-}} + n\,\mathrm{H_2O(l)} \rightleftharpoons \mathrm{(Fe^{III})_2(Fe^{II})_4(OH)_{12}CO_3\cdot}n\mathrm{H_2O(s)} + 2\,\mathrm{e^-} \quad \text{(A.153)}$$

Recalculations in the present review used SIT activity coefficients (Appendix B) for correction to zero ionic strength and TDB values for the carbonate protonation reaction. An average value of −(0.632 ± 0.009) V *vs.* the standard hydrogen electrode is obtained (2σ uncertainty); however, there is a slight drift to more negative calculated E° values for the lower final Fe^{2+} concentrations. For the solution with an initial ratio of Fe^{2+} to OH^- of 0.60, the recalculated value of E° is −0.625 V. Within the experimental uncertainties, these E° values are the same as those reported by the authors. The number of waters of hydration is not well defined, and the green rust is probably better formulated as $(Fe^{III})_2(Fe^{II})_4(OH)_{12}CO_3\cdot nH_2O(s)$ ($\Delta_{\mathrm{r}}G^{\circ}_{\mathrm{m}}$ (A.153) =

$-$ 120.6 kJ·mol^{-1}). The procedure used to calibrate the pH electrode was not described, and this introduces an additional uncertainty in the measurements. The total (2σ) uncertainty is estimated here as ±2.0 kJ·mol^{-1}.

Eventually, further oxidation of the green rust occurred according to

$$(\mathrm{Fe^{III}})_2(\mathrm{Fe^{II}})_4(\mathrm{OH})_{12}\mathrm{CO_3}\cdot n\mathrm{H_2O(s)} \rightleftharpoons 6\,\alpha\text{-FeOOH} + \mathrm{CO_3^{2-}} + 6\,\mathrm{H^+} + n\,\mathrm{H_2O(l)} + 4\,\mathrm{e^-}. \tag{A.154}$$

for solids formed from solutions with initial ratios of Fe^{2+} to OH^- between 0.61 and 0.56, whereas the final iron-containing product from green rusts formed from solutions with lower ratios was magnetite. The authors did not use potentials for Reaction (A.154) to determine other thermodynamic quantities, as the particle size of the goethite was not measured.

[1995KOM/WES]

Careful heat-capacity measurements were made on natural samples of deerite (analysis consistent with $(\mathrm{Fe^{2+}_{4.87}Fe^{3+}_{2.76}Mn_{1.07}Mg_{0.15}Ti_{0.15}O_3})(\mathrm{Si_{5.94}Al_{0.03}Ti_{0.03}O_{17}(OH)_5})$(cr) and grunerite (analysis consistent with $(\mathrm{Fe^{2+}_{5.38}Fe^{3+}_{0.66}Mn_{0.08}Mg_{0.80}Ca_{0.05}})(\mathrm{Si_8O_{22}})\{(\mathrm{OH})_{13}\mathrm{Cl_{0.03}O_{0.60}}\}$)(cr). Adiabatic calorimetry was used for temperatures between 10 and 350 K, and differential-scanning calorimetry at higher temperatures (338.5 to 696.4 K for deerite, 340.2 to 997.5 K for grunerite). For both compounds, in the temperature overlap region (near 340 K) the results from the two types of calorimetry agreed within the uncertainty limits (< 1%).[1] The deerite sample began to lose weight (~0.1%) when heated to temperatures greater than 500 K, whereas the grunerite sample changed colour on heating above 600 K, and gained between 0.1 and 0.2% in weight (possibly indicating oxidation of some iron(II)).

From the smoothed adiabatic calorimetry measurements the following values were reported for 298.15 K

$$C^{\circ}_{p,\mathrm{m}}((\mathrm{Fe^{2+}_{4.87}Fe^{3+}_{2.76}Mn_{1.07}Mg_{0.15}Ti_{0.15}O_3})(\mathrm{Si_{5.94}Al_{0.03}Ti_{0.03}O_{17}(OH)_5}),\mathrm{cr}) = 786.1\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

$$C^{\circ}_{p,\mathrm{m}}((\mathrm{Fe^{2+}_{5.38}Fe^{3+}_{0.66}Mn_{0.08}Mg_{0.80}Ca_{0.05}})(\mathrm{Si_8O_{22}})\{(\mathrm{OH})_{13}\mathrm{Cl_{0.03}O_{0.60}}\},\mathrm{cr}) = 684.9\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

The authors reported standard deviations of 0.05 and 0.19% for the values of $C^{\circ}_{p,\mathrm{m}}/T$ at 298.15 K for the deerite and grunerite sample, respectively (±0.8 J·K^{-1}·mol^{-1} and ±2.6 J·K^{-1}·mol^{-1}, 2σ).

The entropy contributions between 10 and 298.15 K were also calculated and reported:

$$[\Delta S^{\circ}_{\mathrm{m}}]^{298.15\,\mathrm{K}}_{10\,\mathrm{K}}(\mathrm{Fe^{2+}_{4.87}Fe^{3+}_{2.76}Mn_{1.07}Mg_{0.15}Ti_{0.15}O_3})(\mathrm{Si_{5.94}Al_{0.03}Ti_{0.03}O_{17}(OH)_5}) =$$

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[1] The parameters reported for the authors' equation 1 do not provide a good representation of the DSC deerite values in their Table 3, and are inconsistent with the molar values of $C_{p,m}/R$ values in their Table 5. The reported value of the a_3 parameter may be too negative.

$$791.6\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$[\Delta S^{\circ}_{\text{m}}]^{298.15\,\text{K}}_{10\,\text{K}}(\text{Fe}^{2+}_{5.38}\text{Fe}^{3+}_{0.66}\text{Mn}_{0.08}\text{Mg}_{0.80}\text{Ca}_{0.05})(\text{Si}_8\text{O}_{22})\{(\text{OH})_{13}\text{Cl}_{0.03}\text{O}_{0.60}\} = 698.3\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

From these, the authors estimated entropy values for the end-member compositions. The value

$$S^{\circ}_{\text{m}}(\text{Fe}^{\text{II}}_6\text{Fe}^{\text{III}}_3\text{O}_3(\text{Si}_6\text{O}_{17})(\text{OH})_5) = 801.4\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

was obtained, but the authors indicated that an additional indeterminate configurational entropy contribution (maximum 47.6 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) should be added to this value.

The value

$$S^{\circ}_{\text{m}}(\text{Fe}^{\text{II}}_7(\text{Si}_8\text{O}_{22})(\text{OH})_2) = 748.4\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

requires an additional contribution for magnetic excess entropy at $T < 10$ K, a contribution that the authors concluded could not be reliably evaluated without further measurements.

[1995MIL/YAO]

Millero and coworkers applied the Pitzer ion-interaction model and a specific ion-pairing model to the existing literature data for Fe(II) and Fe(III) in a wide range of electrolytes, ultimately with the aim of determining their speciation in sea water and the solubility of iron-bearing phases in sea water.

The results of this study are considered to be outside the scope of the present review.

[1995PAR/KHO]

This was an important review of the thermodynamic properties of iron species. In the review some experimental results are recorded that have not been published elsewhere. Some of these results are discussed in the present synopsis, however, in all cases much of the experimental detail was not reported.

(1) Heats of solution of FeCl_3(cr) and FeBr_3(cr) in perchloric acid solutions.

These results were attributed to Efimov, Fukaluk and Evdokimov, and cited as Zhur. Fiz. Khim. (in press), but the paper never appeared.

A recalculation of the work of Efimov *et al.* [1995PAR/KHO] indicates that the heat of solution of FeCl_3(cr) extrapolated to infinite dilution is ~ – 158.3 $\text{kJ}\cdot\text{mol}^{-1}$ (– 157 $\text{kJ}\cdot\text{mol}^{-1}$ if the results from the highest-ionic-strength solutions are omitted). The results are inconsistent with the less extensive work of Novikov *et al.* [1984NOV/BEL] (dissolution of FeCl_3(cr) into 0.68 $\text{mol}\cdot\text{kg}^{-1}$ HClO_4(sln)), and the large difference in the heat of dissolution (~ 7%) is difficult to rationalize. However, $\varepsilon_{\text{L}}(\text{Fe}^{3+}, \text{ClO}_4^-)$ (where ε_{L} is defined as $(\partial\varepsilon / \partial T)_p$ [1997GRE/PLY2]) is then calculated to be ~ – 0.3 × 10^{-3} $\text{kg}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, very different from the value 0.56 × 10^{-3} $\text{kg}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ deduced from the heat of dissolution of Fe(cr) in $HClO_4$(sln). Indeed, even the sign is different. The value of $\Delta\varepsilon_L$ as calculated from the dissolution of $FeBr_3$(cr) in aqueous $HClO_4$ solutions is similar to the value of $\Delta\varepsilon_L$ as calculated from the dissolution of $FeCl_3$(cr). The very sparse heat-of-solution data for 298 K in HCl(sln) [1958SHC/VAS2], [1976COR/OUW], [1980STU/FER], on extrapolation to $I = 0$, might appear to lead to a limiting heat of solution value more consistent with Novikov *et al.* [1984NOV/BEL]. However, if the enthalpy of complexation of Fe^{3+} with Cl^- is 20 kJ·mol^{-1}, and $FeCl^{2+}$ is the major species on dissolution in solutions of HCl greater than 0.1 mol·kg^{-1}, then the enthalpy of solution of $FeCl_3$(cr) to form $Fe^{3+} + 3\,Cl^-$ is ~ – 160 kJ·mol^{-1}, in agreement with the value from the Efimov *et al.* measurements in perchlorate medium. The recalculation of the work of Efimov *et al.* [1995PAR/KHO] for the heat of solution of $FeBr_3$(cr) indicates that the value extrapolated to infinite dilution is ~ – 152.2 kJ·mol^{-1}. The uncertainties estimated in the present review are ± 3.0 kJ·mol^{-1}.

Table A-53: Unpublished $FeCl_3$(cr) and $FeBr_3$(cr) heat-of-solution results of Efimov, Furkaluk and Evdokimov, as reported by Parker and Khodakovskii [1995PAR/KHO].

$FeCl_3$/ mol·kg^{-1}	$HClO_4$/ mol·L^{-1}	$\Delta_{sln}H$ / kJ·mol^{-1}	$FeBr_3$/ mol·kg^{-1}	$HClO_4$/ mol·L^{-1}	$\Delta_{sln}H$ / kJ·mol^{-1}
0.00304	1.0257	– 144.879	0.00431	1.0257	– 139.360
0.00381	1.0257	– 144.136	0.00504	1.0257	– 139.301
0.00444	1.0257	– 144.885	0.00841	1.0257	– 139.312
0.00474	1.0257	– 144.743	0.00659	3.110	– 128.230
0.002676	3.08	– 131.630	0.00719	3.110	– 128.246
0.004276	3.08	– 131.981	0.00576	3.903	– 118.813
0.002604	3.903	– 121.763	0.00629	3.903	– 120.018
0.004279	3.903	– 121.273			

(2) Heats of solution of $FeCl_2$(cr) and $FeBr_2$(cr) in perchloric acid solutions.

These results also were attributed (in 1995) to "90EFI/FUR" Efimov, Furkaluk and Evdokimov, and cited as "Zhur. Fiz. Khim. (in press)", but the paper never appeared.

These sparse measurements for dissolution of $FeCl_2$(cr) and $FeBr_2$(cr) are in reasonable agreement with those from other heat-of-solution studies [1952LI/GRE], [1977CER/HEP], [1982COB/MUR].

Table A-54: Unpublished $FeCl_2(cr)$ and $FeBr_2(cr)$ heat-of-solution results of Efimov, Furkaluk and Evdokimov, as reported by Parker and Khodakovskii [1995PAR/KHO].

$FeCl_2$/ $mol\cdot kg^{-1}$	$HClO_4$/ $mol\cdot L^{-1}$	$\Delta_{sln}H$ / $kJ\cdot mol^{-1}$
0.00459	0.001	−82.680
0.00422	0.001	−82.639
0.00550	0.001	−82.502
0.00849	0.001	−81.925

$FeBr_2$/ $mol\cdot kg^{-1}$	$HClO_4$/ $mol\cdot L^{-1}$	$\Delta_{sln}H$ / $kJ\cdot mol^{-1}$
0.004273	0.001	−86.442
0.004958	0.001	−86.803
0.007585	0.001	−86.116
0.004918	0.010	−85.960
0.003777	0.1085	−84.322
0.005925	1.085	−82.611

[1995WEI/OSS]

The initial product from the reaction between Fe(II) and S(−II) ions in aqueous solution was studied using a stopped-flow spectrophotometric technique. The absorbance-time curve showed that an intermediate product formed quickly within the first few seconds of the reaction and that this material subsequently decomposed slowly to other species. From the absorbance spectra of the aqueous solutions of Fe(II) ion alone, S(−II) ion alone and the mixture of Fe(II) and S(−II) ions at various pH values, the absorbance at 500 nm was assigned to be from the initial intermediate product. From the observation of the change in the 500 nm absorbance with time, concentrations of Fe(II) and S(−II), and the ratio of Fe(II) and S(−II), the intermediate product was estimated to be $Fe(HS)^+$ with a stability constant of (4.34 ± 0.15) at 25 °C and $I = 0$. The uncertainty from the assumption of regarding the concentrations as equal to the activities was estimated by calculating the activity coefficients using the Davies equation and had been included in the uncertainty given above. The later process was considered to be $Fe(HS)^+ \rightarrow FeS(s) + H^+$ or $Fe(HS)^+ + HS^- \rightarrow Fe(HS)_2(s)$ and $Fe(HS)_2(s) \rightarrow FeS(s) + H_2S(sln)$, but no experimental evidence for this conclusion was given. The experiments and the analysis were carried out appropriately and the result of this paper can be relied on. Although the reported stability constant for $Fe(HS)^+$ is considered reliable, this review takes this value only for information, as this complex is the intermediate product and not the equilibrium species.

[1995ZIE/JON]

The solubility of crystalline magnetite, Fe_3O_4, was measured from 21 to 288 °C in nine alkaline solutions of sodium phosphate (5.34×10^{-4} to 0.1071 $mol\cdot kg^{-1}$ phosphate; $pH_{25°C} = 10.21$ to 11.34) and three ammonia solutions (7.9×10^{-5} to 7.05×10^{-4} $mol\cdot kg^{-1}$ ammonia; $pH_{25°C} = 9.36$ to 10.14) using a platinum-lined flow-through autoclave. The synthesized solid consisted of 0.6 to 1.2 mm spheres with a density of 4.59 $g\cdot cm^{-3}$. The solid was thoroughly characterized using XRD, SEM, XPS, and Mössbauer and emission spectroscopy. The hydrogen concentration in the feed solution was calculated to be (237 ± 13) $\mu mol \cdot kg^{-1}$. The flow rate of the feed solution was varied to determine the optimum rate to obtain equilibrium. Care was taken to minimize contamination of the solution samples during the analysis for iron by graphite-furnace AA (uncertainly of ± 5%). XPS of the post-experimental solid charge led the authors to conclude the $Fe(OH)_2(s)$ is the solubility determining phase at low temperatures. The authors claim that 14 aqueous iron species were identified from a least-squares analysis of their data, *viz.*: Fe^{2+}; $FeOH^+$; $Fe(OH)_2(aq)$; $Fe(OH)_3^-$; $Fe(OH)_3(aq)$; $Fe(OH)_4^-$; $Fe(OH)(HPO_4)^-$; $Fe(OH)_2(HPO_4)^{2-}$; $Fe(OH)_3(HPO_4)^{2-}$; $Fe(OH)(NH_3)^+$; $Fe(OH)_2(PO_4)^{3-}$; $Fe(OH)_4(HPO_4)^{3-}$; $Fe(OH)_2(H_2PO_4)^-$; and $Fe(OH)_3(H_2PO_4)^-$. Thus, it is believed that significant quantities of Fe(II) and (III) species exist under the prevailing experimental conditions.

This system is highly complex with proposed variations in the oxidation state of iron in solution, a proposed alteration of magnetite to iron(II) hydroxide at low temperatures (transformation predicted to occur at 116 °C at p_{H_2} = 1 atm) and the multiple complexed iron species predicted to exist in solution obtained from data collected over a relatively small range of pH. The suggested discontinuities in the $m_{Fe_{total}}$ *vs.* temperature curves are tenuous given the experimental uncertainties in the data and the system, given the above-mentioned complexities, appears to be over-fitted. The uncertain nature of the $Fe(OH)_2(s)$ deposit precludes any useful thermodynamic data from being extracted in the low-temperature regime (see Section VII.2.18.1).

Regarding the ammonia data, the scatter in Runs 11 and 11a at the higher ammonia concentrations $(7.05 - 7.46) \times 10^{-4}$ $mol \cdot kg^{-1}$ is large (13 – 15% in $m_{Fe_{total}}$) and the statement that amine complexation increases with temperature is erroneous; amine complexes with at least divalent metals are destabilized with increasing temperature.

[1996BAR/PAL]

The acid dissolution equilibrium for jarosite is as follows:

$$KFe_3(SO_4)_2(OH)_6(s) + 6\,H^+ \rightleftharpoons K^+ + 3\,Fe^{3+} + 2\,SO_4^{2-} + 6\,H_2O(l).$$

The authors synthesized jarosite and then characterized their product by XRD, SEM/EDX, TGA, FTIR and by wet chemical analysis, although there was no discussion of particle size. These analyses indicate that the material was crystalline with an approximate formulae, $K_{0.98}(H_3O)_{0.02}Fe_{2.79}(SO_4)_2(OH)_{5.37}\cdot 0.63H_2O$. The dissolution experiments were carried out in batch mode with relatively high solid to liquid ratios, 5 to 30 mg in 20 mL. The experiments were performed in triplicate and extended for up to 176 days with 80 days being considered sufficient to attain equilibrium. Very fine 0.1 μm filters were used to minimize particulate contamination of the sample solutions. There was no mention of how the pH of the solutions was measured or how the pH electrodes were standardized. The authors used a combination of the Davies equation for estimation of activity coefficients and literature values for the complexation (ion pair) constants for $FeSO_4^+$, $FeHSO_4^{2+}$, $Fe(SO_4)_2^-$ and KSO_4^-, as well as reasonable hydrolysis constants for Fe^{3+}.

Based on a preliminary assessment using the Debye-Hückel limiting law and NEA recommended $^*K(HSO_4^-)^o$ and a preliminary value of $\log_{10}{}^*K_{1,1}^o = -2.12$ the derived $\log_{10}{}^*K_s$ values from the 25 °C solubility experiments are shown in the following table, ignoring the molar to molal conversion factors (< 1%).

Run Nr. KJAR-	Reported $\log_{10}{}^*K_s$	Re-evaluated $\log_{10}{}^*K_s$
1.5	– 10.81	– 7.65
2.0	– 11.36	– 9.74
2.3	– 11.03	– 9.79
2.6	– 11.06	– 9.73
3.0	– 10.89	– 8.72

The first and fifth experiments involved the lowest and highest pH solutions indicating that the discrepancies can be traced to the significance of the assumed complexation constants and the limited hydrolysis scheme used in the re-evaluation.

[1996GEN/OLO]

Sulfate-containing green rust 2 was prepared by precipitation from mixing of aqueous solutions of NaOH (at an effective final molarity of 0.20 M if precipitation had not occurred) and $FeCl_2·4H_2O$ (a slight molar excess such that the initial ratio of Fe^{2+} to OH^- was 0.55 to 0.62). Solutions of Na_2SO_4 then were added so that the final sulfate molarity was 0.6 M ($I \approx 2$ m). The cell potential (platinum electrode with a calomel reference electrode) for each solution was measured during the oxidation to form green rusts, but the solution temperature (~25 °C? [1995DRI/REF]) was not reported. The uncertainties in the measured potentials were given as 0.005 V and uncertainties in the pH as ± 0.05 pH–presumably 1σ.

The calculated E^o values for the reaction:

$$6\,Fe(OH)_2(s) + SO_4^{2-} + n\,H_2O(l) \rightleftharpoons (Fe^{III})_2(Fe^{II})_4(OH)_{12}SO_4\cdot nH_2O(s) + 2\,e^- \quad (A.155)$$

and assumed sulfate activities were reported for solutions with initial ratios of Fe^{2+} to OH^- from 0.55 to 0.62.

In a recalculation of the E^o value for the solution with an initial ratio of Fe^{2+} to OH^- of 0.60, SIT activity coefficients (Appendix B) for correction to zero ionic strength were used. A value of -0.543 V *vs.* the standard hydrogen electrode was obtained ($\Delta_r G_m^o$ (A.155) = -104.7 kJ·mol^{-1}). This is in good agreement with the value -0.538 V reported by the authors, and a value of -0.550 V obtained by recalculation of some earlier measurements from their own group.

Further oxidation of the green rust occurred according to

$$(\mathrm{Fe^{III}})_2(\mathrm{Fe^{II}})_4(\mathrm{OH})_{12}\mathrm{SO_4}\cdot n\mathrm{H_2O(s)} \rightleftharpoons 6\,\mathrm{FeOOH}(\gamma) + \mathrm{SO_4^{2-}} + 6\,\mathrm{H^+} + n\,\mathrm{H_2O(l)} + 4\,\mathrm{e^-} \quad (A.156)$$

for solids resulting from initial solution ratios of Fe^{2+} to OH^- between 0.61 and 0.56. The authors reported 0.565 V as the potential (E°) for Reaction (A.156) (initial ratio of Fe^{2+} to OH^- of 0.60), and this was recalculated in the present review to be 0.567 V ($\Delta_r G_m^\circ$ (A.156) = 109.4 kJ·mol^{-1}).

[1996LUT/RIC]

The stoichiometry and stability constants for the (bi)sulfide complexes of Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} have been determined in seawater (I = 0.7 M) and chloride solutions of ionic strength of 0.35 and 0.07 M at 25 °C. To determine the stability constants, the peak potential and peak current for the reaction, $HS^- + Hg(l) \rightarrow HgS(s) + H^+ + 2\,e^-$, at the dropping mercury electrode were monitored in the titration of 1 to 10 μM sulfide solutions of $Na_2S\cdot 9H_2O$ or Na_2S by the metal ion solution. The function, $F_0(X) = 1 + \beta_1[X] + \beta_2[X]^2 + \ldots + \beta_n[X]^n$ where [X] is the analytical concentration of the metal ion, was related to the peak potential (E_p) and peak current (I_p) by $F_0(X) = \text{antilog}\{[0.434nF/RT][(E_p)_s - (E_p)_c] + [\log_{10}(I_p)_s/(I_p)_c]\}$, where $n = -2$, and c indicates complexed sulfide and s indicates free or uncomplexed sulfide. $F_0(X)$, $F_1(X) = [F_0(X) - 1]/[X]$, $F_2(X) = [F_1(X) - \beta_1]/[X]$, … , and $F_n(X) = [F_{n-1}(X) - \beta_{n-1}]/[X]$ were plotted *vs.* metal ion concentration to determine β_n values. For Fe(II), $\log_{10}\beta_n$ values are obtained to be (5.07 ± 0.09) ($FeSH^+$), (10.07 ± 0.04) ($Fe_2(SH)^{3+}$) and (16.15 ± 0.06) ($Fe_3(SH)^{5+}$) in seawater (I = 0.7 M), (5.07 ± 0.16) ($FeSH^+$), (9.71 ± 0.35) ($Fe_2(SH)^{3+}$) and (16.03 ± 0.11) ($Fe_3(SH)^{5+}$) in I = 0.35 M, and (5.17 ± 0.01) ($FeSH^+$), (10.17 ± 0.15) ($Fe_2(SH)^{3+}$) and (16.82 ± 0.21) ($Fe_3(SH)^{5+}$) in I = 0.07 M. From the E_p *vs.* pH plots obtained by the acid-base titrations of 10μM of sulfide and metal in 0.545 M NaCl, the complexes are claimed to be bisulfide (HS^-) complexes. All the species such as HS^-, $H_2S(aq)$ and sulfides complexed with metal ion were assumed to be similarly electroactive and labile and to behave similarly at and near the mercury electrode; the difference in the speciation changes the peak potential. However, the relation of the electrode reaction or electrode response to the equilibrium concentrations of the sulfide species, such as HS^-, $H_2S(aq)$ and sulfides complexed with metal ion, is uncertain. Also in the data processing, the differences between the analytical concentrations and the equilibrium concentrations are not well considered. If we take the set of the stability constants reported, the speciation calculation with these values indicates that $Fe_3(SH)^{5+}$ always predominates as the complexed species in the metal ion concentration range used in the experiment (2×10^{-6} to 1.2×10^{-5} M). The contributions of $FeSH^+$ and $Fe_2(SH)^{3+}$ are not large enough for their stability constants to be reliably determined. Thus, this review does not accept the results in this paper.

[1996STO/GLO]

Previous work had shown that the decomposition of wüstite to Fe_3O_4(cr) and Fe(cr) under controlled conditions is a two-step process, with initial precipitation of Fe_3O_4(cr) and a concomitant shift in wüstite composition to about $Fe_{0.99}O$. A mixture of metastable, near-stoichiometric wüstite ($Fe_{0.990\pm0.005}O$), Fe_3O_4(cr) and Fe(cr) was obtained by controlled, partial decomposition of a homogeneous wüstite precursor with the composition $Fe_{0.9374}O$. This was achieved *in situ* in the calorimeter by gradual, stepwise heating to 535 K while monitoring the heat flow due to the decomposition reaction; further heating at somewhat higher temperatures leads to the equilibrium assemblage of Fe(cr) and Fe_3O_4(cr). Analysis by neutron diffraction and magnetic measurements yielded the mole fractions 0.915 $Fe_{0.990\pm0.005}O$, 0.078 Fe_3O_4(cr), and 0.007 Fe(cr). Twenty-one $C^{\circ}_{p,\mathrm{m}}$ measurements are presented for the as-quenched $Fe_{0.9374}O$ at 313.02 to 471.01 K, with 267 measurements for the three-phase assemblage between 11.441 and 444.66 K. Heat capacities and derived thermodynamic values for $Fe_{0.99}O$ at rounded temperatures up to 450 K were extracted by correcting for the known properties of Fe_3O_4(cr) and Fe(cr). The tabulated values also include:

$$C^{\circ}_{p,\mathrm{m}}\ (\mathrm{Fe_{0.99}O, cr, 298.15\ K}) = 47.43\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

$$S^{\circ}_{\mathrm{m}}\ (\mathrm{Fe_{0.99}O, cr, 298.15\ K}) = 60.45\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}.$$

No uncertainty is given, but the authors state that there is a relatively large uncertainty in the composition, which was estimated from the unit cell dimension, a_0 = (4.326 ± 0.002) Å, compared with (4.304 ± 0.002) Å for the homogeneous precursor. Rather, they conclude that the value of S°_{m} (FeO, cr, 298.15 K) = (61 ± 1) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, calculated in a critical review by Grønvold *et al.* [1993GRO/STO], "remains a reasonable estimate" for the hypothetical, exactly stoichiometric composition.

Special attention is paid in the discussion to the Néel transition of wüstite, which is particularly sharp for $Fe_{0.99}O$, showing that "the magnetic order-disorder transition in $Fe_{0.99}O$ is much more cooperative than earlier observed for wüstite with composition further from stoichiometry [1951TOD/BON], [1993GRO/STO].". The Verwey transition of the precipitated Fe_3O_4(cr) is also discussed. A small additional C_p anomaly near 150 K is tentatively ascribed to wüstite.

[1997ARU/KAT]

Heat-capacity measurements for $FeBr_2$(cr) were carried between 1 and 20 K. The main purpose of the study was to investigate the dependence of the temperature and shape of the heat-capacity anomaly as a function of the magnetic field. However, the authors' Figure 1 shows $C_{p,\,\mathrm{mag}}\ T^{-1}$ as a function of T. Digitization and integration of the curve indicates that the contribution to the molar entropy from the magnetic anomaly is (5.5 ± 0.5) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$. Because only the calculated magnetic contributions as calculated by the authors (not their experimental specific heats) are reported, estimation of the magnetic contribution above 17 K (if any) leads to the rather large uncertainty.

[1997RIC2]

A kinetic study of the reaction FeS(mackinawite) + H_2S(aq) → FeS_2(pyrite) + H_2(g) was carried out, and the rate for temperatures between 25 and 125 °C were described by the equation $d(FeS_2)/dt = k(FeS)[H_2S(aq)]$ where the second-order rate constant k varied between 1.03×10^{-3} $L\cdot mol^{-1}\cdot s^{-1}$ at 25 °C and 3.20×10^{-3} $L\cdot mol^{-1}\cdot s^{-1}$ at 125 °C. The reaction was surprisingly fast at ambient temperature with up to 50 % reaction being completed within one day. The mechanism was suggested [1997RIC/LUT] to be the process using a 'H_2S-pathway' where H_2S acted as an oxidizing agent. Later, Benning *et al.* [2000BEN/WIL] showed in their careful experimental work that mackinawite is stable for up to 4 months as long as reducing conditions are maintained, and claimed that some degree of oxidation is required for mackinawite to react to form pyrite. The freeze-dried mackinawite showed a faster rate of conversion to pyrite, indicating that despite the efforts to avoid oxidation in the freeze-drying procedure, the freeze-dried material such as in [1997RIC2] must have been partially oxidized.

[1997RIC/LUT]

See [1997RIC2].

[1997TAY/OWE]

The maghemite was prepared by heating magnetite powder ("Mapico Black", nominally Fe_3O_4) in air at 250 °C for 2 hours. The maghemite was converted to hematite by further heating in air at 500 °C for 10 days. The specific surface areas of the three powders were (8.8 ± 0.4) $m^2\cdot g^{-1}$ for magnetite, (8.64 ± 0.09) $m^2\cdot g^{-1}$ for maghemite, and (6.0 ± 0.8) $m^2\cdot g^{-1}$ for hematite. XRD showed a common magnetite impurity and the maghemite, γ-Fe_2O_3, was considered as being a persistent, metastable intermediate in the reaction:

$$4\,Fe_3O_4(cr) + O_2(g) \rightarrow 6\,\gamma\text{-}Fe_2O_3 \rightarrow 6\,\alpha\text{-}Fe_2O_3$$

Maghemite is stabilized by the presence of phosphate and silica in solution, apparently due to surface complexation. As an aside by the reviewer, experience has shown that maghemite is a common impurity in magnetite prepared at or near room temperature; a phenomenon that has gone largely undetected. As expected the Fe_3O_4/γ-Fe_2O_3 couple is less reducing than the corresponding Fe_3O_4/α-Fe_2O_3 couple.

The solubilities of α- and γ-Fe_2O_3 were measured in individual batch experiments at 25 °C in four dilute HNO_3 solutions (initial concentrations 0.0098 to 0.0492 M) with no colloids being detected in the equilibrated solutions. The pH was calculated from mass balance. Equilibration times were up to 5736 hours for low solid to solution ratios (0.02 g/10 mL) and 4512 hours for 0.4 g/10 mL. Equilibrium was not reached in the former case, although the authors extrapolated their time-dependent data to infinite time using an undisclosed kinetic equation. The Davies equation was used to calculate activity coefficients and the resulting ${}^{*}K_{s,0}$ values, corrected for the contribution of ${}^{*}K^{\circ}_{1,1}$ taken from [1955MIL/VOS], showed an ionic-strength dependence that could not be explained.

The dissolution rates of hematite and maghemite are illustrated in Figure A-49, for the experiments at the 0.02 g/10 mL solid to liquid ratio.

Figure A-49: The change in the molality of iron(III) with time for the two experiments conducted at a lower solid to liquid ratio at 25 °C.

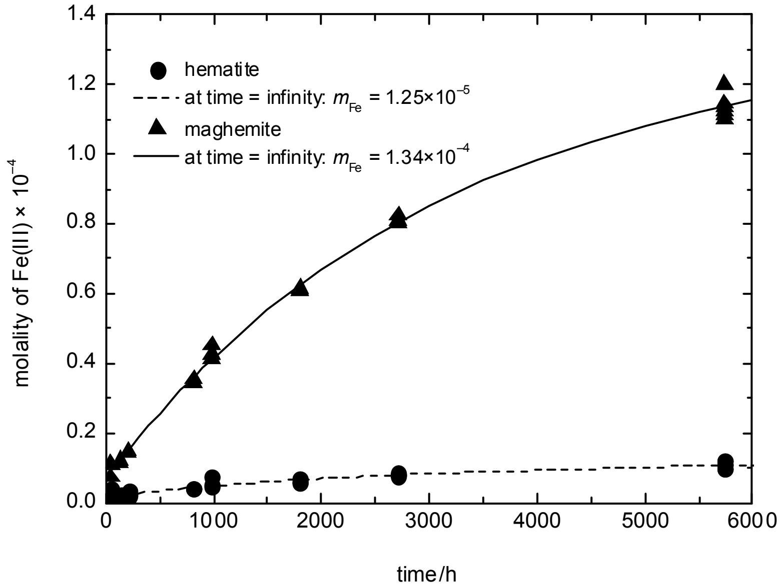


Figure A-49 shows the time dependence of the solubility for both phases at the lowest mass of solid to volume of liquid ratio, where the curves are simply the results of third-order polynomial fits. Table A-55 summarizes the experimental results.

Table A-55: Summary of recalculated solubility results showing only the equilibrated converted molalities of initial nitric acid and iron(III).

g Fe_2O_3/mL	$m_{\text{initial}}(HNO_3)$/mol·dm^{-3}	m_{Fe}(hematite)/mol·dm^{-3}	m_{Fe}(maghemite)/mol·dm^{-3}
0.002	0.0292	1.25×10^{-4} (a)	1.34×10^{-3} (a)
0.04	0.00980	1.10×10^{-5} (b)	1.42×10^{-4} (c)
0.04	0.0196	4.41×10^{-5} (b)	7.70×10^{-4} (c)
0.04	0.0476	5.60×10^{-4} (b)	3.98×10^{-3} (c)

(a) obtained by extrapolation to infinite time (Fig. 1); (b) after 4512 hours; (c) after 1488 hours.

The dissolution equilibrium can be written as:

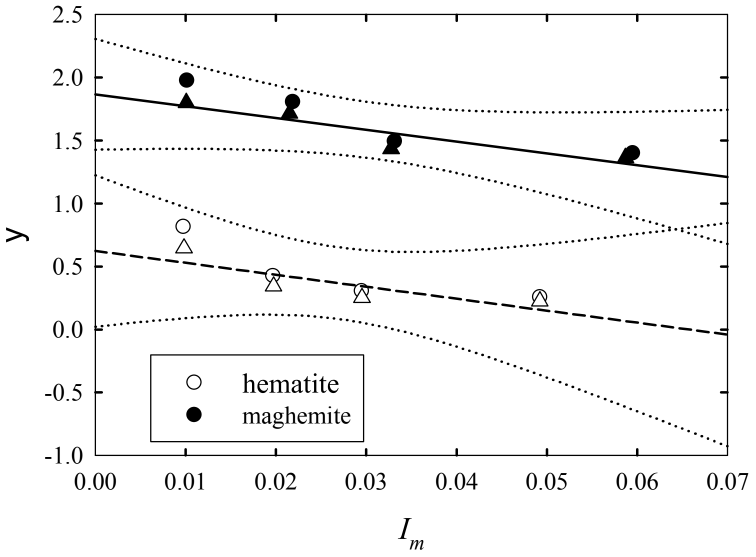
$$\tfrac{1}{2}\,Fe_2O_3(s) + 3\,H^+ \rightleftharpoons Fe^{3+} + 1\tfrac{1}{2}\,H_2O(l) \qquad (A.157)$$

for which:

$$\log_{10}{}^{*}K^{o}_{s,0} - 6D + 1\tfrac{1}{2}\log_{10}a_w = \log_{10}{}^{*}K^{o}_{s,0} - \Delta\varepsilon I_m \qquad (A.158)$$

Plots of the LHS of Equation (A.158) (y) *vs.* I_m are shown in Figure A-50.

Figure A-50: Plot of the LHS of Eq. (A.158) *vs.* ionic strength where the circles represent results for hematite (open) and maghemite (filled) with allowance for the first hydrolysis constant for Fe^{3+} whereas the triangles represent the uncorrected results. The dotted curves correspond to the 95% confidence limits.



The $\log_{10}{}^{*}K^{o}_{s,0}$ values for hematite and maghemite estimated from the intercepts of the linear regressions in Figure A-50 are (0.79 ± 0.52) (3σ) and (2.06 ± 0.37) (3σ), respectively, with no correction for the hydrolysis equilibria and where the uncertainties are simply the standard deviations from the four individual measurements. Using the expression describing $\log_{10}{}^{*}K_{1,1}$ as a function of I_m (see Section VII.1.3.1), the corresponding corrected $\log_{10}{}^{*}K^{o}_{s,0}$ values for hematite and maghemite are (0.62 ± 0.42) (3σ) and (1.87 ± 0.30) (3σ), respectively. This implies the following Gibbs energy of transformation:

$$\Delta_{\mathrm{trs}}G_{\mathrm{m}}^{\mathrm{o}}\ (\mathrm{Fe_2O_3},\ \gamma\rightarrow\alpha,\ 298.15\ \mathrm{K}) = -(13.0 \pm 1.3)\ \mathrm{kJ\cdot mol^{-1}}.$$

A significant residual ionic-strength dependence of K_s was found, similar to that observed for goethite, α-FeOOH, by Hsu and Marion [1985HSU/MAR]. The reason for this remains unclear, and it precludes accurate calculation of Gibbs energies for the individual oxides.

Note that the low ionic strength range of these measurements in nitrate media preclude any meaningful interpretation of the slopes of the lines in Figure A-50 in terms of $\Delta\varepsilon$ that yielded for example, $-(9.5 \pm 4.6)$ and $-(9.4 \pm 2.9)$ kg·mol^{-1}, respectively.

[1997THE/LUT]

Solutions of $\mathrm{Fe(NH_4)_2(SO_4)_2\cdot 6H_2O}$ and $\mathrm{Na_2S\cdot 9H_2O}$ were titrimetrically combined with seawater and the peak current near -1.1 V in square wave voltammogram was measured as a function of an activity corrected ion-activity product (IAP). The computer program MINEQL [1976WES/ZAC] was used to calculate the activity coefficients for $\mathrm{Fe^{2+}}$ and $\mathrm{HS^-}$ in seawater matrix at the appropriate pH. The current of the peak was not measurable, or was negligible, until the IAP exceeds the solubility product, $K_s = (\gamma_{\mathrm{Fe^{2+}}} c_{\mathrm{Fe^{2+}}}\ \gamma_{\mathrm{HS^-}} c_{\mathrm{HS^-}})/a_{\mathrm{H^+}}$, of FeS(nanoparticulate mackinawite). Above K_s, the current linearly increased with the IAP suggesting a 1:1 stoichiometry for this electroactive species. This peak appeared in the voltammogram within 5 seconds of addition of titrant, and the current did not change on repeated measurements. From the intersection of the zero current points with those that increased linearly, K_s was calculated to be $10^{-2.94\pm0.10}$. The authors claimed that this current increase with the IAP is due to the formation of a soluble FeS(aq) species, which may be some oligomeric/polymeric cluster. However, if FeS(aq) is in equilibrium with other species in solution and with the precipitated FeS(mackinawite), the concentration of FeS(aq) should increase with IAP below K_s and reach a constant above K_s since the reaction, FeS(mackinawite) $\rightleftharpoons$ FeS(aq), does not depend on IAP. Probably, this peak is due to the nanoparticulate FeS(mackinawite) or to the excess $\mathrm{HS^-}$ if the added analytical concentration of Fe(II) was constant. Therefore, this review considers that the speciation of aqueous soluble cluster, FeS(aq), is not adequately established. However, the value of K_s can be accepted since the intersection corresponds to the solubility product. This review takes $\log_{10} K_s = -(2.9 \pm 0.3)$ at $I = 0$ and 298 K considering the uncertainty in the measurement, activity correction, ionic strength and temperature, *etc*.

[1997ZHA]

The work from this thesis was used directly in the subsequent paper of Zhao and Pan [2001ZHA/PAN]. Details are discussed in the Appendix A entry for [2001ZHA/PAN].

[1998DAV/BUF]

Normal pulse polarography and cyclic voltammetry were applied to the samples of naturally anoxic waters containing Fe(II) and S(−II) and their synthetic analogues. Differential-pulse polarography and dc-sampled polarography scans indicated that the signal at ~ -0.6 V (*vs*. the saturated calomel electrode) is the result of the reduction of HgS to Hg and S($-$II), where HgS is formed by the spontaneous reaction of mercury with labile S($-$II) species (H_2S(aq), HS^-, S^{2-}) at potentials more positive than ~ -0.6 V. Fe(II), predominantly present as the aquo ion is reduced at ~ -1.35 V. The signal at ~ $-$ 1.1 V was tentatively ascribed to reduction of a soluble iron sulfide species. This signal was only observed when the concentrations of Fe(II) and S($-$II) were sufficiently high for the ion activity product of FeS to approach the laboratory estimate of the solubility product for amorphous FeS, and increased concomitantly with the Fe(II) and S($-$ II) concentrations. The effect of the initial potential on these signals was examined. When an initial potential more positive than ~-0.6 V was used, the polarographic signal reflected reduction of iron sulfide species formed at the electrode surface due to the release of sulfide from the reduction. If the initial potential was more negative than ~ -0.6 V, the surface species could not form *in situ*, but there was a contribution to the polarographic signal from the adsorption of a soluble iron sulfide species. The soluble species formed slowly (minutes-hours) in solution, suggesting that its stoichiometry was not simple, and may possibly have been polynuclear. However, the species must have been small, as it diffused as rapidly as Fe^{2+}. Since the surface concentration of the adsorbed species was independent of initial potential, this species was considered to be neutral. The result supports the existence of 'soluble' polynuclear neutral species such as Fe_nS_n or $Fe_n(HS)_{2n}$. However, it was described that this signal was only observed when the activities of Fe(II) and S(–II) were sufficiently higher than the solubility product of amorphous FeS. If the proposed species are truly 'soluble' neutral complex species, the concentration of the complex should increase even below the concentrations corresponding to the solubility product and the signal should be observed. This reviewer considers that the paper is of value for reference purposes, but still believes that the characterization of the species is not completely clarified.

[1998DIA]

This is a very useful, comprehensive review of heat capacity, enthalpy of transformation, and solubility data, including particle-size effects, on maghemite (γ-Fe_2O_3). It predates the high-precision studies of Majzlan *et al.* ([2003MAJ/GRE], [2003MAJ/LAN]). Based on detailed re-evaluation of original data, this paper recommends the value $\Delta_f H^\circ_m$ (Fe_2O_3, γ, 298.15 K) = $-(805.8 \pm 5.7)$ kJ·mol^{-1} for both ordered and disordered maghemite, and the entropy difference between the two variants at 298.15 K was estimated to be 4 J^{-1}·K^{-1}·mol^{-1}. The specific treatment of individual, key papers is discussed in the corresponding synopses ([1937FRI/ZER], [1967FER], [1975KOR/FAD], [1976DEM], [1988SAD/LIN]).

[1998DIA2]

This review of the thermodynamic properties of lepidocrocite resembles the same author's work on goethite [1994DIA/KHO] and maghemite [1998DIA]. The evaluation was hampered by the scarcity of experimental data. The recommended value of

$\Delta_f H^o_m$ (FeOOH, γ, 298.15 K) = $-(556.4 \pm 2.0)$ $kJ \cdot mol^{-1}$ is derived from a single heat-of-dissolution measurement on natural lepidocrocite from [1937FRI/ZER]; the uncertainty limit is over-optimistic. No reliable conclusions could be drawn from solubility [1973HAS/MIS], potential [1968DOY] or solid-state decomposition measurements [1975KOR/FAD].

Seven $C^o_{p,m}$ values for lepidocrocite at 336 to 490 K are reproduced from Korobeinikova (Ph.D. Thesis, Moscow State University, 1975). The specimen, initial composition $FeOOH \cdot 0.215H_2O$, was dried to constant weight at 443 K prior to the $C^o_{p,m}$ measurements; the onset of FeOOH dehydration to Fe_2O_3 was observed at 490 K.

This review has been largely superseded by the recent detailed experimental studies of [2003MAJ/GRE], [2003MAJ/LAN], and [2007MAJ/MAZ].

[1998JAM/DUT]

This is a detailed review (314 references) of the occurrence, crystal structure, characterization, synthesis, composition, sorption properties, and transformation reactions of ferrihydrite. There is some discussion of TG and DTA studies of the conversion of ferrihydrite to more stable, crystalline phases, and a useful schematic showing the major synthetic and interconversion reactions among the main iron oxide and oxyhydroxide phases (derived from [1991SCH/COR]). While the review is thus a valuable source of general information on ferrihydrite, it does not include any explicit discussion of thermodynamic stability, and there is only a passing mention of the solubility product of "ferric hydroxide".

[1998LAB/NAV]

Enthalpy relationships between synthetic iron oxides and oxyhydroxides (goethite, akaganéite, lepidocrocite, hematite, maghemite, and magnetite) were measured by transposed temperature-drop (TTD) calorimetry, and by high-temperature drop-solution (DS) calorimetry using molten sodium molybdate[1] as a solvent, all at a final temperature of 979 K. The data treatment includes rather large and uncertain corrections for surface area and excess water. A number of minor inconsistencies between the tables, figures, and text make this paper difficult to evaluate. The study is largely superseded by more refined measurements, including surface-area-dependent studies, from the same laboratory: [2003MAJ/GRE], [2005MAZ/NAV], [2006MAZ/DEO], [2007MAJ/MAZ]. For the purposes of the current review, this paper is treated as a preliminary study and the results are not used in the final assessment, but uncorrected data are summarized below. The values ΔH_{TTD} and ΔH_{DS} are the measured enthalpy changes by the TTD and DS methods, respectively, for an initial state of the indicated solid substance at 298 K and a final state of either α-Fe_2O_3 (TTD method) or Fe_2O_3 dissolved in a sodium

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[1] The sodium molybdate composition was not specified by [1998LAB/NAV]; later work from the same laboratory used the composition $3Na_2O \cdot 4MoO_3$ [2005MAZ/NAV].

molybdate melt (DS method), plus the stoichiometric quantity of $H_2O(g)$, at 979 K. A flow of oxygen through the calorimeter assured that iron was fully oxidized to, or maintained in, the iron(III) state.

Table A-56: Summary of transposed temperature-drop (TTD) and high-temperature drop-solution (DS) calorimetric data for iron oxides and hydroxides from [1998LAB/NAV].

Specimen	Surface area/$m^2 \cdot g^{-1}$	ΔH_{TTD}/kJ·mol^{-1}	ΔH_{DS}/kJ·mol^{-1}
α-FeOOH·0.09H_2O	41.2	110.12 ± 0.4 (8)[d]	105.87 ± 1.3 (8)
α-FeOOH·0.08H_2O	39.2	106.56 ± 0.7 (8)	106.68 ± 1.2 (8)
β-FeOOH·0.13H_2O [a]	40.2	108.82 ± 0.9 (9)	105.03 ± 3.1 (7)
γ-FeOOH·0.10H_2O	35.2	97.03 ± 0.5 (8)	95.04 ± 0.7 (8)
α-Fe_2O_3	1.0	100.0 ± 1.1 (9)	93.56 ± 2.9 (9)
γ-Fe_2O_3·0.01H_2O [b]	24.4	90.26 ± 0.8 (9)	84.86 ± 2.2 (8)
γ-Fe_2O_3·0.01H_2O [c]	27.6	86.90 ± 1.3 (8)	83.06 ± 0.8 (8)
Fe_3O_4	27.6	25.10 ± 0.5 (8)	17.11 ± 2.9 (8)

a The akaganéite (β-FeOOH) specimen contained 0.032 moles Cl per mole Fe.

b Disordered (cubic) form.

c Ordered (tetragonal) form; the specimen contained 3 mol% Fe_3O_4; tabulated data are uncorrected.

d The figure in parentheses is the number of tests.

[1998MOU/SEW]

The solubility of troilite (end member of pyrrhotite) was measured as a function of pH and of $\log_{10} m_{H_2S_{total}}$. FeS(s) was prepared by sealing elemental Fe and S in large volume glass ampoules. These were evacuated, filled with N_2 and placed in an 800 °C oven for 6 hours. XRD analysis showed the characteristic peaks of troilite. FeS solubility measurements were carried out using a flow-through column contained in a heated oven (22 °C). Reduced sulfur was added by bubbling the solution with a N_2-H_2S gas mixture, the composition of which was determined by the concentration of reduced sulfur. Solution pH was adjusted by addition of NaOH or $HClO_4$. After the solution was forced through the column and collected in the effluent syringe, its total sulfide concentration ($m_{S_{total}}$) concentration and pH were measured. This was followed by acidification and bubbling with nitrogen and analysis for total Fe by flame atomic absorption. To check the dissolution equilibrium, the flow rate was varied between 50 and 500 mL·h^{-1}. Iron concentrations decreased to a relatively constant value of about 70 – 80 µg·kg^{-1} and were not dependent on the flow rate. Further experiments were carried out at relatively high flow rates (>200 mL·h^{-1}). The logarithm of the solubility of iron ($m_{Fe_{total}}$) between pH 3 and 5.5 decreased with pH with a slope of – 1, and did not depend on $\log_{10} m_{S_{total}}$ ($\log_{10} m_{S_{total}}$: –2 to – 1). From these slopes, the solution species was assigned as $FeHS^+$, assuming the species to be monomeric. The slope of -1 for $\log_{10} m_{\mathrm{Fe_{total}}}$ *vs.* pH is different from the slope of -2 observed for mackinawite by [1999DAV/PHI] and [2006RIC]. Although the solid phase is confirmed to be troilite, the solubility determining solid is considered to be mackinawite in this experiment. Since mackinawite is known to be in the form of nanoparticles ([1989RIC], [1997THE/LUT], [2000BEN/WIL], [2005LUT/RIC], [2005RIC/MOR], [2006OHF/RIC]), the separation between solid and solution in this experiment is considered to have been inadequate. The effect of flow rate seems strange to the reviewer, as the equilibrium was reached at higher flow rates (shorter contact time). This review does not accept the speciation assigned in the paper.

[1999DAV/PHI]

The solubility of Fe(II) in 0.1 M $NaClO_4$ equilibrated at (20.0 ± 0.1) °C with various partial pressures of H_2S ($p_{\mathrm{H_2S}}$ = 0.1, 0.001, 0.0001, 0.00001 MPa) was measured in the pH range 3.1 – 7.9. To 75 mL of a solution of 0.1 M $NaClO_4$, an aliquot of deoxygenated 0.1 M NaOH was added to adjust the pH to the desired range. After degassing, 0.5 mL of a solution of deoxygenated 0.1 M $Fe(ClO_4)_2$ was added. After further degassing, the inflowing gas was switched from nitrogen to the appropriate H_2S/N_2 mixture. Equilibrium was established within 1 – 6 hours when amorphous FeS was the solid phase, and the Fe(II) in the solution was analyzed colourimetrically. Values obtained for $\log_{10} c_{\mathrm{Fe(II)_{total}}}$ were plotted against pH at various $p_{\mathrm{H_2S}}$. At each partial pressure, $\log_{10} c_{\mathrm{Fe(II)_{total}}}$ decreased with pH with a slope of -2, then reached a constant value in a region of higher pH (pH 5 to 9). The pH-dependent region (with a slope of -2) extended to the higher pH values with a decrease in the partial pressure, suggesting that the constant value at higher pH depends on $[H_2S(aq)]$. The results were explained by the reactions $FeS(am) + H^+ \rightleftharpoons Fe^{2+} + HS^-$ where $\log_{10} {}^*K_s = -(3.00 \pm 0.12)$ (2σ), and $Fe^{2+} + 2\,HS^- \rightleftharpoons Fe(HS)_2(aq)$ where $\log_{10} \beta_2 = (6.45 \pm 0.12)$ (2σ). The first dissociation constant of H_2S was measured in 0.1 M $NaClO_4$ and a value of $-(7.011 \pm 0.019)$ was obtained for $\log_{10} {}^*K_1$. Thus, $\log_{10} {}^*K_s$ corresponds to $\log_{10} {}^*K = 4.01$ for $FeS(am) + 2\,H^+ \rightleftharpoons Fe^{2+} + H_2S(aq)$. Any soluble species of the form $Fe_x(HS)_{2x}$ where $x \geq 1$, was claimed to fit the data equally well. In the analysis, $[H_2S(aq)]$ was calculated using the tabulated fugacity and the activity coefficients (in $I \approx 0.1$ M solution) of the solution species from MINTEQ. Therefore, the constants are the values at $I = 0$. The uncertainties from the activity corrections and the estimation of $[H_2S(aq)]$ from the partial pressure of H_2S are properly considered, and are well within the uncertainties given by the authors. The iron sulfide which was referred to as amorphous FeS is considered to be nanoparticulate mackinawite. Although this study seems to have been carried out carefully, the result that $c_{\mathrm{Fe(II)_{total}}}$ in the higher pH region was independent of pH but dependent on $p_{\mathrm{H_2S}}$ is different from what was found by Rickard [2006RIC] where $c_{\mathrm{Fe(II)_{total}}}$ in the alkaline region was independent of $p_{\mathrm{H_2S}}$. Rickard [2006RIC] claimed the reaction to be $FeS(mackinawite) \rightleftharpoons FeS(cluster)$ where FeS(cluster) means a quantum-sized particle or complex which contains a discrete number of atoms in a molecule or ion that is small enough to behave as a dissolved species. The experimental differences in these studies are the starting materials ($Fe(ClO_4)_2$ or $Fe(NH_4)_2(SO_4)_2{\cdot}H_2O$), media ($NaClO_4$ or NaCl) and the way equilibrium was reached (FeS(mackinawite) was precipitated and its solubility measured or FeS(mackinawite) was precipitated by adding OH^- to an acidic solution of Fe(II) and S(−II)). In these studies, the speciation in the solution phase and the surface or ageing property of the FeS(mackinawite) still remain unclear. So far, the reviewer cannot discern a reason for the difference in the experimental results in the higher pH region. Moreover, the formation of the 2:1 complex $Fe(HS)_2(aq)$ without formation of a 1:1 complex $Fe(HS)^+$ needs some molecular or structural explanation. Thus, this review accepts the solubility constant as $\log_{10}{}^*K = (4.0 \pm 0.3)$ for FeS(am) + $2H^+ \rightleftharpoons Fe^{2+}$ + $H_2S(aq)$ but suspends judgment on the speciation in higher pH region and the relevant stability constant.

[1999DIA/SCH]

The solubility of synthetic hematite (α-Fe_2O_3 in 2-4 μm size range) was measured from 60 to 300 (±1) °C ($0.007 \le m_{NaOH} \le 2.0$) at p_{sat} (3 to 13 bar O_2 at 25 °C) and the results of these experiments were interpreted in terms of the equilibrium: $\tfrac{1}{2}Fe_2O_3(cr)$ + $2\tfrac{1}{2}H_2O(l) \rightleftharpoons Fe(OH)_4^-$ + H^+, *i.e.*, the tetrahydroxoiron(III) species was assumed to be the dominant form of iron in solution. The oxide was well characterized by XRD, BET, SEM (*ca.*, 1 μm spheres) and Mössbauer spectroscopy. Solution samples were double filtered using 2 and 0.1 μm filters prior to acidification to avoid the common problem of colloid entrainment. Experiments were sampled for up to 82 days and one experiment at 60 °C was reversed to approach equilibrium from supersaturation in order to verify that equilibrium had been attained. Analytical uncertainty associated with the iron(II) analyses was given as ±15%.

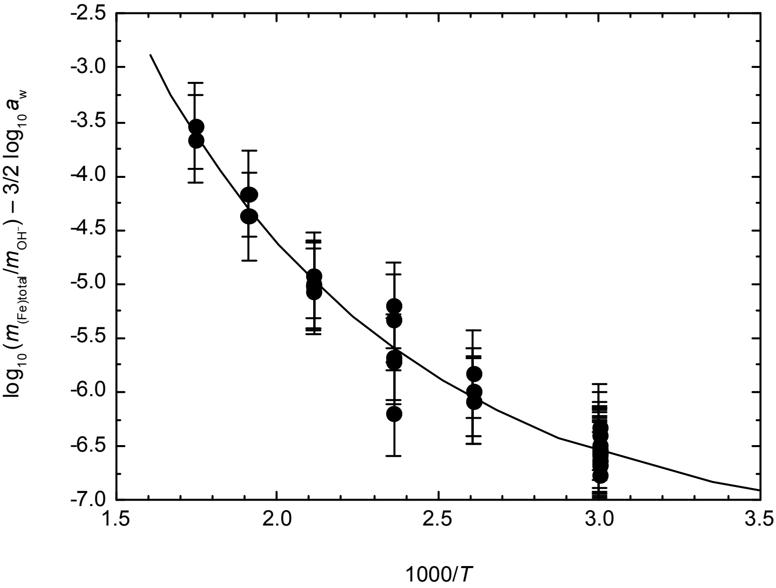
The dissolution equilibrium can be written in basic form: $\tfrac{1}{2}Fe_2O_3(cr)$ + $1\tfrac{1}{2}H_2O(l) + OH^- \rightleftharpoons Fe(OH)_4^-$, which eliminates the Debye-Hückel term in fitting the solubility constants. In order to extrapolate these data, which were generally obtained at relatively low ionic strengths (≤ 0.2001 $mol{\cdot}kg^{-1}$ (H_2O)), to 25 °C this form of the equilibrium should provide the most conservative (more linear) approach. Taking the activities of water for NaCl solution from Archer [1992ARC] and assuming that only $Fe(OH)_4^-$ was produced led to Figure A-51.

A constant uncertainty of ±0.4 log units was assigned to each data point giving rise to the following best-fit equation:

$$\log_{10}\beta^{\circ}_{s,4}(T) = -(14.81 \pm 2.26) + (878.0 \pm 464.0)(T/K)^{-1} + (1.688 \pm 0.267) \times 10^{-2}(T/K).$$

The scatter in the data at each temperature exceeds any isothermal trends with ionic strength due to the assumptions made concerning ignoring the differences in the activity coefficients of hydroxide ion and $Fe(OH)_4^-$. The degree of curvature in this plot is surprising when compared to analogous plots for the corresponding aluminium system considering the isocoulombic nature of the equilibrium. Nevertheless, the fitting equation used (see figure caption) gives a 25 °C value for $\log_{10} \beta^{\circ}_{s,4}$ of $-(6.8 \pm 2.9)$, which would correspond to a value of $\log_{10} {}^{*}\beta^{\circ}_{s,4}$ of $-(20.8 \pm 2.9)$.

Figure A-51: Solubility of crystalline hematite as a function of reciprocal temperature (kelvin).



[1999FAR/BER]

The conditional stability constants of sulfide complexes of Ag^+, Cd^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+} and Al^{3+} were determined in pH 8 seawater at salinities (the dissolved salt content of a body of water, expressed as parts per thousand by weight) of 35, 21 and 10.5 by monitoring free sulfide concentrations by flow-analysis, with detection by cathodic-stripping voltammetry. Seawater used in the experiments was obtained from the North Sea and UV-irradiated for 3 hours to eliminate organic matter that could interfere with the metal-sulfide complexation measurements. This water was diluted with UV-irradiated Milli-Q water to obtain lower salinities. In the case of Fe^{2+}, 200 nM of sulfide was titrated with Fe^{2+}, where Fe^{2+} was prepared from Fe(III) in an aqueous solution of hydroxylammonium hydrochloride at a concentration 10 times higher than that of iron. The addition of 100 µL of the TRIS buffer (1 M tris(hydroxymethyl)methylamine buffer in 0.5 M HCl) in 10 mL of seawater served to maintain the pH at 8. With a deposition time of 15 s and deposition potential of -0.2 V, the -0.3 to -0.8 V range was scanned. The height of the peak (a mercury reduction peak) at around -0.56 V decreased with the addition of Fe^{2+}. In each scan, the peak heights of 4 titration points (data points) were obtained and the stability constant of the iron sulfide complex was calculated by assuming that the peak height was directly dependent on the concentration of free sulfide. It was assumed that the metal-sulfide species were of the bisulfide-type and the $\log_{10} K$ values for $Fe^{2+} + HS^- \rightleftharpoons Fe(HS)^+$ obtained were (6.07 ± 0.06) at a salinity of 35, (5.97 ± 0.04) at a salinity of 21, and (5.86 ± 0.02) at a salinity of 10.5. In this paper, no supporting evidence for the speciation, such as the pH dependence of the peak, was given. The logarithm of the solubility of FeS(mackinawite) is reported to decrease with pH with a slope of -2, and then reach a constant value ([1999DAV/PHI], [2006RIC]). If we accept the speciation $Fe(HS)^+$, there should be a region where the logarithm of the solubility of FeS(mk) decreases with a slope of -1. Therefore, although some reaction is proceeding under this experimental condition, this review does not accept the speciation and the constants reported in this paper.

[1999INA/FUN]

The authors used EXAFS to determine the relative mole fractions of $Fe(H_2O)_6^{3+}$ and $FeCl(H_2O)_5^{2+}$ in aqueous acid solutions ($HClO_4$) with 0.194 M Fe(III), Cl^- 0.000 to 0.501 M^{-1} and an acid concentration of 1.0 M. The reported value for K_1 was (3.8 ± 0.4) M^{-1}. There is no indication that the measurements were done at a constant ionic strength. Therefore, the reported formation constant value, though reasonably consistent with values from earlier studies (*e.g.*, [1963HEI/CLE]) was not used in the SIT calculations in the present review. The method used was effective for detection and measurement of the concentration of the $FeCl^{2+}$ inner-sphere complex. This investigation provides direct proof of the existence of such a species in aqueous solutions. However there is no mention of second-sphere chloride ions, probably because of the lack of sensitivity of the method within the concentrations ranges chosen for determination of the formation constant.

[1999LIU/MIL]

Note that Millero had earlier (Millero, F.J., Earth Planet. Sci., 154, 323-330 (1998)) concluded that solubility measurements based on dialysis techniques are unreliable. In the current study, iron(III) hydroxide spiked with ^{59}Fe was precipitated *in situ* and samples of the solution were obtained after filtration through 0.02 μm syringe filters over a three week period. The temperature was maintained at (25.0 ± 0.1) °C for the series of ionic strengths from 0.01 to 5.0 $mol \cdot L^{-1}$ NaCl. Two additional sets of data at 5 and 50 °C (0.7 $mol \cdot L^{-1}$ NaCl) were also tabulated. The pH of the samples was measured immediately with a combination glass electrode calibrated on the hydrogen ion molarity scale, although no liquid-junction corrections appear to have been made. Although no reliable solubility equilibrium constants can be obtained from this study, treatment of the iron(III) solubility – pH – ionic strength data may yield useful hydrolysis constants for the higher-order hydroxide species in particular which are difficult to obtain by other methods.

After conversion to the molality scale the data sets at 0.01, 0.105, 0.711 and 5.609 mol·kg^{-1} ionic strength (25 °C) were fitted as $\log_{10} m_{\mathrm{Fe}}$ *vs.* pH_m according to the equilibria:

$$\mathrm{Fe(OH)_3(am)} + n\,\mathrm{H^+} \rightleftharpoons \mathrm{Fe(OH)}_{3-n}^{n} + n\,\mathrm{H_2O(l)} \qquad \text{(A.159)}$$

for $n = 2$ to -1. For $n = 3$, the value was fixed according to their Equation (17), noting that the $\mathrm{Fe^{3+}}$ was always a minor species under their conditions. The resulting plots are shown in Figure A-52 to Figure A-55. The fits converged only when the $\mathrm{Fe(OH)_3(aq)}$ species was ignored which seems contrary to data for hematite and goethite where this species dominates the near neutral pH region at higher temperatures. Nevertheless, the fits shown in Figure A-52 to Figure A-55 yielded the solubility constants given in Table A-57 with the corresponding hydrolysis constants listed in Table A-58.

Figure A-52: Plot of $\log_{10} m_{\mathrm{Fe}}$ *vs.* $-\mathrm{pH}_m$ for the solubility of “presumably” amorphous iron(III) hydroxide at 25 °C in NaCl medium at $I_m = 0.01$.

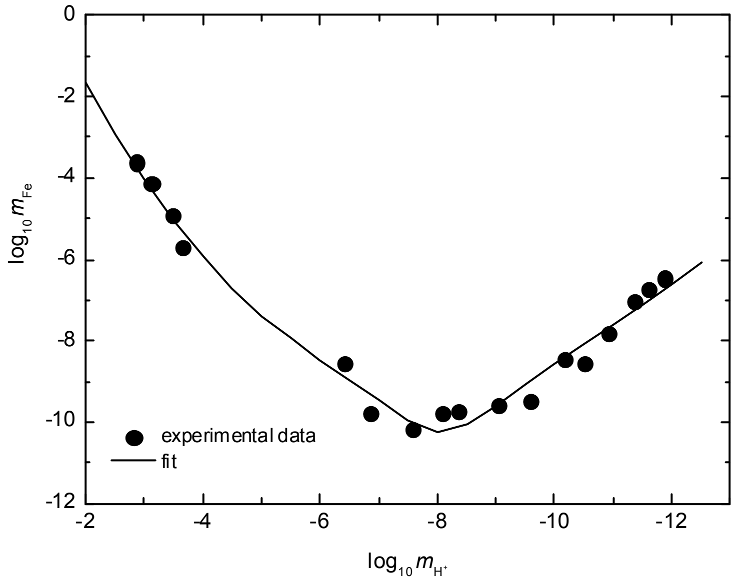


Figure A-53: Plot of $\log_{10} m_{Fe}$ *vs.* $-$ pH$_m$ for the solubility of "presumably" amorphous iron(III) hydroxide at 25 °C in NaCl medium at I_m = 0.105.

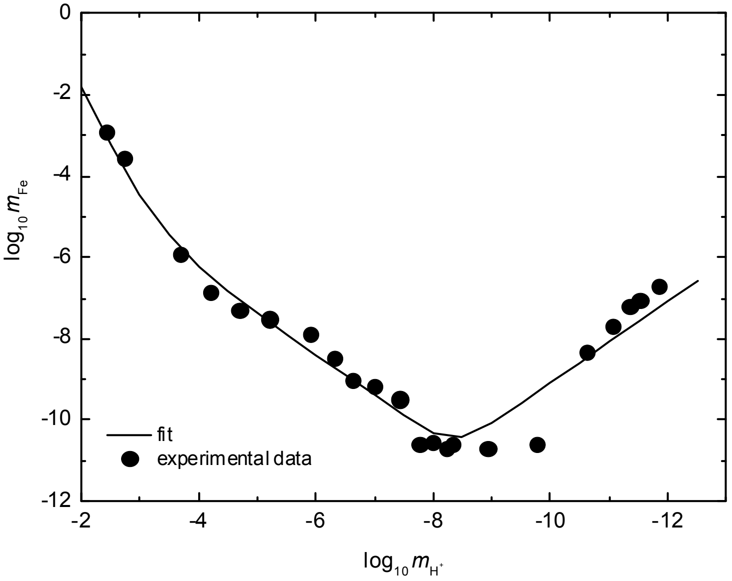


Figure A-54: Plot of $\log_{10} m_{Fe}$ *vs.* $-$pH$_m$ for the solubility of "presumably" amorphous iron(III) hydroxide at 25 °C in NaCl medium at I_m = 0.711.

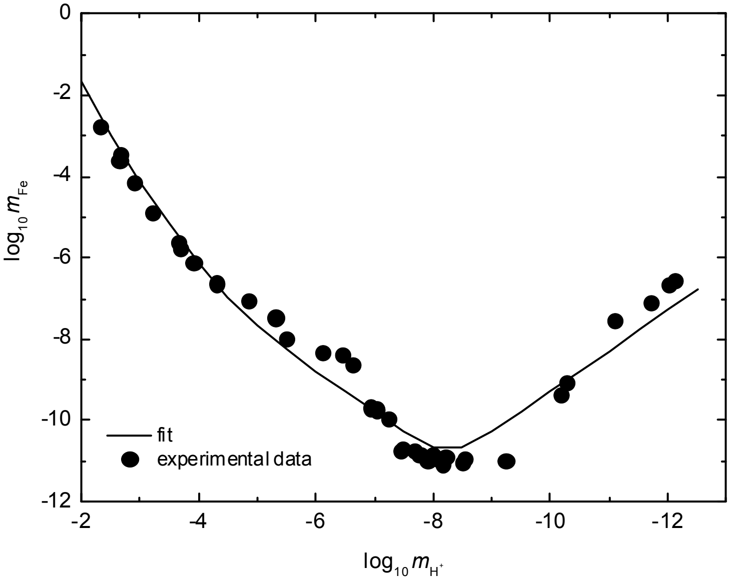


Figure A-55: Plot of $\log_{10} m_{\mathrm{Fe}}$ *vs.* $-\mathrm{pH}_m$ for the solubility of “presumably” amorphous iron(III) hydroxide at 25 °C in NaCl medium at $I_m = 5.609$.

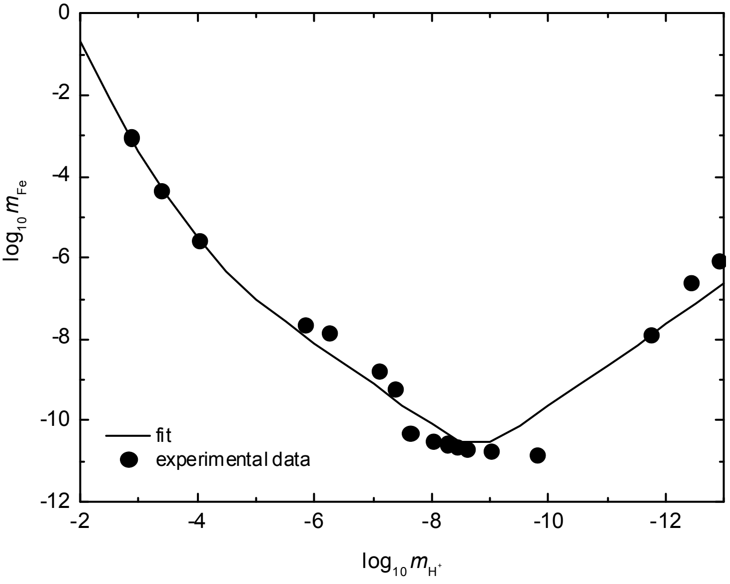


Table A-57: Molal solubility constants of “presumably” amorphous iron(III) hydroxide as a function of ionic strength ($\mathrm{mol \cdot kg^{-1}}$) at 25 °C.

equilibrium	0.01	0.105	0.711	5.609
$\log_{10} {}^*K_{s,0}$	4.14	4.12	4.20	5.26
$\log_{10} {}^*\beta_{s,1}$	1.90 ± 0.20	1.25 ± 0.66	1.76 ± 0.34	2.32 ± 0.44
$-\log_{10} {}^*\beta_{s,2}$	2.48 ± 0.19	2.41 ± 0.15	2.79 ± 0.12	2.11 ± 0.17
$-\log_{10} {}^*\beta_{s,4}$	18.60 ± 0.11	19.08 ± 0.17	19.28 ± 0.16	19.64 ± 0.22

Table A-58: Molal hydrolysis constants of “presumably” amorphous iron(III) hydroxide as a function of ionic strength ($\mathrm{mol \cdot kg^{-1}}$) at 25 °C.

equilibrium	0.01	0.105	0.711	5.609
$-\log_{10} {}^*K_{2,1}$	4.38 ± 0.28	3.66 ± 0.68	4.55 ± 0.36	4.43 ± 0.47
$-\log_{10} ({}^*\beta_{s,4}/{}^*\beta_{s,2})$	16.12 ± 0.22	16.67 ± 0.23	16.49 ± 0.20	17.53 ± 0.28

The two hydrolysis equilibria extracted from these data are:

$$\mathrm{FeOH^{2+} + H_2O(l) \rightleftharpoons Fe(OH)_2^+ + H^+} \qquad {}^*K_{2,1} \tag{A.160}$$

$$\mathrm{Fe(OH)_2^+ + H_2O(l) \rightleftharpoons Fe(OH)_4^- + 2\,H^+} \qquad {}^*\beta_{s,4}/{}^*\beta_{s,2}\,. \tag{A.161}$$

Application of the SIT to Eq. (A.160) results in the weighted linear regression shown in Figure A-56 with $\log_{10} {}^*K^{\circ}_{2,1} = -(3.3 \pm 0.2)$ and $\Delta\varepsilon = (0.00 \pm 0.08)$ kg·mol^{-1}. Similarly, for Eq. (A.161) the weighted linear regression, which is shown in Figure A-57, results in $\log_{10}({}^*\beta^{\circ}_{s,4}/{}^*\beta^{\circ}_{s,2}) = -(17.38 \pm 0.16)$ and $\Delta\varepsilon = -(0.17 \pm 0.07)$ kg·mol^{-1}. These values are useful because of the dearth of hydrolysis data for the higher-order species, but are not recommended due to the metastable nature of these measurements.

Figure A-56: Plot of $\log_{10} {}^*K_{2,1} + 2D - \log_{10} a_w$ vs. I_m for Reaction (A.160) at 25 °C and 1 bar.

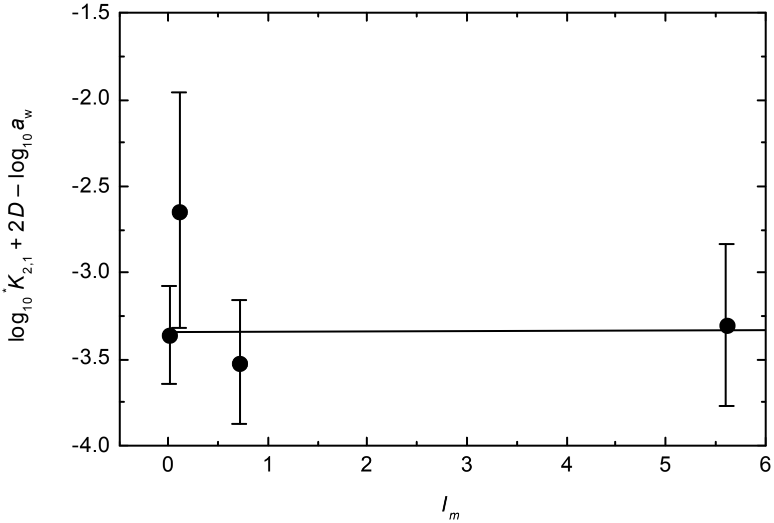
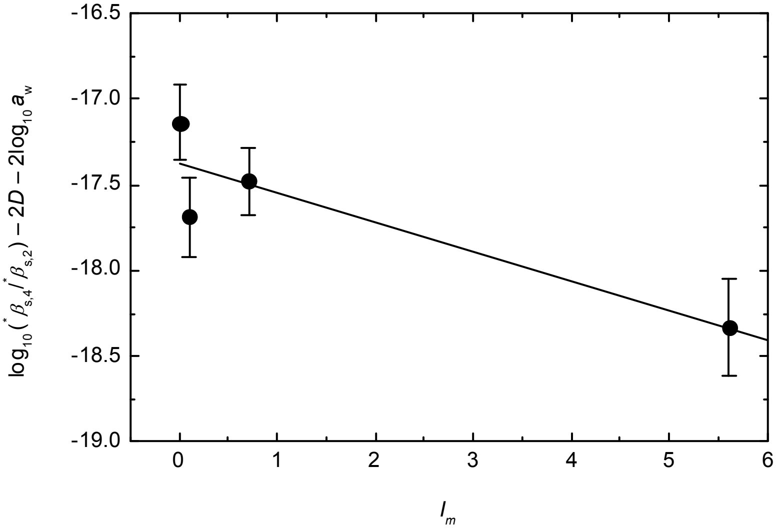


Figure A-57: Plot of $\log_{10}({}^*\beta^{\circ}_{s,4}/{}^*\beta^{\circ}_{s,2}) - 2D - 2\log_{10}a_w$ *vs.* I_m for Reaction (A.161) at 25 °C and 1 bar.



[1999MOL/GON]

This paper simply reworks of the experimental molality and water-activity data of Kálamán [1970KAL], the details of which are found in the 1970 PhD dissertation by Kálamán [1970KAL2].

The derived activity coefficients for aqueous $Al(ClO_4)_3$ were not considered further by this review.

[1999REF/BON]

Sulfate-containing green rust 2 was prepared by precipitation from mixed aqueous solutions of NaOH (at an effective final molarity of 0.20 M if precipitation had not occurred) and $FeSO_4{\cdot}7H_2O$(cr) (a molar excess such that the initial ratio of Fe^{2+} to OH^- was 0.60). The redox potentials of solutions were measured by cyclic voltammetry using a three-electrode system with platinum-wire electrodes and a calomel reference electrode. The potentials were varied from −0.655 to −0.425 V, and the solution temperature was (25.0 ± 0.5) °C. The uncertainties in the measured potentials were given as 0.007 V and uncertainties in the pH as ± 0.10–presumably 1σ.

Total solution concentrations of dissolved iron- and sulfur-containing aqueous species were determined by inductively-coupled plasma atomic-emission spectroscopy (ICP-AES). These analyses confirmed parallel changes in the sulfate and iron solution concentrations as the green rust was formed and then, on further oxidation, converted to lepidocrocite.

Transmission Mössbauer spectroscopy was used to confirm that the stoichiometry of the green rust did not change substantially during the oxidation.

The measured equilibrium potential for the reaction

$$6\,\mathrm{Fe(OH)_2(s)} + \mathrm{SO_4^{2-}} + n\,\mathrm{H_2O(l)} \rightleftharpoons \mathrm{(Fe^{III})_2(Fe^{II})_4(OH)_{12}SO_4}\cdot n\mathrm{H_2O(cr)} + 2\,\mathrm{e^-} \quad \text{(A.162)}$$

is reported as $-(0.497 \pm 0.007)$ V *vs.* the standard hydrogen electrode. This was obtained at a pH of (8.0 ± 0.1) for a solution $(1.3 \pm 0.1) \times 10^{-2}$ M in total dissolved iron, and $(11.0 \pm 0.3) \times 10^{-2}$ M in dissolved sulfate ($I \approx 0.35$ m). With the activity of sulfate ion (0.0225) recalculated using the SIT equations in Appendix B, the value of E° becomes -0.546 V ($\Delta_r G_m^{\circ}$ (A.162) $= -105.3$ kJ·mol^{-1}).

Measurements were also performed at potentials that correspond to $\mathrm{(Fe^{III})_2(Fe^{II})_4(OH)_{12}SO_4}\cdot n\mathrm{H_2O(s)} \rightleftharpoons 6\,\mathrm{FeOOH(\gamma)} + \mathrm{SO_4^{2-}} + 6\,\mathrm{H^+} + n\,\mathrm{H_2O(l)} + 4\,\mathrm{e^-}$, but the authors reported that the voltammetry features were "less pronounced", and did not use the results for thermodynamic calculations.

This paper also provides a solubility measurement for $\mathrm{Fe(OH)_2(s)}$, albeit as a transient, fresh precipitate without direct characterization (a Mössbauer spectrum, their Fig. 4(a), refers to a separate preparation). Solubility equilibrium for freshly precipitated $\mathrm{Fe(OH)_2(s)}$ at (25.0 ± 0.5) °C was defined by pH = (8.0 ± 0.1), $[\mathrm{Fe^{II}}$(aq, total)] = (15 ± 1) mM, and $[\mathrm{SO_4}$(aq, total)] = (113 ± 3) mM, with charge balance by $\mathrm{Na^+}$. The authors derive the equilibrium activity relationship: $-\log_{10} K = 2\,\mathrm{pH} + \log_{10} a_{\mathrm{Fe^{2+}}} = (13.32 \pm 0.18)$, and hence $\Delta_f G_m^{\circ}$ ($\mathrm{Fe(OH)_2}$, s, 298.15 K) $= -(489 \pm 1)$ kJ·mol^{-1}.

[1999SER/SUL]

The solubility of synthetic crystalline α-$\mathrm{Fe_2O_3}$ (grain size 0.1 - 0.2mm) was measured at 200 °C (±2 − 5 °C) in acidic ($0.010 < m_{\mathrm{HClO_4}} < 0.316$ mol·kg^{-1}) and basic ($0.112 < m_{\mathrm{NaOH}} < 0.301$ mol·kg^{-1}) perchlorate media at 0.1 and 0.316 mol·kg^{-1} ionic strength ($\mathrm{NaClO_4}$) and saturation vapour pressure (a preliminary report on this work appears to have been presented at a conference a decade earlier [1988SER/SUL]). Experiments were run for time periods of up to 85 days and it was demonstrated that equilibrium was attained within two days for acidic solutions and eight days in basic solutions. The pH of the initial and quenched solutions were measured with a glass electrode (±0.04) calibrated against standard buffer solutions. Spectrophotometric iron analyses were performed to (±2 - 6%).

The equilibria and corresponding constants are reported as:

$$\tfrac{1}{2}\mathrm{Fe_2O_3(cr)} + 3\,\mathrm{H^+} \rightleftharpoons \mathrm{Fe^{3+}} + 1\tfrac{1}{2}\mathrm{H_2O(l)} \qquad \log_{10} {}^{*}K_{s,0}^{\circ} = -(4.54 \pm 0.36)\ (473.15\ \mathrm{K})$$

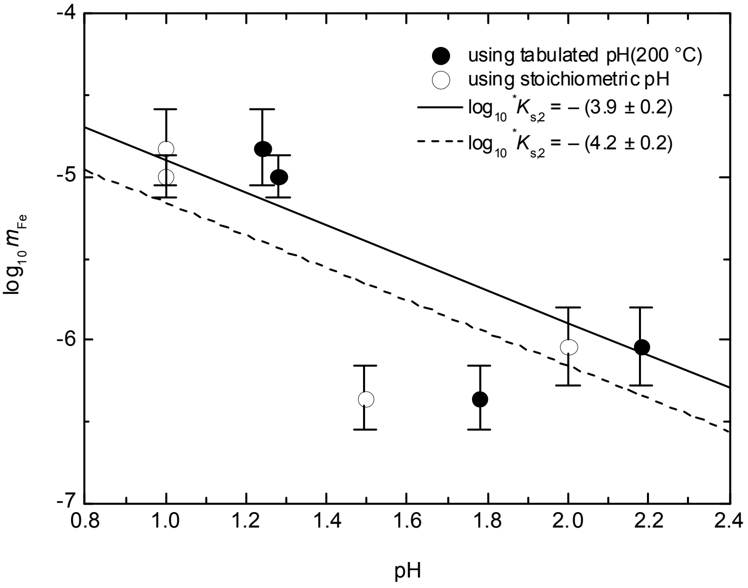
$$\tfrac{1}{2}\mathrm{Fe_2O_3(cr)} + 2\,\mathrm{H^+} \rightleftharpoons \mathrm{FeOH^{2+}} + \mathrm{H_2O(l)} \qquad \log_{10} {}^{*}\beta_{s,1}^{\circ} = -(3.88 \pm 0.36)\ (473.15\ \mathrm{K})$$

$$\tfrac{1}{2}\mathrm{Fe_2O_3(cr)} + \mathrm{OH^-} + 1\tfrac{1}{2}\mathrm{H_2O(l)} \rightleftharpoons \mathrm{Fe(OH)_4^-} \qquad \log_{10} {}^{*}\beta_{s,4}^{\circ} = -(4.56 \pm 0.10)\ (473.15\ \mathrm{K})$$

These values were derived from a consideration of other thermodynamic data taken from the literature.

Only 8 of the 28 experiments in dilute $HClO_4$ were performed with a significant excess of supporting electrolyte, $NaClO_4$, *i.e.*, *ca.* > 10% with an additional 5 at a 0.1 / 0.316 molal ratio. Given this serious limitation and the fact that at least one of the reported iron(III) concentrations appears to be incorrect, a plot of the logarithm of their averaged weighted Fe(III) molality *vs.* pH is badly scattered as shown in Figure A-58.

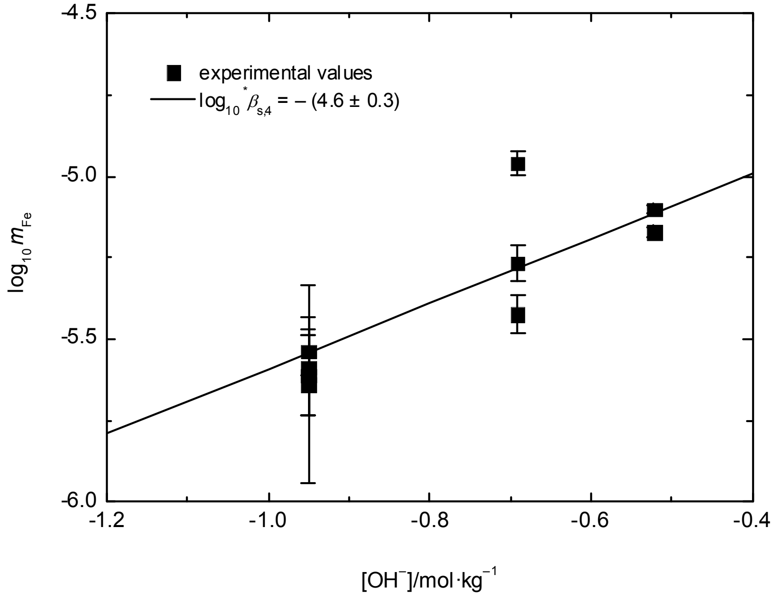
Figure A-58: Plots of the logarithm of the averaged hematite solubility *vs.* pH for 10 experiments at I_m = 0.316 that only approximately follow the swamping electrolyte criterion whereby one set uses their reported pH values calculated from the quenched pH(25 °C) values whereas the second set relies on the tabulated stoichiometric $HClO_4$ values which are significantly different from the quenched values for reasons that are not clear.



The provisional assumption is made by this reviewer that given the scatter in the limited data presented in either form in this figure, a unit slope can be applied to the regression to obtain a solubility constant for the equilibrium: $\frac{1}{2}Fe_2O_3(cr) + H^+ + \frac{1}{2}H_2O(l) \rightleftharpoons Fe(OH)_2^+$ $\log_{10}{}^*\beta_{s,2} = -(4.0 \pm 0.4)$ (473.15 K). However, this regression cannot be favored over one representing $\log_{10}{}^{*}\beta_{\mathrm{s},1}$, and considering the uncertainties in these few data, the measurements in acidic media are not considered to be reliable.

Ten experiments were conducted in basic media at three NaOH concentrations ranging from 0.1121 to 0.3008 mol·kg^{-1} with I_m = 0.316. If these results are treated according the third solubility equilibrium above, which is in the isocoulombic form, such that the failure to have a significant excess of supporting electrolyte does not completely invalidate their treatment, then the plot below can be used to derive a value for $\log_{10}\beta_{\mathrm{s},4}$ of $-(4.6 \pm 0.3)$ (473.15 K).

Figure A-59: Plot of the dependence of the solubility of hematite *vs.* hydroxide molality at 200 °C at an ionic strength of 0.316.



[1999YU/HEO]

This was a field study of streams affected by acid-mine drainage in Korea combined with data from an analogous stream in Ohio, USA. Despite the uncertainties in over- and under-saturation with respect to the two solid phases believed to control the iron(III) levels, the crystallinity and stoichiometry of these phases, temperature variations (15 ± 5) °C and the possible presence of colloids (filter used was 0.45 µm) the apparent solubility constants (treated using the WATEQ4F computer code) offer some approximate solubility limits for these phases. The solubility equilibria for these semi-crystalline solid phases are:

$(FeO(SO_4)_x(OH)_{1-0.25x}\cdot nH_2O$ (schwertmannite) $+ (3 - 0.25x)H^+ \rightleftharpoons Fe^{3+} + xSO_4^{2-} + (2 - 0.25x + n)H_2O(l)$, where $0.218 \le x \le 0.233$ and $1.02 \le n \le 1.08$; (A.163)

$$\tfrac{1}{2}(Fe_2O_3\cdot 1.6H_2O(\text{ferrihydrite})) + 3\,H^+ \rightleftharpoons Fe^{3+} + 2.3\,H_2O(l)$$

Schwertmannite is metastable with respect to goethite, and the compositions of the samples deviated considerably from the synthetic samples prepared by Majzlan *et al.* (and their idealized formulation $(FeO(SO_4)_{0.125}(OH)_{0.75})$ [2004MAJ/NAV]). Also, the stoichiometric sulfate content was generally greater than the maximum (1.75/8) indicated by Brigham *et al.* [1994BIG/CAR] in the original description of the mineral. Although these authors split the data into two 5 °C temperature ranges, they proposed a mean value for $\log_{10} {}^*\beta^\circ$ (A.163) of (10.5 ± 2.5)/8 for schwertmannite.

These estimates of the equilibrium solubility constants of schwertmannite and ferrihydrite provide possible limits on iron(II) concentrations in streams affected by acid-mine drainage. However, as the samples were not equilibrium samples, and there was variation in the compositions and deposition temperatures, the results are not used further in the present review.

[2000BEN/WIL]

Nanoparticulate mackinawite, FeS(mk), precipitated by adding NaOH to the solution of Mohr's salt, $Fe(NH_4)_2(SO_4)_2\cdot 6H_2O$, was aged or transformed under various reducing and slightly oxidizing conditions at pH 3 – 12 and at temperatures 25 – 95 °C. The effect of freeze-drying was also examined. At different time intervals (5 minutes to 4 months), samples of the suspension were withdrawn and filtered through 0.2 µm polycarbonate filters. The pH, total dissolved iron, total dissolved sodium and total reduced sulfur in the filtered solution were measured. Ionic strengths were calculated to be from 0.18 to 0.90 $mol\cdot kg^{-1}$ depending on the experimental conditions. The solids were transferred into an oxygen-free N_2-filled desiccator and dried under vacuum. Within 10 – 30 minutes, the samples were characterized using X-ray diffraction and scanning electron microscopy. In addition, the magnetic state of the dried powders was checked with a hand magnet. The experimental results showed that in reduced sulfur solutions at low temperatures, the mackinawite was stable for up to 4 months. Below 100 °C, the rate of pyrite formation from the mackinawite was insignificant in solutions equilibrated solely with $H_2S(aq)$. Controlled experiments involving deliberate oxidation at temperatures below 100 °C and over a wide range of pH (3.3 – 12) indicated that the mackinawite to pyrite transformation occurs in slightly oxidizing environments. The freeze-dried mackinawite showed the faster rate of conversion to pyrite, indicating that despite the efforts to avoid oxidation in the freeze-drying procedure, the freeze-dried material such as in [1997RIC2] must have been oxidized. By using the data from these ageing experiments, the solubility of crystalline mackinawite at temperatures below 100 °C and at pH 3.2 − 5 was determined. Two data points at pH 7.39 and 8.15 at 80 °C, which were not compatible with the overall trend, were excluded from the analysis since there may be an effect from the formation of $FeHS^+$ and/or $Fe(HS)_2(aq)$ in near neutral to alkaline solutions, and the available data obtained in this study were insufficient to determine the iron sulfide speciation at high pH values. The dissolution reaction of mackinawite was assumed to be $FeS(mk) + 2H^+ \rightleftharpoons Fe^{2+} + H_2S(aq)$ based on the results obtained by other researchers, and the activity coefficients of Fe^{2+} and HS^- were calculated by means of the Davies equation. The logarithms (base 10) of the equilibrium constants, $\log_{10} K^\circ_{FeS}$, were calculated to be 3.21 (25 °C), 2.47 (50 °C), 1.84 (75 °C), 1.72 (80 °C), 1.50 (90 °C) and 1.29 (100 °C) or $\Delta_r G^\circ = -(18.31 \pm 1.10)$ (25 °C), $-(15.27 \pm 1.90)$ (50 °C), $-(12.24 \pm 1.30)$ (75 °C), $-(11.63 \pm 1.30)$ (80 °C), $-(10.41 \pm 1.40)$ (90 °C) and $-(9.20 \pm 1.40)$ (100 °C) $kJ \cdot mol^{-1}$. The temperature dependence of the equilibrium constant obtained was $\log_{10} K_{FeS} = 2848.799/T - 6.347$, which leads to $\Delta_r H^\circ = -54.55$ $kJ \cdot mol^{-1}$ and $\Delta_r S^\circ = -122$ $J \cdot K^{-1} \cdot mol^{-1}$ for the enthalpy and entropy of the reaction (assuming a value of $\Delta_r C^\circ_{p,m} = 0$ $J \cdot K^{-1} \cdot mol^{-1}$). In the data analysis, activity coefficients for the species at ionic strengths from 0.18 to 0.90 at each temperature were estimated using the Davies equation. The contribution to the difference in the $\log_{10} K$ value for this reaction ($\Delta z^2 = 2$) from use of the Davies equation instead of the SIT equation in this ionic strength range, is estimated to be at most ± 0.2. Each value at a given temperature was obtained from only two or three data points measured at a nearly constant pH. The change in the temperature may affect the ageing state and the surface condition of the precipitate, which in turn, affects the solubility of the precipitate. Considering the uncertainties in activity coefficients, this review takes the value of $\log_{10} K^\circ_{FeS} = (3.2 \pm 0.5)$ at 25 °C, giving a fairly large uncertainty, and does not take values for other temperatures.

[2000BRU/DUR]

This paper is the response by Bruno and Duro to the comments by Hummel [2000HUM] on an earlier study by Bruno *et al.* [1992BRU/STU] on the solubility of hematite in carbonate-containing solutions. No new experimental work was reported, but the points raised by Hummel [2000HUM] were discussed.

Bruno and Duro concurred with Hummel's comment concerning errors in calculation of values for $\beta_{1,1,1}$ and $\beta_{2,1}$ and the values that he reported ($\log_{10}\beta_{1,1,1} = 14.9$ for $FeCO_3OH(aq)$ and $\log_{10}\beta_{2,1} = 26.5$ for $Fe(CO_3)_2^-$).

Bruno and Duro agreed that these values are unreasonably large and with the suggestion that the hematite surface might be covered by ferrihydrite (and hence that the actual complexation constants for carbonate with iron could be smaller). Extrapolation of their results to zero ionic strength led to $\log_{10} \beta^\circ_{1,1,1} = 7.7$ for $FeCO_3OH(aq)$ and $\log_{10} \beta^\circ_{2,1} = 19.6$, values close to those recommended by Hummel.

The species $FeCO_3OH(aq)$, which had been introduced to explain the first part of the hematite solubility curve as a function of pH, was considered to be dubious by

Hummel. Bruno and Duro carried out new simulations with and without $FeCO_3OH(aq)$ and found that the introduction of this species matched better with the experimental results. However, as the proposed formula of this complex was based only on accepting a value of zero for the slope of a plot of soluble Fe(III) *vs*. pH, other reasonable hypotheses could be invoked, for example mixtures of $Fe(OH)_2^+$ and $Fe(CO_3)_2^-$.

This paper and the two previous discussions of the same data [1992BRU/STU], [2000HUM] are important in assessing information on the Fe(III) carbonate system. They show that carbonate complexation must be taken into account to predict the behaviour of Fe(III) in the natural waters when the CO_2 partial pressure is greater than 1 kPa. However confirmation of the species' stoichiometries and thermodynamic quantities were not firmly established.

[2000BYR/LUO]

The authors carried out potentiometric titrations with a Ross combination glass electrode calibrated on the free hydrogen ion concentration scale in NaCl (2.84 M) and 0.01 to 6.0 M $NaClO_4$ at 25 °C. Redox potentials were also monitored. Liquid-junction potentials were estimated using the relationship: $E_{lj} = C_0 + C_1[H^+]$. No raw experimental results were provided. The iron(III) and iron(II) concentrations were quite low at 5×10^{-5} M (2×10^{-5} M in 0.01 M $NaClO_4$). The data for the ionic strength dependence of $\log_{10}{}^*\beta_{1,1}$ at 25 °C are shown in Table A-59 and those for the temperature dependence at a fixed I_c are given in Table A-60.

From the results in Table A-59, using an unconventional extended Debye-Hückel term, the authors report a $\log_{10}{}^*\beta^{\circ}_{1,1}$ value at 25 °C of $-(2.18 \pm 0.01)$ and a corresponding $\Delta_r H_{1,1}$ of (42.7 ± 1.3) kJ·mol^{-1} at $I_m = 0.75$. The remainder of the manuscript was devoted to recalculation of the next two hydrolysis constants and the solubility product of $Fe(OH)_3(s)$ without introduction of any new experimental results.

Table A-59: $\log_{10}{}^*\beta_{1,1}$ values converted to molal units at 25 °C.

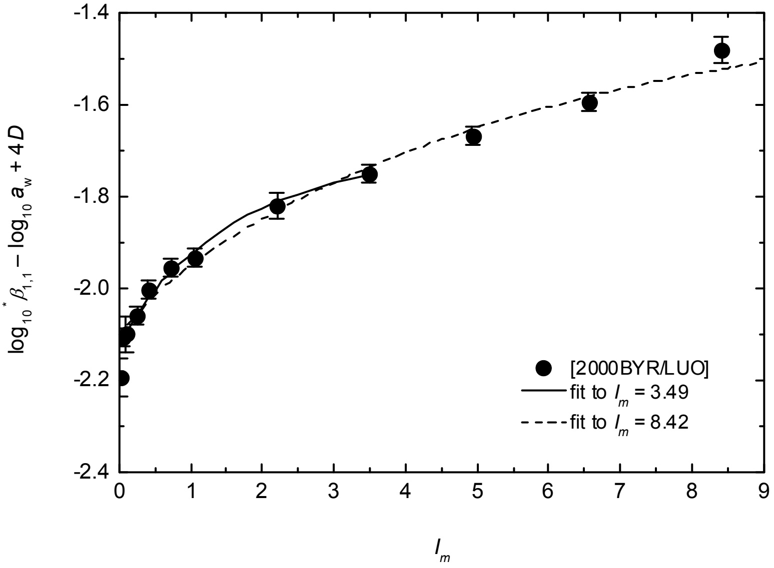
I_m	$\log_{10}{}^*\beta_{1,1}$	1σ
0.01	– 2.37	0.04
0.0501	– 2.45	0.02
0.1005	– 2.54	0.04
0.2530	– 2.65	0.02
0.4076	– 2.67	0.02
0.7235	– 2.73	0.02
1.049	– 2.77	0.02
2.206	– 2.79	0.03
3.493	– 2.80	0.02
4.935	– 2.79	0.02
6.563	– 2.78	0.02
8.418	– 2.73	0.03

Table A-60: $\log_{10}{}^*\beta_{1,1}$ values converted to molal units as a function of temperature.

t, °C	I_m	$\log_{10}{}^*\beta_{1,1}$	1σ
5	0.750	– 3.30	0.03
10	0.751	– 3.11	0.03
25	0.752	– 2.70	0.02
40	0.753	– 2.37	0.03
56	0.754	– 2.04	0.03

This appears to be a very well executed study. Application of the SIT *via* a weighted fit leads to the results shown in Figure A-60 and, if application of SIT is limited to $I_m \le 3.49$, $\log_{10}{}^*\beta^{\circ}_{1,1} = -(2.14 \pm 0.02)$ at 25 °C with an ionic strength dependent $\Delta\varepsilon/\text{kg}\cdot\text{mol}^{-1} = -(0.22 \pm 0.04) + (0.19 \pm 0.07)\log_{10} I_m$ with uncertainties at the 2σ level. This limited ionic strength range complies with the generally accepted limit of the SIT, noting that the value of $\log_{10}{}^*\beta^{\circ}_{1,1}$ was identical when fitted to the results $I_m \le$ 2.11, but increased if higher ionic strengths were included in the fit and this was the criterion for limiting the fit. On the other hand, in order to gain predictions at higher ionic strength, application of the SIT over the whole range of ionic strength gives the dashed curve in Figure A-60 that fits almost all the data to within 1σ. However, this weighted fit gives only a slightly higher value of $\log_{10}{}^*\beta^{\circ}_{1,1} = -(2.11 \pm 0.03)$ with $\Delta\varepsilon/\text{kg}\cdot\text{mol}^{-1} = -(0.16 \pm 0.02) + (0.10 \pm 0.02)\log_{10} I_m$.

Figure A-60: Plot of $\log_{10}{}^*\beta_{1,1} - \log_{10} a_\text{w} + 4D$ *vs.* I_m in an SIT analysis of the results of [2000BYR/LUO] at 25 °C.



[2000HUM]

This paper is a critique of the solubility measurements of hematite in hydrogen carbonate solutions as reported by Bruno *et al.* [1992BRU/STU]. No new experimental work was reported. Corrections were proposed, though a different interpretation of the data was presented.

The author pointed out major errors in the data treatment, and questioned whether the solubility-controlling phase actually was hematite.

In a response, Bruno and Duro [2000BRU/DUR] addressed the data-treatment problems, and Grivé later attempted to do similar solubility measurements using better characterized solids (*cf.* the Appendix A entry for [2005GRI]).

[2000RIC/BRA]

The vapour pressures of $AlCl_3$ solutions were measured in the temperature range 298 to 342 (±0.05) K over the range of molalities: 0.421 to 3.033 $mol{\cdot}kg^{-1}$. They used a strain-gauge pressure sensor with an absolute uncertainty of ±0.06%. The temperature range was limited to 342 K to avoid the complication of HCl generated by aluminium hydrolysis contributing significantly to the measured vapour pressure. The authors extrapolated their water activities to 298.15 K and the corresponding osmotic coefficients were shown graphically to be consistent with the much older results of Mason [1941MAS], and Robinson and Stokes [1949ROB/STO]. These osmotic coefficients were calculated here at molalities of 0.421, 1.071, 1.765, 2.566 and 3.033 $mol{\cdot}kg^{-1}$ to be 0.95, 1.44, 2.19, 3.24 and 3.54, respectively.

Considering the limited number and accuracy of these results, and the extrapolation required to 298.15 K, these osmotic coefficient measurements were not included in the final SIT fit for $AlCl_3$(sln).

[2000SCH/COR]

This monograph deals primarily with the synthesis and characterization of iron oxides and oxyhydroxides, with emphasis on the reliable synthesis of pure phases. There are several general chapters, plus individual chapters dealing with individual phases: goethite, lepidocrocite, feroxyhyte, ferrihydrite, akaganéite, hematite, magnetite, maghemite, and iron hydroxy salts.

Note: the first edition is [1991SCH/COR].

[2000TAG/DIA]

The cell used in this study of E°_{T} (Fe^{3+}/Fe^{2+}) was a non-isothermal cell that was designed for measurements of the normal potential of the Fe(III)/Fe(II) couple at temperatures between 20.8 and 90 °C.

$$\mathrm{Pt,H_2}\mid \mathrm{HClO_4}\,(m) \;\vdots\vdots\; \mathrm{HClO_4}\,(m) \;\vdots\; \mathrm{HClO_4}(m),\ \mathrm{Fe(ClO_4)_2}\,(x),\ \mathrm{Fe(ClO_4)_3}\,(y) \mid \mathrm{Pt}$$

reference at 25 °C liquid junction test at 20.8 to 90 °C

Activity coefficients were calculated from an extended Debye-Hückel expression [1975KHO]. Junction potentials were calculated for 25 °C, and changes in temperature were taken into account using Walden's rule. Hydrolysis was taken into account, and E°_{T} as function of the temperature was given by Equation (A.164).

$$E^{\circ}_{T}/\mathrm{V} = 0.600 - 3.091 \times 10^{-3}(T/\mathrm{K}) + (6.435 \times 10^{-4}\,(T/\mathrm{K})\ln(T/\mathrm{K})) \qquad \text{(A.164)}$$

From this, assuming the constant heat-capacity change for the temperature range to be $\Delta_r C^{\circ}_p$ = 62.09 J·K^{-1}·mol^{-1} [1988HOV], the calculated values of $\Delta_r G^{\circ}$, $\Delta_r H^{\circ}$, and $\Delta_r S^{\circ}$ were – (74.27 ± 0.17) kJ·mol^{-1}, – (39.34 ± 1.88) kJ·mol^{-1}, and (117.15 ± 6.28) J·K^{-1}·mol^{-1}, respectively, if the values of $\Delta_r G^{\circ}$ and $\Delta_r S^{\circ}$ are used to calculate $\Delta_r H^{\circ}$.

1. Standard potential

To apply the SIT formalism to the experimental results for the determination of the standard potential, the authors' equation (5) was used, but without the correction terms that were necessary only when the temperature of the test half cell was different from 25 °C (A.165):

$$\begin{aligned} E = {} & E^{\circ}(\mathrm{Fe^{3+}/Fe^{2+}}) - (RT/F)\ln(m_{\mathrm{Fe^{2+}}}/m_{\mathrm{Fe^{3+}}}) - (RT/F)\ln(\gamma_{\mathrm{Fe^{2+}}}/\gamma_{\mathrm{Fe^{3+}}}) \\ & + E_j - (RT/F)\ln m_{\mathrm{H^+}} - (RT/F)\ln \gamma_{\mathrm{H^+}}\,. \end{aligned} \qquad \text{(A.165)}$$

Here, for convenience, we define a potential $E^{\ddagger}$ for the Fe^{2+}/Fe^{3+} couple at total ionic strength I_m and perchlorate molality $m_{\mathrm{ClO_4^-}}$.

$$E^{\ddagger} = E + (RT/F)\ln(m_{\mathrm{Fe^{2+}}}/m_{\mathrm{Fe^{3+}}}) + (RT/F)\ln m_{\mathrm{H^+}} + (RT/F)\ln \gamma_{\mathrm{H^+}} - E_j \qquad \text{(A.166)}$$

and therefore

$$E^{\ddagger} = E^{\circ} - (RT/F)\ln(\gamma_{\mathrm{Fe^{2+}}}/\gamma_{\mathrm{Fe^{3+}}}) \qquad \text{(A.167)}$$

where E_j is the junction potential.

Thus, the value of E° is calculated by applying the SIT Equation (A.168):

$$E^{\ddagger} = E^{\circ} - (5D)(0.05916)(\varepsilon(\mathrm{Fe^{2+}, ClO_4^-}) - \varepsilon(\mathrm{Fe^{3+}, ClO_4^-}))\, m_{\mathrm{ClO_4^-}} \qquad \text{(A.168)}$$

where: 0.05916 is the value of $RT(\ln(10))/nF$ for $n = 1$, $T = 298.15$ K, 5 is the value of $z^2(\mathrm{Fe^{3+}}) - z^2(\mathrm{Fe^{2+}})$, z being the charge of the ions, and D is the SIT Debye-Hückel term at 298.15 K.

As discussed in the main text, Section VI.1.2.1.1, Equation (A.168) is not adequately represented by a straight line, which means that $\Delta\varepsilon$ is not a constant. So two kinds of extrapolation to zero ionic strength have been carried out (see Figure A-61): a linear fit (SIT$_1$) which is only an approximation ($R^2 \approx 0.984$),

$$E^{\ddagger} + (5D)(0.05916) = E^{\circ} - 0.05916(\varepsilon(\mathrm{Fe^{2+}, ClO_4^-}) - \varepsilon(\mathrm{Fe^{3+}, ClO_4^-}))\; m_{\mathrm{ClO_4^-}} \qquad \text{(A.169)}$$

and a fit to a function (A.170) in which $\varepsilon(\mathrm{Fe}^{3+}, \mathrm{ClO}_4^-)$ is not constant but equal to:

$\Delta(\varepsilon_1 + \varepsilon_2 \log_{10} I_m.)$ (SIT$_2$ with $R^2 = 0.995$)

$$E^{\ddagger} + (5D)(0.05916) = E^{\mathrm{o}} - 0.05916\{\varepsilon(\mathrm{Fe}^{2+}, \mathrm{ClO}_4^-) - \varepsilon_1(\mathrm{Fe}^{3+}, \mathrm{ClO}_4^-) - \varepsilon_2(\mathrm{Fe}^{3+}, \mathrm{ClO}_4^-)\log_{10} I_m)\}\, m_{\mathrm{ClO}_4^-} \quad \text{(A.170)}$$

The R^2 value in the latter case is better than 0.99. The fit of $E^{\ddagger} = \mathrm{f}(m_{\mathrm{ClO}_4^-})$ according to Eq. (A.170) is shown in Figure A-62.

The final results from these SIT treatments for the data of Tagirov *et al.* at 25 °C yield, after rounding and assigning the uncertainties.

SIT$_1$: $E_0^{\mathrm{o}} = (0.778 \pm 0.05)$ V;

$\varepsilon(\mathrm{Fe}^{3+}, \mathrm{ClO}_4^-) = (0.67 \pm 0.05)\ \mathrm{kg\cdot mol^{-1}}$

using $\varepsilon(\mathrm{Fe}^{2+}, \mathrm{ClO}_4^-) = (0.37 \pm 0.04)\ \mathrm{kg\cdot mol^{-1}}$

SIT$_2$: $E_0^{\mathrm{o}} = (0.775 \pm 0.04)$ V;

$$\varepsilon(\mathrm{Fe}^{3+}, \mathrm{ClO}_4^-) = ((0.73 \pm 0.05) - (0.23 \pm 0.03)\log_{10} I_m)\ \mathrm{kg\cdot mol^{-1}} \quad \text{(A.171)}$$

using $\varepsilon(\mathrm{Fe}^{2+}, \mathrm{ClO}_4^-) = (0.37 \pm 0.04)\ \mathrm{kg\cdot mol^{-1}}$

Figure A-61: SIT$_1$ treatment of the experimental data of [2000TAG/DIA] at 25 °C. Linear fit of $E^{\ddagger} + (5D)(0.05916) = E_0^{\mathrm{o}} - 0.05916\Delta\varepsilon\, m_{\mathrm{ClO}_4^-}$, $\Delta\varepsilon$ = constant.

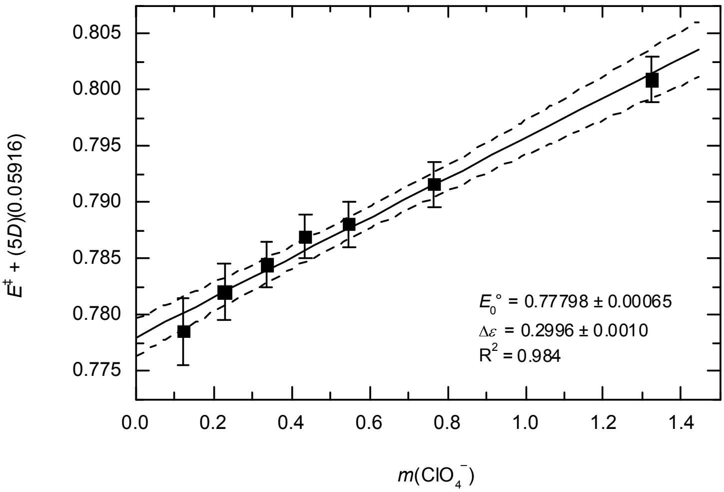
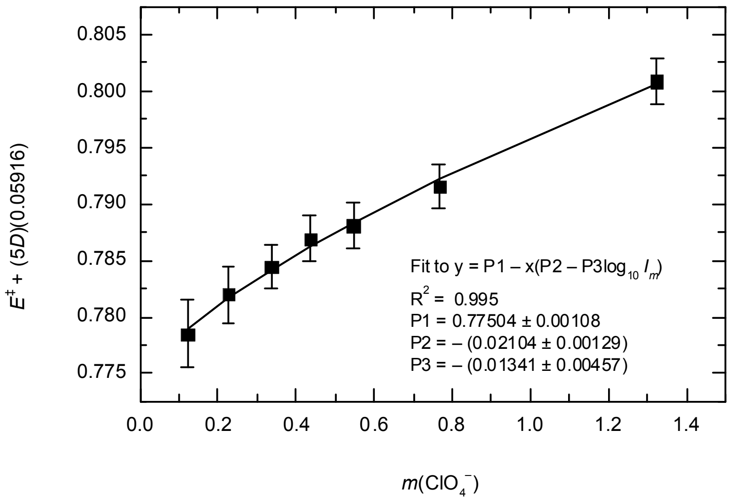


Figure A-62: SIT$_2$ treatment of the experimental data of [2000TAG/DIA] at 25 °C. Fit to the equation: $y = \mathrm{P1} - x(\mathrm{P2} - \mathrm{P3}\log_{10} I_m)$ representing $E^{\ddagger} + (5D)(0.05916) = E^{\circ} - 0.05916\Delta\varepsilon m_{\mathrm{ClO}_4^-}$. Here: $\mathrm{P1} = E^{\circ}$, $\mathrm{P2} = 0.05916\ (\varepsilon(\mathrm{Fe}^{2+}, \mathrm{ClO}_4^-) - \varepsilon_1(\mathrm{Fe}^{3+}, \mathrm{ClO}_4^-))$; $\mathrm{P3} = 0.05916\ \varepsilon_2(\mathrm{Fe}^{3+}, \mathrm{ClO}_4^-)$.



The $\varepsilon(\mathrm{Fe}^{3+}, \mathrm{ClO}_4^-)$ values obtained by treating the Tagirov *et al.* data by SIT$_1$- or SIT$_2$- type formulations are different from the recommended values of this review. The latter stem from cell-potential data obtained over a larger range of ionic strengths and especially data at low ionic strengths. That corresponds to an increase in the curvature of the function $E^{\ddagger} + (5D)(0.05916) = E_0^{\circ} - 0.05916\Delta\varepsilon\ m_{\mathrm{ClO}_4^-}$ at low ionic strength, and is taken into account by a strong increase in the $\varepsilon_2\ (\log_{10} I_m)$ contribution.

In the present review, in addition to the two functions illustrated by the plots in Figures A-61 and A-62, second- and third-degree polynomial fitting functions were considered for extrapolation to $m_{\mathrm{ClO}_4^-} = 0$.

For the fit of $E^{\ddagger} + (5D)(0.05916) = \mathrm{f}(m_{\mathrm{ClO}_4^-})$ to a third-degree polynomial equation one has:

$$E^{\ddagger} + (5D)(0.05916) = E^{\circ} + \mathrm{A}\, m_{\mathrm{ClO}_4^-} + \mathrm{B}\, m^2_{\mathrm{ClO}_4^-} + \mathrm{C}\, m^3_{\mathrm{ClO}_4^-} \qquad (\mathrm{A.172})$$

where A, B and C are the third-degree polynomial fitting coefficients. That implies:

$$-\,0.05916\Delta\varepsilon\ m_{\mathrm{ClO}_4^-} = \mathrm{A}\, m_{\mathrm{ClO}_4^-} + \mathrm{B}\, m^2_{\mathrm{ClO}_4^-} + \mathrm{C}\, m^3_{\mathrm{ClO}_4^-} \qquad (\mathrm{A.173})$$

and

$$\varepsilon(\mathrm{Fe}^{2+}, \mathrm{ClO}_4^-) - \varepsilon(\mathrm{Fe}^{3+}, \mathrm{ClO}_4^-) = -\,(1/0.05916)(\mathrm{A} + \mathrm{B}\, m_{\mathrm{ClO}_4^-} + \mathrm{C}\, m^2_{\mathrm{ClO}_4^-}) \quad (\mathrm{A.174})$$

$$\varepsilon(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-) = \varepsilon(\mathrm{Fe}^{2+},\mathrm{ClO}_4^-) + (1/0.05916)\,(\mathrm{A} + \mathrm{B}\,m_{\mathrm{ClO}_4^-} + \mathrm{C}\,m^2_{\mathrm{ClO}_4^-}) \quad (\mathrm{A}.175)$$

For the second-degree polynomial,

$$\varepsilon(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-) = \varepsilon(\mathrm{Fe}^{2+},\mathrm{ClO}_4^-) + \mathrm{A}/0.05916 + (\mathrm{B}/0.05916)\,m_{\mathrm{ClO}_4^-} \quad (\mathrm{A}.176)$$

We calculated values of $\varepsilon(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-)$ by applying Equations (A.175) and (A.176) to solutions with ionic strengths varying from 0.1 to 4 m. The data of Tagirov *et al.* for 25 °C served to determine the necessary parameters for the four different types of fitting described above. The results are given in Table A-61.

It can be seen that the linear fit yields a constant but rather high value of $\varepsilon(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-)$, when compared to 0.56 $\mathrm{kg\cdot mol^{-1}}$, the value listed in previous TDB tables (*e.g.* [1992GRE/FUG]). The linear fit does not adequately reflect the shape of the function: $E^{\ddagger} + (5D)(0.05916) = \mathrm{f}(m_{\mathrm{ClO}_4^-})$.

The fits to second- and third-degree polynomial functions provide a better representation of the data, but the unrealistic low values of $\varepsilon(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-)$ from the second-degree polynomial, and high values from the third-degree polynomial outside the range of the experimental data at high ionic strengths (I > 1.5) show that these functions cannot be used beyond the experimentally investigated and fitted range of $m_{\mathrm{ClO}_4^-}$.

Table A-61: Comparison of the $\varepsilon(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-)$ and $E^{\circ}_0(\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+})$ values obtained by different fitting of the function: $E^{\ddagger} + (5D)(0.05916) = \mathrm{f}(m_{\mathrm{ClO}_4^-})$ applied only to the data of [2000TAG/DIA], $\varepsilon(\mathrm{Fe}^{2+},\mathrm{ClO}_4^-) = 0.37\ \mathrm{kg\cdot mol^{-1}}$.

I_m^*	$\varepsilon(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-)/\mathrm{kg\cdot mol^{-1}}$			
$m(\mathrm{ClO}_4^-)$↓	SIT_1	2nd degree polynomial**	3rd degree polynomial***	SIT_2 (Eq. (A.171))
0.1	0.67	0.772	0.974	0.952
1	0.67	0.705	0.713	0.725
2	0.67	0.63	0.867	0.657
4	0.67	0.48	2.58	0.589
5	0.67	0.405	4.137	0.568
$E^{\circ}_0(\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+})/\mathrm{V}$ →	0.778 ± 0.005	0.776 ± 0.003	0.774 ± 0.003	0.775 ± 0.003
R^2 →	0.0983	0.990	0.994	0.995

* For these calculations only, the simplifying assumption is made that $I_m = m(\mathrm{ClO}_4^-)$.

** $\mathrm{A} = 0.410\ \mathrm{mol\cdot kg^{-1}}$, $\mathrm{B} = -0.0750\ \mathrm{mol^2\cdot kg^{-2}}$ (Eq. (A.176)).

*** $\mathrm{A} = 0.657\ \mathrm{mol\cdot kg^{-1}}$, $\mathrm{B} = -0.548\ \mathrm{mol^2\cdot kg^{-2}}$, $\mathrm{C} = 0.234\ \mathrm{mol^3\cdot kg^{-3}}$ (Eq. (A.175)).

The two-term function with a logarithmic term seems more adequate, and has been proposed previously in earlier TDB reviews (Appendix B, Eq. B 24, but also see the comments in Appendix B of Rand *et al.* [2008RAN/FUG]), so this is the chosen

SIT_2 treatment. The high $\varepsilon(Fe^{3+}, ClO_4^-)$ values at low ionic strengths are still a subject of discussion and must be considered with other types of data.

2. E^o as a function of the temperature

2.1. SIT treatment of the data as a function of the ionic strength at various temperatures.

Tagirov *et al.* determined the quasi standard potentials $E^o(T)$ (E'^o extrapolated to 0 ionic strength) of the Fe^{3+}/Fe^{2+} redox couple at temperatures other than 298.15 K.

We treated the data of [2000TAG/DIA] at temperatures other than 25 °C by the SIT_1 and SIT_2 methods; the results are listed in Table A-62. The values for D at the different temperatures were calculated using the Debye-Hückel $A(T)$ values in Table B-2 of the present volume, and the recommended temperature-independent value of 1.5 $kg^{½}·mol^{-½}$ for Ba_j.

Table A-62: Comparison of E_t^o calculated by the SIT formalism and by [2000TAG/DIA] from their experimental results and values of $dE^{o\prime}/dT$.

t/°C	Corrections#/ V	$E_t^{o\,\#}$/V *vs.* SHE	E_t^o SIT_1^*/V *vs.* SHE	E_t^o SIT_2^*/V *vs.* SHE	$dE_t^o/dt^{\#}$/ mV	dE_t^o/dt SIT_1/mV	dE_t^o/dt SIT_2/mV
20.8	− 0.0023	0.765	0.773 ± 0.005	0.770 ± 0.004	1.262	1.216	1.179
25	0.0000	0.770	0.778 ± 0.005	0.775 ± 0.004	1.243	1.157	1.087
35	0.0055	0.783	0.789 ± 0.005	0.784 ± 0.004	1.216	1.060	0.938
40	0.0082	0.789	0.794 ± 0.005	0.789 ± 0.004	1.213	1.034	0.900
45	0.0110	0.795	0.800 ± 0.005	0.794 ± 0.004	1.216	1.023	0.886
50	0.0137	0.801	0.805 ± 0.005	0.798 ± 0.004	1.225	1.027	0.896
55	0.0165	0.807	0.810 ± 0.005	0.803± 0.004	1.241	1.047	0.931
60	0.0192	0.813	0.816± 0.005	0.808 ± 0.004	1.264	1.082	0.989
70	0.0247	0.826	0.827 ± 0.005	0.819 ± 0.005	1.329	1.197	1.180
75	0.0275	0.833	0.833 ± 0.005	0.823 ± 0.005	1.371	1.278	1.311
80	0.0302	0.840	0.839 ± 0.005	0.830 ± 0.006	1.419	1.373	1.467
85	0.0329	0.848	0.848 ± 0.005	0.839 ± 0.007	1.475	1.484	1.647
90	0.0357	0.854	0.851 ± 0.006	-	1.536	-	-

\# [2000TAG/DIA], the values of the corrections are those given by Tagirov *et al.* to take into account the fact that their cell was not isothermal (Eq. 12 of the original article).

* SIT_1 linear extrapolation to $m_{ClO_4^-} = 0$ of all $E^{o\prime}(t)$ (Tagirov *et al.* formal potentials at t) calculated using Eq. (A.169) to get the E_t^o values;(pseudo standard potentials);

SIT_2 fit of the data using Eq. (A.170) to get the E_t^o values (pseudo standard potentials).

The influence of hydrolysis has been taken into account as described above for the [1972WHI/LAN] work. Here, in spite of the higher acidities, it is not a secondary correction because of the larger temperature range investigated. The 1:1 species $FeOH^{2+}$

plays a significant role, especially at the higher temperatures because of the positive $\Delta_r H$. This species can represent 26% of the total Fe(III), well beyond the 5% limit claimed in the original paper. The amount of $\mathrm{Fe_2(OH)_2^{4+}}$ is negligible, especially at higher temperatures because of the negative $\Delta_r H$ value for the dimerization constant.

The slopes $\mathrm{d}E^{\circ}/\mathrm{d}T$ of the functions $E^{\circ}(T) = \mathrm{f}(t/°\mathrm{C})$ have been determined by calculating the values of the derivatives of the equation $E^{\circ}_T = \mathrm{f}(T)$. This arbitrary equation has been established by fitting the data to a third-degree polynomial. Three series of calculation were carried out:

(a) using the E°_T values from the original paper (Table 1),

(b) using the $\mathrm{SIT_1}$ E° values obtained from a linear fit of

$E^{\circ}(t) + (5D)(RT(\ln(10))/\mathrm{F}) = \mathrm{f}(m_{\mathrm{ClO_4^-}})$ (to Eq. (A.169))

(c) using $\mathrm{SIT_2}$ (a fit of $E^{\circ}(t) + (5D)(RT(\ln(10))/\mathrm{F}) = \mathrm{f}(m_{\mathrm{ClO_4^-}})$ to Eq. (A.170))

Rather large discrepancies are observed between the $\mathrm{d}E^{\circ}_T/\mathrm{d}T$ values; even between those calculated with $\mathrm{SIT_1}$ or $\mathrm{SIT_2}$. Such differences were not observed between the values obtained using the $\mathrm{SIT_2}$ treatment of the single ionic-strength data of [1951CON/MCV], [1953MAG/HUI] or [1972WHI/LAN] (see main text). This indicates again that the extrapolations of the Tagirov *et al.* data to zero ionic strength by different methods are not equivalent. The difference between the $\mathrm{SIT_1}$ and $\mathrm{SIT_2}$ analyses is due to the fact that $\mathrm{SIT_2}$ is better at taking the low ionic strength data into account. However, as the $\mathrm{SIT_2}$ formulation imposes an increasing slope at low ionic strength, the E° value at zero ionic strength at each temperature is more sensitive to small scatter in the data points, especially if the number of points is limited. So, for obtaining the recommended value of $\mathrm{d}E^{\circ}_T/\mathrm{d}T$ only the Tagirov *et al.* data obtained between 20.8 and 40 °C were used (see the main text).

2.2. SIT treatment of the data as a function of the temperature at various ionic strengths.

Another way to treat the Tagirov *et al.* data at various temperatures by the SIT formalism is to consider the experimental values of E at each ionic strength and to extrapolate the values to zero ionic strength by using the SIT relations (A.177) to (A.180) to calculate $\mathrm{Fe^{3+}}$ and $\mathrm{Fe^{2+}}$ activities.

$$\log_{10}\gamma_j = -z_j^2 D + \textstyle\sum_k \varepsilon(j,k,I_m)\, m_k \qquad (A.177)$$

where j designates an ion of charge z_j which interacts with the ions k of opposite charge, present at molality m_k, in a solution of ionic strength I_m.

So $$\log_{10}\gamma_{\mathrm{Fe3+}} = -9\,D + 0.73\, m_{\mathrm{ClO_4^-}} \quad \mathrm{SIT_1} \qquad (A.178)$$

$$\log_{10}\gamma_{\mathrm{Fe3+}} = -9\,D + (0.78 - 0.41\log_{10}(I_m))\, m_{\mathrm{ClO_4^-}} \quad \mathrm{SIT_2} \qquad (A.179)$$

$$\log_{10}\gamma_{\mathrm{Fe2+}} = -4\,D + 0.37\, m_{\mathrm{ClO_4^-}} \quad \mathrm{SIT_1}\ \text{and}\ \mathrm{SIT_2} \qquad (A.180)$$

The values $E^{\circ}(t)$ so obtained have been plotted as a function of *t*. They all fall on quasi-straight lines with $R^2 > 0.999$, as did the $E^{\circ}(T)$ -values of the original paper. The results of these calculations are listed in Table A-63.

Table A-63: Slopes $\mathrm{d}E^{\circ}(T)/\mathrm{d}T$ of the data of Tagirov *et al.* $E^{\circ}(T)$ as determined by the SIT_1 and SIT_2 formalisms.

$I/\mathrm{mol\cdot kg^{-1}}$	$\mathrm{d}E^{\circ}(T)/\mathrm{d}T \times 10^3/\mathrm{V}$ and R^2 (SIT_1)	$\mathrm{d}E^{\circ}(T)/\mathrm{d}T \times 10^3/\mathrm{V}$ and R^2 (SIT_2)	$\mathrm{d}E^{\circ}(T)/\mathrm{d}T \times 10^3/\mathrm{V}$ [2000TAG/DIA] and R^2
0*			1.28 (0.9989)
0.133	1.32 ± 0.011 (0.9992)	1.31 ± 0.011 (0.9992)	
0.239	1.37 ± 0.012 (0.9990)	1.36 ± 0.012 (0.9990)	
0.348	1.38 ± 0.012 (0.9990)	1.38 ± 0.011 (0.9992)	
0.558	1.38 ± 0.011 (0.9994)	1.36 ± 0.010 (0.9994)	
0.778	1.37 ± 0.010 (0.9996)	1.35 ± 0.006 (0.9998)	
1.336	1.36 ± 0.012 (0.9992)	1.35 ± 0.012 (0.9992)	

* $E^{\circ}(T)$ values obtained by the authors of the original paper using their own extrapolation method to zero ionic strength and their own correction for hydrolysis.

Contrary to what is observed in Table A-62, the SIT_1 and SIT_2 methods of extrapolation of *E* to zero ionic strength yield the same slopes —slopes that do not differ as much from the slope deduced from the $E^{\circ}(T)$ values in the original paper.

The linearity of the function $E^{\circ}(T)$ = f(*T*) (*T* in K) suggests that $\Delta_{\mathrm{r}}C_p^{\circ} \approx 0$ for the reaction $\mathrm{Fe^{3+} + ½H_2(g) \rightleftharpoons H^+ + Fe^{2+}}$. However, we know from the work of Hovey [1988HOV] that $\Delta_{\mathrm{r}}C_p^{\circ}$ differs from zero and that $\Delta_{\mathrm{r}}C_p^{\circ}$ varies as a function of temperature. The data of Hovey have been fitted to Eq. (A.181). The values of the parameters P_1 to P_5, can be used to calculate $\Delta_{\mathrm{r}}S^{\circ}(T)$ by applying Eq. (A.182)

$$\Delta_{\mathrm{r}}C^{\circ}_{p,\mathrm{m}}(T)\ /\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = P_1 + P_2T + P_3T^2 + P_4T^{-1} + P_5T^{-2}$$

or

$$\Delta_{\mathrm{r}}C^{\circ}_{p,\mathrm{m}}(T) = P_1 + P_2(T-273.15) + P_3(T-273.15)^2 + P_4(T-273.15)^{-1} + P_5(T-273.15)^{-2} \quad \text{(A.181)}$$

$$[\,\mathrm{d}E^{\circ}(T)/\mathrm{d}T\,] = \Delta_{\mathrm{r}}S^{\circ}\,(298.15\ \mathrm{K})/F + (1/F)\int_{T_0}^{T}(\Delta_{\mathrm{r}}C_p^{\circ}(T)/T)\mathrm{d}T \quad \text{(A.182)}$$

$P_1 = -\ (364.30 \pm 43.73)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$

$P_2 = (11.746 \pm 1.14)\ \mathrm{J\cdot K^{-2}\cdot mol^{-1}}$

$P_3 = -\ (0.1149 \pm 0.0101)\ \mathrm{J\cdot K^{-3}\cdot mol^{-1}}$

$P_4 = (6082.2 \pm 664.3)\ \mathrm{J\cdot mol^{-1}}$

$P_5 = -\ (24470 \pm 3342)\ \mathrm{J\cdot K\cdot mol^{-1}}$

As was the case for the Whittemore and Langmuir [1972WHI/LAN] data, the term $(1/F)\int_{T_0}^{T}(\Delta_r C_p^o(T)/T)\mathrm{d}T$ is small compared to $\Delta_r S^o$ (298.15 K)/F, and to get the value of $\Delta_r S^o$ (298.15 K) using a constant average value of 57.2 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ for $\Delta_r C_p^o$ simplifies the calculation without significantly changing the final result. Two methods of $\mathrm{d}E°(T)/\mathrm{d}T$ correction at 298.15 K which take into account the value of $\Delta_r C_p^o$ are used. The simplest one is based on Eq. (A.183) in which $T_{½}$ (= 328.15 K) is the mid-temperature of the temperature range of the data set.

$$\Delta[\,\mathrm{d}E^o(T)/\mathrm{d}T\,]_\mathrm{T} = [\,\mathrm{d}E^o(T)/\mathrm{d}T\,]_{\mathrm{T}_{½}} + (\Delta_r C_p/F\ \ln(T/T_{½}))] \qquad \text{(A.183)}$$

with

$$(\Delta_r C_p/F\ \ln(T/T_{½}))\Delta = (57.2/96485.4)\ \ln(298.15/328.55) = -\ 5.76\times10^{-5}\ \mathrm{V{\cdot}K^{-1}}$$

Using the average of the SIT$_2$ slopes, (0.001350 ± 0.000005) $\mathrm{V{\cdot}K^{-1}}$, one obtains:

$$[\,\mathrm{d}E^o(T)/\mathrm{d}T\,]_{298.15\ \mathrm{K}} = (0.00129 \pm 0.00001)\ \mathrm{V{\cdot}K^{-1}}$$

and

$$\Delta_r S^o\ (298.15\ \mathrm{K}) = (124.5 \pm 10.0)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}.$$

The ±10 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ uncertainty is our estimate based on the numerous possible systematic uncertainties, the main contribution being from the extrapolations to zero ionic strength.

The value of $\Delta_r S^o$ (298.15 K) given by the authors was (117.15 ± 6.28) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$. The application of the present method of evaluation applied to their $E^o(T)$ data yields (117.7 ± 10.0) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$. The overlap of the uncertainty range of the original value with the one calculated here using the SIT$_2$ formulation is much better than that obtained by the SIT$_2$ treatment of the data reported above in part 2.1 of this synopsis. As discussed there, the low curvature found for the $E^o(T)$ = f(T) plot is probably due mainly to the uncertainties in the methods used for extrapolation to zero ionic strength.

The second method to calculate $\mathrm{d}E^o(T)/\mathrm{d}T$ is to use Eq. (A.184):

$$E^o(T) - ((\Delta_r C_p^o/F)(T_0 - T) + T(\Delta_r C_p^o/F)\ln(T/T_0) = -\ \Delta_r H^o\ (298.15\ \mathrm{K})/F + T\Delta_r S^o\ (298.15\ \mathrm{K})/F \qquad \text{(A.184)}$$

The linear fit of $E^o(T) - ((\Delta_r C_p^o/F)\ (T_0 - T) + T(\Delta_r C_p^o/F)\ln(T/T_0) = \mathrm{f}(T)$ yields the value of $\Delta_r S^o$ (298.15 K)/F.

As previously found for the [1972WHI/LAN] data, the two methods of calculation lead to similar slope corrections for the linear function $E^o(T)$ = f(T). Using Eq. (A.184) yields a correction of – 0.00006 $\mathrm{V{\cdot}K^{-1}}$, essentially identical to – 0.0000574 $\mathrm{V{\cdot}K^{-1}}$ calculated by use of Eq. (A.183).

Taking into account the value of (124.5 ± 10.0) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ for $\Delta_r S^o$ (298.15 K) and – (74.78 ± 0.20) $\mathrm{kJ{\cdot}mol^{-1}}$ for $\Delta_r G^o$ (298.15 K) as found by applying the SIT_2 formulation, the value of $\Delta_r H^o (298.15\ K)$ is – (37.66 ± 3.00) $kJ.mol^{-1}$, in reasonable agreement with the value in the original paper – (39.33 ± 2.1) $kJ\cdot mol^{-1}$.

For estimating the recommended values of $\Delta_r S^o (298.15\ K)$ and $\Delta_r H^o (298.15\ K)$ from electrochemical data (see main text) we gathered the literature dE/dT values from 5 to 40 °C. Only the lower temperature data of Tagirov *et al.* has been used. This selection is justified by the available literature—there have been several investigations to 35 °C which give results in good agreement. For the higher temperatures, one can expect problems with the kind of cell used by Tagirov *et al.*, such as changes of solution composition due to evaporation or unstable temperatures profiles.

3. Studies in hydrochloric acid medium.

Similar potential measurements from 20.8 to 90 °C were carried out using the cell

$$Pt(s),H_2 \mid HCl(m) \vdots HCl(m)\ ,\ FeCl_2\ (x),\ FeCl_3\ (y)\ |Pt(s).$$

Comparison of the data obtained in hydrochloric acid with those obtained in perchloric acid and the extrapolation of the results to zero ionic strength at 25 °C led to the reported value of 33.1 $kg\cdot mol^{-1}$ for the overall formation constant (inner + outer sphere complexation) for Reaction (A.185) ($\log_{10} \beta_1^o = (1.52 \pm 0.10)$. At 90 °C, the authors found $K_1^o (388.15\ K) = 269.1\ kg\cdot mol^{-1}$. The formation constant values for $FeCl^{2+}$ as a function of the temperature permitted the authors to calculate values of $\Delta_r H_m^o$ and $\Delta_r C_{p,m}^o$.

$$Fe^{3+} + Cl^- \rightleftharpoons FeCl^{2+} \qquad (A.185)$$

$$\log_{10} \beta_1^o = 0.018(T/K) + 420.12/(T/K) - 5.23^1 \qquad (A.186)$$

$$\Delta_r H_m^o = -8.0249 + 0.341(T/K)^2\ kJ\cdot mol^{-1} \qquad (A.187)$$

and

$$\Delta_r C_{p,m}^o = 0.6820(T/K)\ J\cdot K^{-1}\cdot mol^{-1} \qquad (A.188)$$

These results were based on the experimental work in the paper and on additional values taken from the work of Vasil'ev and Lobanov [1967VAS/LOB2]. The results of Vasil'ev and Lobanov were corrected to zero ionic strength, $\Delta_r H_m^o$ by applying an extrapolation equation proposed by Khodakovsky [1975KHO], and the calculation method of Johnson *et al.* [1992JOH/OEL]. From these, $\Delta_r H_m^o (A.185) = 22.47\ kJ\cdot mol^{-1}$ ($\Delta_r S_m^o (A.185) = 104.46\ J\cdot K^{-1}\cdot mol^{-1}$) and $\Delta_r C_{p,m}^o (A.185) = 48.60\ J\cdot K^{-1}\cdot mol^{-1}$ at 298.15 K and zero ionic strength.

The authors also reviewed the literature for the thermodynamic properties of $FeCl_2^+$ and $FeCl_3(aq)$. From the rather scattered values of K_2 for the process $FeCl^{2+}$ +

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[1] There are minor rounding inconsistencies in the values and equations provided by Tagirov *et al.*

$Cl^- \rightleftharpoons FeCl_2^+$ at various ionic strengths they evaluated K_2° by applying the equation proposed by Khodakovsky [1975KHO]:

$$\log_{10} K - \Delta z^2 A_\gamma I^{1/2}/(1 + 4B_\gamma I^{1/2}) = \log_{10} K^\circ + bI$$

where Δz^2 is the difference in the square of charges (products minus reactants); A_γ and B_γ are the Debye-Hückel coefficients, and I is the molal ionic strength. The extrapolation to zero molality yielded a value of 7.08 for K_2° (*cf.* [2000TAG/DIA] Figure 10, $\log_{10} K_2^\circ = (0.85 \pm 0.2)$).

The standard entropy, $\Delta_r S_m^\circ$ and heat capacity $\Delta_r C_{p,m}^\circ$ at 298.15 K and 100 kPa for the reaction $Fe^{3+} + 2Cl^- \rightleftharpoons FeCl_2^+$ were estimated using an *ab initio* calculation of ionic association proposed by Akinfiev [1995AKI]. The model used the previously estimated thermodynamic properties of $FeCl^{2+}$, the interionic distance of the Fe-Cl bond and the frequency of the bond oscillation. That resulted in the values 149.8 $J\cdot K^{-1}\cdot mol^{-1}$ for $\Delta_r S_m^\circ$ and 378.65 $J\cdot K^{-1}\cdot mol^{-1}$ for $\Delta_r C_{p,m}^\circ$.

The literature formation constant values for $FeCl_3(aq)$ were too scattered to permit an extrapolation to zero ionic strength.

Finally the authors proposed a set of thermodynamic constants of formation for the Fe^{3+} ion and its first two chlorido complexes as shown below. These values are not very different from the recommended values given in the main text of the present review. The experimental data from this paper were re-evaluated using the SIT, and appear in the main text (Section VIII.2.3.1.1).

Table A-64: Values of the thermodynamic formation constants for Fe^{3+}, Cl^- and the 1:1 and 2:1 chlorido complexes of Fe(III) at 298.15 K and 100 kPa (based on the authors' Table 12 [2000TAG/DIA]).

	$\Delta_f G_m^\circ$ /kJ·mol^{-1}	$\Delta_f H_m^\circ$ /kJ·mol^{-1}	S_m° /J·K^{-1}·mol^{-1}	$C_{p,m}^\circ$ /J·K^{-1}·mol^{-1}
Fe^{3+}	− 17.24	− 52.93	− 288.28	− 104.39
Cl^-	− 131.29	− 167.07	56.9	− 122.59
$FeCl^{2+}$	− 157.36	− 197.53	− 126.36	− 23.85
$FeCl_2^+$	− 293.53$^{(a)}$	− 356.10$^{(a)}$	− 24.69	29.29

(a) Corrected. In preparing the values for their table (and abstract) the authors appear to have calculated $\Delta_f G_m^\circ(FeCl_2^+)$ using $\log_{10}(K_2^\circ \beta_2^\circ)$ rather than $\log_{10} \beta_2^\circ$.

[2001BEN/ABD]

The authors confirmed that in the presence of phosphate ions a mixture of the carbonate green rust, goethite and ferrihydrite converted spontaneously to a mixture of siderite and magnetite. This confirms that the carbonate green rust, one of the more stable green rusts, is metastable with respect to a siderite-magnetite mixture. Also, no phosphate-containing green rust was formed.

The paper quotes a value of -3590 kJ·mol^{-1} for the Gibbs energy of formation of $(Fe^{III})_2(Fe^{II})_4(OH)_{12}CO_3(s)$ (ignoring waters of hydration) from Génin *et al.* [1998GEN/BOU]. The value is indeed in that reference, but in turn cites an as-then-unpublished article by Refait *et al.*, apparently [1999REF/BON]. However, that reference provides only a value for the sulfate-containing green rust, and that value differs by 5 kJ·mol^{-1} from the value in [1998GEN/BOU] (as does the value for γ-FeOOH). The reference seems to be to the methodology rather than the value. It is not clear what concentration or activity was used for carbonate in the calculation.

[2001CHA/RIC]

Pure sodium tetrasulfide (Na_2S_4) was prepared and reacted with divalent cations of Mn, Fe, Co, Ni, Cu and Zn in aqueous solution at 25 °C, and at concentrations below 10 μM of S_4^{2-}. Square-wave voltammetry and cyclic voltammetry at mercury electrodes were used to monitor the S_4^{2-} peak and to determine (i) the stoichiometry of the metal tetrasulfide complexes, (ii) the extent of protonation of the tetrasulfide in the complex, and the pK_a of the complexes, and (iii) the stability constants of the complexes. The successive-extrapolation method was used to determine the formation constants of complexes, where the function, $F_0(X) = 1 + \beta_1[X] + \beta_2[X]^2 + \ldots + \beta_n[X]^n$ ([X] is the analytical concentration of the metal ion) was related to the peak potential (E_p) and peak current (I_p) by $F_0(X) = \text{antilog}\{[0.434nF/RT][(E_p)_s - (E_p)_c] + [\log_{10}(I_p)_s/(I_p)_c]\}$ ($n = -2$, c indicates complexed S_4^{2-} and s indicates free S_4^{2-}). $F_0(X)$, $F_1(X) = [F_0(X) - 1]/[X]$, $F_2(X) = [F_1(X) - \beta_1]/[X]$, … , and $F_n(X) = [F_{n-1}(X) - \beta_{n-1}]/[X]$ were calculated to determine β_n values. For Fe(II), $\log_{10}\beta_n$ the values (5.98 ± 0.14) ($FeS_4(aq)$) and (11.24 ± 0.21) ($Fe_2(S_4)^{2+}$) were obtained in 0.50 M Na_2SO_4 and (5.97 ± 0.09) ($FeS_4(aq)$) and (11.34 ± 0.06) ($Fe_2(S_4)^{2+}$) were obtained in 0.55 M NaCl. Analytical concentrations were used and no activity corrections were made in the authors' calculation. The relation of the electrode reaction or $F_0(X)$ to the equilibrium concentrations of the uncomplexed and complexed species is not strongly enough established. Also in the data processing, the difference between the analytical concentrations and the equilibrium concentrations are not well considered. The values obtained for $\log_{10}\beta_1$ for Mn(II), Fe(II), Co(II) and Ni(II) listed in Table 2 in the paper indicates that, in some cases, $\log_{10}\beta_2/\beta_1$ are larger than $\log_{10}\beta_1$. This is unreasonable because it means that, with the increase in [M], S_4^{2-} or $M_2(S_4)^{2+}$ always predominates and the determination of $\log_{10}\beta_1$ for $MS_4(aq)$ is difficult. This review does not accept the values from this paper.

[2001CHE/SUN]

The following equations from the assessment of Chen and Sundman have been used in the present review to calculate the thermodynamic quantities for iron metal between 800 and 1800 K at 0.101325 MPa.

R is the gas constant 8.31451 kJ·mol^{-1}, T/K is the temperature.

For the bcc $G(T)$ and $C_\mathrm{p}(T)$ equations

$T_\mathrm{C} = 1043\ \mathrm{K}$

$\beta = 2.22$

$\mathrm{p} = 0.37$

$\Theta_\mathrm{E} = 309\ \mathrm{K}$

$\mathrm{G_{IN}} = 1.5R\Theta_\mathrm{E} + 3RT\,ln(1 - \mathrm{e}^{-\Theta_\mathrm{E}/T})$

$\mathrm{D_1} = 0.33471979$

$\mathrm{D_2} = 0.49649686$

$\mathrm{D} = \mathrm{D_1} + \mathrm{D_2}(1/\mathrm{p} - 1)$

$\mathrm{G^{mdo}}(\infty) = -R[T\,ln\,(\beta + 1)][T - 0.38438376\ T_\mathrm{C}/\mathrm{pD}]$

$\tau = T/T_\mathrm{C}$

If $\tau \leq 1$:

$\mathrm{f}(\tau) = 1 - [0.38438376\,\tau^{-1}/\mathrm{p} + 0.63570895\,(1/\mathrm{p} - 1) \times (\tau^3/6 + \tau^9/135 + \tau^{15}/600 + \tau^{21}/1617)]/\mathrm{D}$

$C_p^\mathrm{mag} = R\,ln(\beta + 1)\ [0.63570895(1/\mathrm{p} - 1) \times (2\tau^3 + 2\tau^9/3 + 2\tau^{15}/5 + 2\tau^{21}/7)]/\mathrm{D}$

If $\tau > 1$:

$\mathrm{f}(\tau) = [\tau^{-7}/21 + \tau^{-21}/630 + \tau^{-35}/2975 + \tau^{-49}/8232]/\mathrm{D}$

$C_p^\mathrm{mag} = R\,ln(\beta+1)\ [2\tau^{-7} + 2\tau^{-21}/3 + 2\tau^{-35}/5 + 2\tau^{-49}/7]/\mathrm{D}$

$\mathrm{G^{mo}} = -R[T\,ln\,(\beta + 1)]\ \mathrm{f}(\tau)$

$\mathrm{a_1} = -8.41026596 \times 10^3$

$\mathrm{a_2} = -3.2390815 \times 10^{-3}$

$\mathrm{a_3} = -3.3191339 \times 10^{-14}$

$\mathrm{G_{bcc}} = \mathrm{a_1} + \mathrm{a_2}T^2 + \mathrm{a_3}T^5 + \mathrm{G_{IN}} + \mathrm{G^{mdo}}(\infty) + \mathrm{G^{mo}}$

$C_p^\mathrm{bcc} = 3R(\Theta_\mathrm{E}/T)^2\ \mathrm{e}^{\Theta_\mathrm{E}/T}/(\mathrm{e}^{\Theta_\mathrm{E}/T} - 1)^2 - 2\mathrm{a_2}T - 20\mathrm{a_3}T^4 + C_p^\mathrm{mag}$

For the fcc $G(T)$ and $C_\mathrm{p}\,(T)$ equations

$T_\mathrm{N} = 67\ \mathrm{K}$

$\beta = 0.70$

$\mathrm{p} = 0.25$

$\Theta_\mathrm{E} = 309\ \mathrm{K}$

$G_{IN} = 1.5R\Theta_E + 3RT\,ln(1 - e^{-\Theta_E/T})$

$\Delta G_{2ST} = 9.02352375 \times 10^3 - 2.49522260\,T$

$G_{2ST} = -RT\,ln(1 + e^{-(\Delta G_{2ST}/RT)})$

$D_1 = 0.33471979$

$D_2 = 0.49649686$

$D = D_1 + D_2(1/p - 1)$

$G^{mdo}(\infty) = -R[T\,ln\,(\beta + 1)][T - 0.38438376\,T_C/pD]$

$\tau = T/T_N$

If $\tau \leq 1$:

$$f(\tau) = 1 - [0.38438376\,\tau^{-1}/p + 0.63570895\,(1/p - 1) \times (\tau^3/6 + \tau^9/135 + \tau^{15}/600 + \tau^{21}/1617)]/D$$

$$C_p^{mag} = R\,ln(\beta + 1)\,[0.63570895(1/p - 1) \times (2\tau^3 + 2\tau^9/3 + 2\tau^{15}/5 + 2\tau^{21}/7)]/D$$

If $\tau > 1$:

$$f(\tau) = [\tau^{-7}/21 + \tau^{-21}/630 + \tau^{-35}/2975 + \tau^{-49}/8232]/D$$

$$C_p^{mag} = R\,ln(\beta + 1)\,[2\tau^{-7} + 2\tau^{-21}/3 + 2\tau^{-35}/5 + 2\tau^{-49}/7]/D$$

$$G^{mo} = -R[T\,ln\,(\beta + 1)]\,f(\tau)$$

$$a_1 = -2.61500904 \times 10^3$$

$$a_2 = -2.7933375 \times 10^{-3}$$

$$a_3 = -2.1239087 \times 10^{-14}$$

$$G_{fcc} = a_1 + a_2T^2 + a_3T^5 + G_{IN} + G_{2ST} + G^{mdo}(\infty) + G^{mo}$$

$$C_p^{fcc} = 3R(\Theta_E/T)^2\,e^{\Theta_E/T}/(e^{\Theta_E/T} - 1)^2 - 2a_2T - 20a_3T^4 + C_p^{mag}$$

[2001ZHA/PAN]

The formation of iron(II) chlorido complexes was studied by Zhao and Pan at several temperatures (10, 25, 40, 60, 80 and 100 °C) in NaCl/LiCl solutions of various concentrations by means of UV and near-ir spectrophotometry. The information in this paper is taken directly from the thesis of Zhao [1997ZHA]. The evaluation of formation constants was done using two different models, and the resulting average of the two evaluations was used. The evaluation according to a model of Helgeson *et al.* [1981HEL/KIR] was documented and seems straight forward. A second evaluation was done using the approach of Pitzer [1977PIT]. Temperature derivatives for the Pitzer coefficients for the Fe^{2+}, Cl^- system were taken as similar as those for the Co^{2+}, Cl^- system, and initial $FeCl^+$,Cl^- Pitzer parameters were taken to be analogous to those for the CuCl^+,Cl^- system. References to all of the necessary Pitzer parameters are given, but no attempt has been made to reproduce the complex procedure that was used for the iterative calculation of the parameters for the FeCl^+,Cl^- system.

Re-evaluation of absorption spectra provided in the authors' Figure 3 at 10, 25 and 40 °C was performed according to the procedure given in the Appendix_A entry [1990HEI/SEW], using corrected absorptivities for FeCl^+ (shifted by 4 nm) from the authors' Figure 9. Table A-65 lists the spectra as digitized from the top part of Figure 3 in [2001ZHA/PAN].

Table A-65: 25 °C molar decadic absorption coefficients (columns 2 and 3) extracted from Figure 9 of [2001ZHA/PAN]. The spectrum for FeCl^+ is shifted towards higher wavelengths by 4 nm (see Figure A-40 in the Appendix A entry [1990HEI/SEW]). Digitized absorbances for the system {0.07491 M FeCl_2 in 4.300 m NaCl} at different temperatures are shown in columns 4 to 6. Equally spaced values were obtained from processing digitized data with spline procedures.

Wavelength [nm]	$\varepsilon_{\text{Fe}^{2+}}$ [m^2/mol]	$\varepsilon_{\text{FeCl}^+}$ [m^2/mol]	10 °C	25 °C	40 °C
220	22.12			2.547	2.750
222	21.58		2.244	2.408	2.582
224	20.94	46.55	2.163	2.303	2.457
226	20.28	43.49	2.075	2.202	2.334
228	19.75	41.30	2.000	2.122	2.252
230	19.52	39.53	1.937	2.057	2.164
232	19.08	37.88	1.876	1.985	2.094
234	18.89	36.56	1.828	1.939	2.043
236	18.66	35.31	1.783	1.892	2.003
238	18.38	34.18	1.753	1.864	1.966
240	18.30	33.40	1.725	1.839	1.947
242	18.14	32.71	1.708	1.823	1.943
244	17.76	32.12	1.699	1.815	1.934
246	17.38	31.95	1.683	1.806	1.929
248	16.79	31.71	1.668	1.792	1.920
250	16.01	31.63	1.633	1.768	1.896
252	15.02	31.41	1.588	1.720	1.851
254	13.87	30.88	1.514	1.652	1.786
256	12.54	30.06	1.430	1.561	1.700
258	10.97	29.03	1.313	1.450	1.584
260	9.55	27.58	1.188	1.324	1.458
262	8.15	25.66	1.044	1.181	1.305
264	6.85	23.51	0.906	1.030	1.152
266	5.51	21.19	0.765	0.879	1.001
268	4.51	18.92	0.643	0.741	0.851
270	3.68	16.38	0.517	0.612	0.715

(Continued on next page)

Table A-65 (continued)

Wavelength [nm]	$\varepsilon_{\mathrm{Fe}^{2+}}$ [m^2/mol]	$\varepsilon_{\mathrm{FeCl}^{+}}$ [m^2/mol]	10 °C	25 °C	40 °C
272	2.86	13.98	0.422	0.504	0.593
274	2.27	11.76	0.323	0.394	0.474
276	1.70	9.71	0.242	0.309	0.383
278	1.30	7.92	0.185	0.236	0.301
280	1.04	6.34	0.144	0.179	0.227
282	0.79	4.94	0.100	0.132	0.177
284	0.60	3.80	0.078	0.094	0.129
286		2.96	0.050	0.063	0.089
288		2.21	0.032	0.038	0.061

The densities of solutions for which results are shown in Figure 3 of [2001ZHA/PAN], were calculated according to equations provided by Söhnel and Novotný [1985SOH/NOV]. The concentration quotients $\log_{10}\beta_1$ for the reaction Fe^{2+} + $\mathrm{Cl}^{-} \rightleftharpoons \mathrm{FeCl}^{+}$ at 10, 25 and 40 °C in 4.3 m NaCl solutions were calculated according to the procedure outlined in the Appendix A entry for [1990HEI/SEW] (also see Equation A-2) and are provided in Table A-66.

Table A-66: Logarithm (base 10) of the concentration quotients for $\mathrm{Fe}^{2+} + \mathrm{Cl}^{-} \rightleftharpoons \mathrm{FeCl}^{+}$ at 10, 25 and 40 °C in 4.3 m NaCl.

t	$\log_{10}\beta_1$	I_m
10 °C	-1.095 ± 0.105	4.485
25 °C	-0.918 ± 0.082	4.473
40 °C	-0.772 ± 0.069	4.461

According to equation 19 in TDB-4 [1999PUI/RAR], *i.e.*, by assuming that the standard molar enthalpy of reaction does not vary over the temperature range 10 to 40 °C, the regression of the $\log_{10}\beta_1$ values from Table A-66 against $(1/T_0 - 1/T)$ produces

$$\Delta_r H_m \text{ (4.3 m NaCl, 25 °C)} = (18.2 \pm 6.9)\ \mathrm{kJ\cdot mol^{-1}}$$

and

$$\log_{10}\beta_1 \text{ (4.3 m NaCl, 25 °C)} = -(0.923 \pm 0.049)$$

These values have not been corrected to zero ionic strength.

Figure A-63: Determination of $\Delta_r H_m$ ($Fe^{2+} + Cl^- \rightleftharpoons FeCl^+$) from spectrophotometric data provided in Figure 3 of [2001ZHA/PAN].

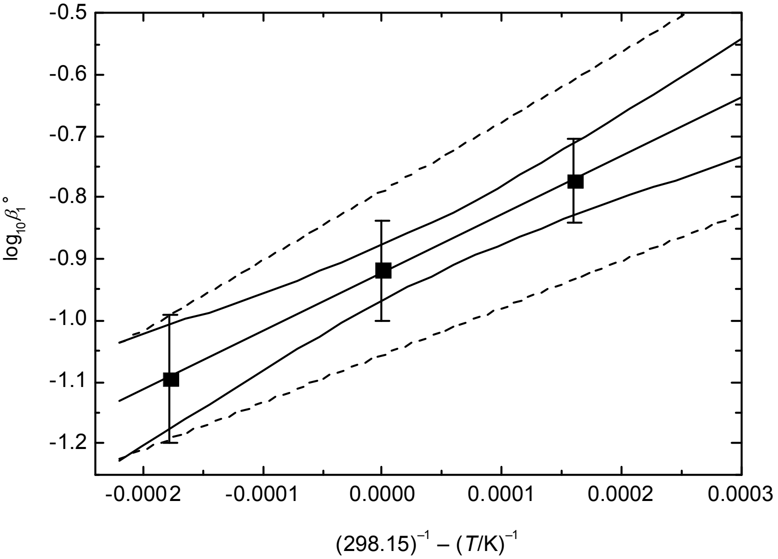
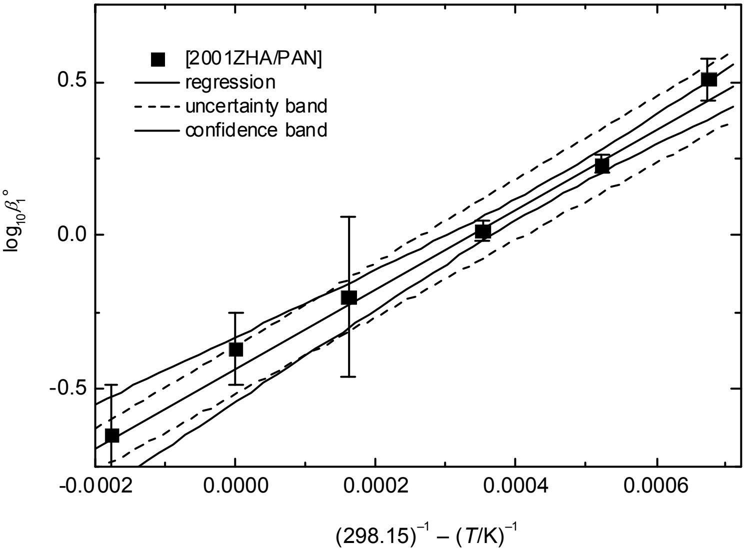


Figure A-64: A regression of $\log_{10}\beta_1^\circ$ vs. $1/T$ using values from Table 2 of [2001ZHA/PAN] but with doubled uncertainties.



The authors listed values for $\log_{10} \beta_1^{\text{o}}$ at different temperatures in their Table 2. Their enthalpy and entropy of reaction values for the formation of the 1:1, 2:1 and 4:1 complexes are shown in Table A-67. The β values were calculated as averages from two different model evaluations of their UV data (and excluding their near-ir spectral data). A regression using the authors' values but doubling their uncertainties (Figure A-64) leads to the values $-(0.436 \pm 0.062)$ for $\log_{10} \beta_1^{\text{o}}$ (FeCl^+, 298.15 K), and $(24.91 \pm 2.54_6)$ $\text{kJ}\cdot\text{mol}^{-1}$ for $\Delta_{\text{r}}H_{\text{m}}$ (298.15 K).

Table A-67: Values for $\log_{10} \beta_i^{\text{o}}$ for 298.15 K and the reported enthalpy of reaction values for the association of Cl^- with Fe^{2+}.

	$\log_{10} \beta_i^{\text{o}}$ (298.15 K) $^{(a)}$	$\log_{10} \beta_i^{\text{o}}$ (298.15 K) $^{(b)}$	$\Delta_{\text{r}}H^{\text{o}\ (b)}$/ $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{r}}S^{\text{o}\ (b)}$/ $\text{J}\cdot\text{K}^{-1}\text{mol}^{-1}$
FeCl^+	– 0.366 0.059	– 0.41 ± 0.28	24.7 ± 1.2	75.0 ± 3.6
$\text{FeCl}_2\text{(aq)}$	– 1.74 ± 0.02	– 1.42 ± 0.36	9.9 ± 1.5	6.1 ± 4.7
FeCl_4^{2-}	———	– 5.4 ± 0.57	71.4 ± 2.5	136 ± 7

(a) based only on data for 298.15 K. The value reported for $\log_{10} \beta_4^{\text{o}}$ at 333.15 K was – 4.1.

(b) based on regression of data from 283.15 to 373.15 K (assuming that $\Delta_{\text{r}}C_p = 0\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)

Considering the small size of the formation constants, neither these nor the enthalpies or entropies of reaction for the higher complexes are recommended values in the present review.

[2002APE/KOR]

Solid $\text{FeCl}_3\cdot6\text{H}_2\text{O}$ (99.9%) was used as the source of the salt. The temperature was controlled to within 0.05 K. The vapour pressures of solutions in contact with solid iron(III) chloride were measured by a hygrometric technique. Their vapour-pressure data are plotted against temperature in Figure A-65, where the solid line is a fit of these data Eq. (A.189) and the dashed line Eq. (A.190) was generated by the authors' equation which includes selected results from [1962KAN/GRO].

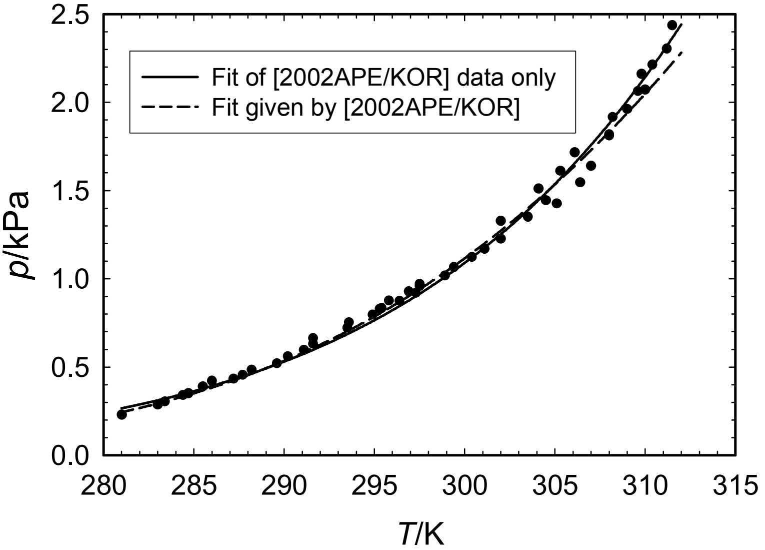
The authors speculate that above 298 K the solutions may be supersaturated with respect to iron(III) chloride.

$$\ln\{ p_{\text{H}_2\text{O}}(\text{FeCl}_3, T, m_{\text{sat}})/\text{kPa}\} = 7.285 - 5663.45(T/\text{K})^{-1} + 2.0477 \ln(T/\text{K}) \quad \text{(A.189)}$$

$$\ln\{ p_{\text{H}_2\text{O}}(\text{FeCl}_3, T, m_{\text{sat}})/\text{kPa}\} = 521.10 - 28436(T/\text{K})^{-1} - 74.723 \ln(T/\text{K}) \quad \text{(A.190)}$$

using p_{sat} for pure water at 298.15 K of 3.1699 kPa and taking $m_{\text{sat}}(\text{FeCl}_3\text{(sln)}) = 5.90\ \text{mol}\cdot\text{kg}^{-1}$ (relative molecular mass of water = 18.0153) from the present study, $\phi = 2.81$ with Eq. (A.189) and $\phi = 2.75$ with Eq. (A.190), although Apelblat and Korin cite a value of 2.73.

Figure A-65: Plot of the vapour pressure (kPa) *vs.* temperature (kelvin) over saturated acidified iron(III) chloride solutions.



As discussed in Section VI.4, the osmotic coefficient derived from their data at 298.15 K for an assumed saturated solution of 5.90 mol·kg^{-1} is anomalously higher than would be anticipated from other studies of undersaturated solutions of iron(III) chloride. Consequently their results were not accepted in the current review.

[2002APE/KOR2]

The vapour pressures of saturated solutions of $AlCl_3$, $Al(NO_3)_3$ and $Al_2(SO_4)_3$ were measured over a narrow range of temperatures, *ca.* 280 to 297 K. The authors report the following osmotic coefficients at 298.15 K: $AlCl_3$, m_{sat} = 3.43 mol·kg^{-1}, ϕ = 3.36; $Al(NO_3)_3$, m_{sat} = 3.25 mol·kg^{-1}, ϕ = 2.24; $Al_2(SO_4)_3$, m_{sat} = 1.094 mol·kg^{-1}, ϕ = 1.927. The molar enthalpies of solution of aluminium chloride hexahydrate, aluminium nitrate nonahydrate and aluminum sulfate octadecahydrate are reported.

The osmotic coefficient results are well beyond the range of linear application of the SIT model and were therefore not considered further in this review.

[2002CHO/SEA]

This paper presents experimental measurements of water-vapour pressures over melanterite-rozenite mixtures ($FeSO_4\cdot7H_2O$-$FeSO_4\cdot4H_2O$) at temperatures from below 40 °C to above 60 °C by a gas-flow method, and by an isopiestic method (similar to that used by Malinin *et al.* [1979MAL/DRA]) at 309.28 K (4.303 kPa), 314.19 K

(5.826 kPa) and 321.45 K (9.234 kPa).[1] The experimental results are completely compatible with the measurements done at lower temperatures [1979MAL/DRA], and the detail provided on characterization of the solids is much more extensive.

The results were used to estimate the enthalpy and Gibbs energy of reaction over the limited temperature range (36.1 to 48.3 °C) for

$$FeSO_4{\cdot}7H_2O(cr) \rightleftharpoons FeSO_4{\cdot}4H_2O(cr) + 3\,H_2O(g). \qquad (A.191)$$

The limited experimental results lead to $\Delta_r H^o_m$(A.191) = (155.9 ± 5.6) kJ·mol^{-1}. For weighting purposes, uncertainties of 50 Pa were estimated; primarily, these uncertainties arise from uncertainties in the vapour pressures assumed for the reference solutions.

[2002CIA/TOM]

The competition between Fe^{2+} and H^+ for the sulfate ion was measured with a glass electrode in 3 mol·dm^{-3} $NaClO_4$ at 25 °C. The results were interpreted in terms of the two complexes $FeSO_4$(aq) and $Fe(SO_4)_2^{2-}$. The paper very carefully discusses the effects of medium changes on the potential differences found for the electrochemical cell (although there seem to be some "cut and paste" misprints in Equation 8).

A key point in the evaluation is the formation constant for HSO_4^-. The simultaneous fit for all three constants leads to $\log_{10} K(HSO_4^-$, 25 °C, 3 M $NaClO_4$) = (1.027 ± 0.005). Separate titrations in the absence of Fe(II) produced $\log_{10} K$ = (1.013 ± 0.005) (3σ). Recalculation to I = 0 produces $\log_{10} K^o(HSO_4^-$, 25 °C) = (1.98 ± 0.16), essentially identical to the value of (1.980 ± 0.050) based on CODATA [1989COX/WAG] and used in the TDB series [1992GRE/FUG]. This excellent agreement of $\log_{10} K(HSO_4^-)$ in two independent experiments and of $\log_{10} K^o(HSO_4^-)$ with the value earlier recommended by the NEA review indicates a high reliability for all constants derived from given experimental data. This is particularly true for $\log_{10} \beta_1(FeSO_4$, aq, 25 °C, 3 M $NaClO_4$) = (0.60 ± 0.05).

It is interesting to note that without applying rigorous corrections of systematic errors caused by medium changes, the evidence for the $Fe(SO_4)_2^{2-}$ complex would not be conclusive. In their recalculation to I = 0 the authors used interaction coefficients that differ slightly from those adopted in the NEA review series[2]:

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[1] Their reanalysis of the earlier work of Milanin for 31.47 °C uses the tabulated relative humidity values for saturated NaBr(sln) from Greenspan [1977GRE] (not the equation, which appears to contain a typographical error).

[2] The authors also discussed the impact of the possible formation of the complex $NaSO_4^-$. However, they did not correct their constants with the factor (1 + $K_{Na}[Na^+]$) (or with powers of it). Note that this factor would range from 1.55 to 1.94 (when considering $\log_{10} K^o_{Na}$ = (0.7 ± 0.1) as mentioned by the authors, with

[2002CIA/TOM]	This review
$\varepsilon(\mathrm{Fe}^{2+}, \mathrm{ClO}_4^-) = 0.33\ \mathrm{kg{\cdot}mol^{-1}}$	$(0.37 \pm 0.04)\ \mathrm{kg{\cdot}mol^{-1}}$
$\varepsilon(\mathrm{Na}^{+}, \mathrm{HSO}_4^-) = (0.04 \pm 0.04)\ \mathrm{kg{\cdot}mol^{-1}}$	$-(0.01 \pm 0.02)\ \mathrm{kg{\cdot}mol^{-1}}$
$\varepsilon(\mathrm{Na}^{+}, \mathrm{SO}_4^{2-}) = -0.11\ \mathrm{kg{\cdot}mol^{-1}}$	$-(0.12 \pm 0.06)\ \mathrm{kg{\cdot}mol^{-1}}$ or $(-(0.184 \pm 0.002) + (0.139 \pm 0.006)\cdot\log_{10} I_m)\ \mathrm{kg{\cdot}mol^{-1}}$, *i.e.*, between -0.108 and $-0.101\ \mathrm{kg{\cdot}mol^{-1}}$ for $3.5 < I_m < 3.94$.
$\varepsilon(\mathrm{FeSO_4}, \mathrm{NaClO_4}) = (0.11 \pm 0.05)\ \mathrm{kg{\cdot}mol^{-1}}$	use of this ε is incompatible with the model used

Additions of $FeSO_4$, Na_2SO_4 and $HClO_4$, necessary to vary the chemical composition, produced test solutions with a range of ionic strengths. For 3 M $NaClO_4$ at 25 °C, the factor for conversion to molal units (based on the density equation from Söhnel and Novotný [1985SOH/NOV]) is $1.1677\ \mathrm{dm^3{\cdot}kg_{H_2O}^{-1}}$, but may become as great as $1.233\ \mathrm{dm^3{\cdot}kg_{H_2O}^{-1}}$ for the maximum ionic strength. In the present case I_m varies from 3.50 to the maximum of $(3.94 - 4\,[\mathrm{FeSO_4}]\ \mathrm{mol{\cdot}kg^{-1}}$ ($I_m = (3.72 \pm 0.22)\ \mathrm{mol{\cdot}kg^{-1}}$)). The potential correction arising from the uncertainty in ionic strength is estimated to be of the order of 0.05 $\log_{10}$-units ($\log_{10}(1.233/1.1677) + 8(D(I_m = 3.94) - D(I_m = 3.5))$), which is already covered by the assessed uncertainty.

[2002CIA/TOM2]

This paper deals with the results of electrochemical potential and spectrophotometric measurements for determination of formation constants for $\mathrm{FeSO_4^+}$, $\mathrm{Fe(SO_4)_2^-}$ and $\mathrm{FeHSO_4^{2+}}$. The equilibria have been investigated at 25 °C in 3 M $NaClO_4$. The concentration $c_{\mathrm{H^+}}$ was maintained sufficiently high, ≥ 0.1 M, to prevent hydrolysis of more than 1% of the iron(III).

The auxiliary values necessary for the determination of the Fe(III) sulfate-species stability constants, such as the formation constants of Fe(II) sulfato complexes and the protonation constant of $\mathrm{SO_4^{2-}}$, were taken from a previous study [2002CIA/TOM]. The total concentration of iron(III) was varied between 0.0001 and 0.005 M and the total sulfate concentration was varied between 0.1 and 0.65 M. Equilibrium constants at zero ionic strength were obtained by applying the SIT treatment.

Potentiometry

Titrations were carried out using two electrochemical redox cells:

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correction to 3 M $NaClO_4$) and would produce additional corrections of (0.24 ± 0.05) $\log_{10}$-units (and (0.48 ± 0.10) $\log_{10}$-units in the case of the $\mathrm{Fe(SO_4)_2^{2-}}$ complex).

Cell G, potential E_G, to measure c_{H^+}

reference ⁝ test solution | glass electrode

Cell R, potential E_R, to measure $c_{Fe^{3+}}$

reference ⁝ test solution, Fe^{3+}, Fe^{2+} | Pt electrode

The reference electrode was

Ag,AgCl | 0.01 M $AgClO_4$, 2.99 M $NaClO_4$ ⁝⁝ 3 M $NaClO_4$

Equations (A.192) and (A.193) express the electrochemical potentials (E_G and E_R), in mV, of the cells G and R.

$$E_G = E_G^{\circ\prime} + (RT(\ln(10))/F)\log_{10} c_{H^+} + E_{jG} \quad (A.192)$$

$$E_R = E_G^{\circ\prime} + (RT(\ln(10))/F)\log_{10} (c_{Fe^{3+}} / c_{Fe^{2+}}) + E_{jR} \quad (A.193)$$

$E^{\circ\prime}_G$ and $E^{\circ\prime}_R$ were assumed constant for each titration. The junction potentials

$$E_{jG} = -17\, c_{H^+} - 23\, c_{SO_4^{2-}}$$

$$E_{jR} = -17\, c_{H^+} - 42\, c_{SO_4^{2-}}$$

were estimated by the authors from the variation of activity coefficients when Na^+ ions were replaced by H^+ [1953BIE/SIL] (the $-17\, c_{H^+}$ terms), and when ClO_4^- ions were replaced by SO_4^{2-} or HSO_4^- [2002CIA/TOM] (the SIT-based terms $-23\, c_{SO_4^{2-}}$ and $-42\, c_{SO_4^{2-}}$).

In this paper [2002CIA/TOM2], the equilibrium constants were designated as $\beta_{q,m,r}$, and refer to the reactions given in Eqs. (A.194) to (A.196). For each species, m was equal to the number of Fe^{3+}, q to the number of H^+, and r to the number of sulfato ligands. Two different complexation models were fitted to the experimental data (80 values based on four titrations). Model (1) considered only two complexes 0:1:1 and 0:1:2 ($FeSO_4^+$ and $Fe(SO_4)_2^-$); model (2) considered three species, 0:1:1, 0:1:2 and 1:1:1 ($FeSO_4^+, Fe(SO_4)_2^-$ and $FeHSO_4^{2+}$).

The choice of model was made by comparing the values of $\Sigma(E_{obs} - E_{calc})^2$, and in the present case the model with the 0:1:1, 0:1:2 and 1:1:1 complexes (model (2)) was slightly better. The authors' values and 3σ uncertainties are:

$$Fe^{3+} + SO_4^{2-} \rightleftharpoons FeSO_4^+$$

$$\log_{10} \beta_{0,1,1c} (\equiv \log_{10} \beta_{1c}) = (1.71 \pm 0.01) \text{ (model (1)) or } (1.65 \pm 0.02) \text{ (model (2))} \quad (A.194)$$

$$Fe^{3+} + 2SO_4^{2-} \rightleftharpoons Fe(SO_4)_2^-$$

$$\log_{10} \beta_{0,1,2c} (\equiv \log_{10} \beta_{2c}) = (2.64 \pm 0.02) \text{ (model (1)) or } (2.68 \pm 0.02) \text{ (model (2))} \quad (A.195)$$

$$Fe^{3+} + H^+ + SO_4^{2-} \rightleftharpoons FeHSO_4^{2+}$$

$$\log_{10} \beta_{1,1,1c} = (2.36 \pm 0.20) \text{ (model (2))} \quad (A.196)$$

Spectrophotometry

The absorbances from 28 test solutions at 18 wavelengths were processed by the HYPERQUAD computer program [1996GAN/SAB] (authors' 3σ uncertainties). Again, the model with three species gave the better fit.

$$\log_{10}\beta_{0,1,1c}\ (\equiv \log_{10}\beta_{1c}) = (1.67 \pm 0.03)\ \text{(model (1)) or } (1.55 \pm 0.12)\ \text{(model (2))}$$

$$\log_{10}\beta_{0,1,2c}\ (\equiv \log_{10}\beta_{2c}) = (2.47 \pm 0.12)\ \text{(model (1)) or } (2.77 \pm 0.20)\ \text{(model (2))}$$

$$\log_{10}\beta_{1,1,1c} = (2.39 \pm 0.26)\ \text{(model (2))}$$

The results from the two techniques are consistent. The authors of the article extrapolated these numbers to zero ionic strength by using the SIT treatment. They obtained:

$$\log_{10}\beta^{\circ}_{0,1,1} = (3.82 \pm 0.17);\ \log_{10}\beta^{\circ}_{0,1,2} = (5.75 \pm 0.17);\ \log_{10}\beta^{\circ}_{1,1,1} = (3.68 \pm 0.35).$$

The values of the interaction coefficients used by Ciavatta *et al.*, both those used in this paper after conversion to the molal scale, and those used by us in the present review are listed in Table A-68. The auxiliary constants, needed to determine the values of the formation constants for the Fe(III) complexes, those of Ciavatta *et al.* converted to the molal scale and those used in this review are compared in Table A-69.

No tables of experimental values are given in this paper. So except for conversion of the results from the molar scale to the molal scale, no reanalysis has been done. There were a large number of experimental measurements, and because of this and the careful reasoning behind the data analysis, the results of this paper were included in the overall selection of values, $\beta^{\circ}_{q,m,r}$, for the formation constants of the complexes, and in evaluation of the interaction coefficients.

Table A-68: Comparison of the SIT interaction coefficients used in this paper [2002CIA/TOM2] with those used in the present review.

Interaction	Ciavatta *et al.* $dm^3 \cdot mol^{-1}$	Ciavatta *et al.* $kg \cdot mol^{-1}$	this review $kg \cdot mol^{-1}$
$\varepsilon(Fe^{2+}, ClO_4^-)$	0.39	0.33	0.37 ± 0.04 [f]
$\varepsilon(Fe^{3+}, ClO_4^-)$	0.64	0.55	0.73 ± 0.04
$\varepsilon(Na^{+}, ClO_4^-)$	0.01	0.01	0.01 ± 0.01
$\varepsilon(Na^{+}, SO_4^{2-})$	– 0.11	– 0.13	-0.12 ± 0.06
$\varepsilon(Fe^{2+}, SO_4^{2-})$	– 0.29 [a]	– 0.25	no value
$\varepsilon(Fe^{3+}, SO_4^{2-})$	– 0.39 [b]	– 0.33	no value
$\varepsilon(Na^{+}, HSO_4^-)$	0.01	0.01	-0.01 ± 0.02
$\varepsilon(Fe^{2+}, HSO_4^-)$	0.39 [c]	0.33	0.37 ± 0.04 [g]
$\varepsilon(Fe^{3+}, HSO_4^-)$	0.64 [d]	0.55	0.73 ± 0.05 [g]

(Continued on next page)

Table A-68 (continued)

Interaction	Ciavatta *et al.* $dm^3\cdot mol^{-1}$	Ciavatta *et al.* $kg\cdot mol^{-1}$	this review $kg\cdot mol^{-1}$
$\varepsilon(H^+, SO_4^{2-})$	0.18 $^{(e)}$	0.15	0.14 ± 0.04 $^{(i)}$
$\varepsilon(H^+, HSO_4^-)$			– 0.03 ± 0.04 $^{(h)}$
$\varepsilon(FeSO_4^+, ClO_4^-)$			0.4 ± 0.1 $^{(j)}$
$\varepsilon(Na^+, Fe(SO_4)_2^-)$			0.24 ± 0.14 $^{(j)}$
$\varepsilon(Na^+, HSO_4^-)$			– 0.01 ± 0.01 $^{(k)}$

(a) From the value of $\varepsilon(Mg^{2+}, SO_4^{2-})$.
(b) From the value of $\varepsilon(Al^{3+}, SO_4^{2-})$.
(c) From the value of $\varepsilon(Fe^{2+}, ClO_4^-)$.
(d) From the value of $\varepsilon(Fe^{3+}, ClO_4^-)$.
(e) From osmotic coefficients of H_2SO_4.
(f) From the value of $\varepsilon(Ni^{2+}, ClO_4^-)$.
(g) Assuming that HSO_4^- interacts as ClO_4^-.
(h) From the value of $\varepsilon(Li^+, SO_4^{2-})$.
(i) From the value of $\varepsilon(H^+, ClO_4^-)$.
(j) Determined in this review.
(k) From the value of $\varepsilon(Na^+, ClO_4^-)$.

Table A-69: Auxiliary values (sulfato complexation constants for iron(II) and the protonation constant of sulfate ion) used by Ciavatta *et al.* [2002CIA/TOM2] and those used in this review. The formation constant values are in concentration (molar) units or molal units as noted, and are appropriate for calculations involving small amounts of the species in 3 M $NaClO_4$(sln)).

	Ciavatta *et al.* $mol^{-1}\cdot dm^3$	Ciavatta *et al.* $mol^{-1}\cdot kg$	this review $mol^{-1}\cdot kg$
$\log_{10}\beta_{1FeSO_4(aq)}$	0.6	0.53	1.314 ± 0.245 *
$\log_{10}\beta_{2Fe(SO_4)_2^-}$	0.87	0.8	no value
$\log_{10}K_{1,1(HSO_4^-)}$	1.01	0.942	1.085 ± 0.200

* Value obtained by assuming $\log_{10}\beta^{\circ}_{1FeSO_4(aq)}$ = (2.44 ± 0.03) and $\varepsilon(Fe^{2+}, ClO_4^-)$ = (0.37 ± 0.03) $mol^{-1}\cdot kg$.

$FeSO_4^+$

In the present review we accept the existence of $FeHSO_4^{2+}$. Therefore, we have applied the SIT formalism to the results of the authors' "model 2", for which $\log_{10}\beta_{1c}$ = (1.60 ± 0.12), the equally-weighted average of their potentiometric and spectrophotometric values. That yields $\log_{10}\beta_{1m}$ = (1.53 ± 0.12). The auxiliary constants values used by the authors were replaced only partially by this those of this review. We calculated $\log_{10}\beta_{1m}$ by replacing $\log_{10} K_{m1,1(\mathrm{HSO}_4^-)}$ = (0.942 ± 0.100) by $\log_{10} K_{m1,1(\mathrm{HSO}_4^-)}$ = (1.085 ± 0.100). For the acidity m_{H^+} = 0.1168, used in most samples, one needs to multiply the original formation constant by $[1 + K_{m1,1(\mathrm{HSO}_4^-)\mathrm{review}} \times 0.1168)]/[1 + (K_{m1,1(\mathrm{HSO}_4^-)\ \mathrm{original}} \times 0.1168)]$. That yields:

$$\log_{10}\beta_{1m} = (1.61 \pm 0.14).$$

This value is incorporated in the plot in Figure IX-3 of the main text.

The value of $\log_{10}\beta_1^{\circ}$ also has been re-evaluated by extrapolation to zero ionic strength (from $m_{\mathrm{ClO}_4^-}$ = 3.5) using Eq. (A.197) and the interaction coefficients recommended in this review.

$$\begin{aligned}\log_{10}\beta_1^{\circ} = {} & \log_{10}\beta_{1m} + 12D - \varepsilon(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-)\,m_{\mathrm{ClO}_4^-} - \varepsilon(\mathrm{Na}^+,\mathrm{SO}_4^{2-})\,m_{\mathrm{Na}^+} \\ & - \varepsilon(\mathrm{H}^+,\mathrm{SO}_4^{2-})\,m_{\mathrm{H}^+} + \varepsilon(\mathrm{FeSO}_4^+,\mathrm{ClO}_4^-)\,m_{\mathrm{ClO}_4^-} \qquad \text{(A.197)}\end{aligned}$$

The terms involving the interactions of Fe^{3+}, SO_4^{2-} and FeSO_4^+ with ions of the opposite charge present in small concentrations such as: $\varepsilon(\mathrm{Fe}^{3+},\mathrm{SO}_4^{2-})\,m_{\mathrm{SO}_4^{2-}}$, $\varepsilon(\mathrm{Fe}^{3+},\mathrm{HSO}_4^-)\,m_{\mathrm{HSO}_4^-}$, $\varepsilon(\mathrm{Fe}^{3+},\mathrm{SO}_4^{2-})\,m_{\mathrm{Fe}^{3+}}$, $\varepsilon(\mathrm{FeSO}_4^+,\mathrm{SO}_4^{2-})\,m_{\mathrm{FeSO}_4^+}$, $\varepsilon(\mathrm{FeSO}_4^+,\mathrm{SO}_4^{2-})\,m_{\mathrm{SO}_4^{2-}}$, and $\varepsilon(\mathrm{FeSO}_4^+,\mathrm{HSO}_4^-)\,m_{\mathrm{HSO}_4^-}$, have been neglected.

That yields: $\log_{10}\beta_1^{\circ}$ = (3.85 ± 0.47).

$\mathrm{Fe(SO_4)_2^-}$

As for the other papers dealing with $\mathrm{Fe(SO_4)_2^-}$ in this review, we will discuss the results by considering the stability constant, $K_{2m} = m_{\mathrm{Fe(SO_4)_2^-}} / (m_{\mathrm{FeSO}_4^+}\,m_{\mathrm{SO}_4^{2-}})$.

Its average (equally-weighted) calculated value from the potentiometric and spectrophotometric investigations (*i.e.*, the reported values of β_{102c}), after conversion to the molal scale ($m_{\mathrm{ClO}_4^-}$ = 3.5) yields:

$$\log_{10} K_{2m} = (1.05 \pm 0.12).$$

The correction to allow for use of different values for the formation constant of HSO_4^- is made by multiplying this value by: $[1 + (K_{m1,1(\mathrm{HSO}_4^-)})_{\mathrm{review}} \times 0.1168)]/ [1 + (K_{m1,1(\mathrm{HSO}_4^-)})_{\mathrm{original}} \times 0.1168)]$.

That yields: $\log_{10} K_{2m}$ = (1.13 ± 0.14).

The extrapolation to zero ionic strength (from $m_{\mathrm{ClO}_4^-}$ = 3.5) can be done by applying Eq. (A.198)

$$\begin{aligned}\log_{10} K_{2m\mathrm{Fe(SO_4)_2^-}} = {} & \log_{10} K_{2m} + 4D - \varepsilon(\mathrm{FeSO}_4^+,\mathrm{ClO}_4^-)\,m_{\mathrm{ClO}_4^-} - \varepsilon(\mathrm{Na}^+,\mathrm{SO}_4^{2-})\,m_{\mathrm{Na}^+} \\ & - \varepsilon(\mathrm{H}^+,\mathrm{SO}_4^{2-})\,m_{\mathrm{H}^+} + \varepsilon(\mathrm{Na}^+,\mathrm{Fe(SO_4)_2^-})\,m_{\mathrm{Na}^+} + \varepsilon(\mathrm{H}^+,\mathrm{Fe(SO_4)_2^-})\,m_{\mathrm{H}^+} \\ & \qquad \text{(A.198)}\end{aligned}$$

That yields: $\log_{10} K_2^{\circ}$ = (1.84 ± 0.61).

$FeHSO_4^{2+}$

In the original paper the formation constant of $FeHSO_4^{2+}$ (the 1:1:1 complex) was expressed as: $\beta_{1,1,1c} = c_{FeHSO_4^{2+}}/(c_{Fe^{3+}}c_{SO_4^{2-}}c_{H^+})$. In this review as in most other papers, the equilibrium constant $K_{mFeHSO_4^{2+}} = m_{FeHSO_4^{2+}}/(m_{Fe^{3+}}m_{HSO_4^-})$ was considered, so we have converted the constants given in [2002CIA/TOM2] to values of $K_{mFeHSO_4^{2+}}$.

The average of the formation constants for the potentiometric and spectrophotometric measurements of the original paper has been calculated, that yields: $\log_{10}\beta_{1,1,1c} = (2.38 \pm 0.16)$ and, converted to molalities, $\log_{10}\beta_{1,1,1m} = (2.25 \pm 0.16)$.

Using $c_{H^+} = 0.1$ and the value of $K_{m1,1(HSO_4^-)}$ from the present review, instead of the value of $K_{m1,1(HSO_4^-)}$ from the original paper produces:

$$\log_{10}\beta_{1,1,1m} = (2.33 \pm 0.16) \text{ and } \log_{10} K_{mFeHSO_4^{2+}} = (1.24 \pm 0.19).$$

This value is shown in Figure IX-5 of the main text.

Using the interaction coefficients proposed in this review and listed in Table A-68, and applying Eq. (A.199) we calculated the value of $\log_{10} K_{mFeHSO_4^{2+}}$ (for $m_{ClO_4^-}$ = 3.5).

$$\begin{aligned}\log_{10} K^{\circ}_{mFeHSO_4^{2+}} = {} & \log_{10} K_{mFeHSO_4^{2+}} + 6D - \varepsilon(Fe^{3+}, ClO_4^-)\,m_{ClO_4^-} - \varepsilon(Na^+, HSO_4^-)\,m_{Na^+} \\ & - \varepsilon(H^+, HSO_4^-)\,m_{H^+} + \varepsilon(FeHSO_4^{2+}, ClO_4^-)\,m_{ClO_4^-} \qquad (A.199)\end{aligned}$$

which yields: $\log_{10} K^{\circ}_{mFeHSO_4^{2+}} = (2.56 \pm 0.98)$.

Within the large uncertainty bounds, this value is consistent with the value recommended in the present review.

[2002CIA/TOM3]

This article deals with the mixed hydroxidosulfato complexes of Fe(III) in aqueous solutions. This subject has been already discussed in this review with reference to the papers of [1969ZVY/LYA], [1977SAP/PAT], [1988KHO/ROB]. The investigation has been carried out by pH measurements using a glass electrode in 3 M $NaClO_4$ at 25 °C. For these conditions it was necessary to have precise values for the stability constants of the binary sulfato complexes and for HSO_4^-, and the authors used results from their own earlier investigations [2002CIA/TOM2], [2002CIA/TOM]. For the formation constants of the binary hydroxido complexes, except $FeOH^{2+}$ and $Fe(OH)_2^+$, they also used results from one of their earlier publications [2001CIA/TOM3]. For $FeOH^{2+}$ and $Fe(OH)_2^+$ they referred to unpublished values obtained by Biedermann, as cited by Schlyter in [1962SCH2].

The total iron(III) and total sulfate concentrations were varied from 0.0025 to 0.03 M and from 0.005 to 0.06 M, respectively. The authors varied the pH between 1.3 to 2.6 by addition of $NaHCO_3$ for 12 acid-base titration runs for fixed iron and total sulfate concentrations. The upper pH-limit for each titration, 2.3 to 2.6, depended on the total iron concentration. Each was the highest attainable without precipitation. For each run, ten pH values were recorded and used to determine the most probable species and their formation constants. Reverse runs were also carried out. A total of 212 data points were produced. These potentiometric data were obtained under conditions such that the activity coefficients were approximately constant. The cell employed for the measurements was:

Ag,AgCl | 0.01 M $AgClO_4$, 2.99 M $NaClO_4$ ⁞⁞ 3 M $NaClO_4$ ⁞ test solution | glass electrode.

Its potential E in mV, at 25 °C, can be expressed as:

$$E = E^{\circ\prime} + (RT(\ln(10))/F)\ \log_{10} c_{\mathrm{H}^+} + E_{\mathrm{j}} \qquad \text{(A.200)}$$

$E^{\circ\prime}$ is a constant for each run and E_{j} is an additive potential which take into account the variations of the H^+ activity coefficients and the junction potentials changes. For calculation of values of E_{j} the authors proposed:

$$E_{\mathrm{j}} = \xi_{\mathrm{H}} c_{\mathrm{H}^+} + \xi_{\mathrm{Fe}} c_{\mathrm{Fe}^{3+}} + \xi_{\mathrm{SO}_4} c_{\mathrm{SO}_4^{2-}} + \xi_{\mathrm{HSO}_4} m_{\mathrm{HSO}_4^-} + \xi_{pqr} c_{\mathrm{Fe}p\mathrm{H}q(\mathrm{SO}_4)r^{(3p+q-2r)+}} \qquad \text{(A.201)}$$

where the ξ_{s} are constants, some of which had been determined in previous investigations: $\xi_{\mathrm{H}} = -(17 \pm 1)$ mV·mol^{-1} [1953BIE/SIL], $\xi_{\mathrm{Fe}} = (26 \pm 1)$ mV·mol^{-1}, $\xi_{\mathrm{SO}_4} = -(23 \pm 3)$ mV·mol^{-1} and $\xi_{\mathrm{HSO}_4} = (0)$ mV·mol^{-1} [2002CIA/TOM] (ξ is the symbol used by the Ciavatta *et al.*, and should not be confused with the usage for the same symbol as indicated in Table II-2 of the present review). The value of the last term in Eq. (A.201) was approximated by treating the data in several iterative calculation cycles in which best estimates of parameters were introduced at the beginning of the process. So the initial value of E_{j} in the first cycle was:

$$E_{\mathrm{j}}/\mathrm{mV} = -\,17\, c_{\mathrm{H}^+} + 26\, c_{\mathrm{Fe_{total}}} - 23\, c_{\mathrm{sulfate_{total}}} \qquad \text{(A.202)}$$

where $c_{\mathrm{Fe_{total}}}$ and $c_{\mathrm{sulfate_{total}}}$ were the total iron and sulfate concentrations, and from the final iteration

$$E_{\mathrm{j}}/\mathrm{mV} = -\,17\, c_{\mathrm{H}^+} + 26\, c_{\mathrm{Fe}^{3+}} - 23\, c_{\mathrm{SO}_4^{2-}} + 8\, c_{\mathrm{FeSO}_4^+} \qquad \text{(A.203)}$$

No details of the experimental data and the methods used to reach the conclusions were given in this paper. According to the authors the best fit to the experimental data was obtained with a model which took into account the species listed in Table A-70. The values used by Ciavatta *et al*, for formation constants for these species also are listed.

Only one mixed hydroxidosulfato complex $FeOHSO_4$(aq) was incorporated in the "best fit" model. As already discussed in the entries for [1969ZVY/LYA], [1977SAP/PAT] and [1988KHO/ROB] it seems difficult to reach any firm conclusion as to the presence or absence of mixed complexes when it is already proposed that there are nine simpler complex species in the solutions. Even if ternary complex species are present, basing the speciation only on data from pH potentiometric measurements seems dubious because the formation constants of the nine binary complexes also are pH-dependent. In the present work [2002CIA/TOM3] the investigation of ternary Fe(III) species by pH measurements probably has been pushed to its limit. The choice of the solution compositions, the preliminary determination of the nine auxiliary constants and the evaluation of changes in activity coefficients and junction potentials with conditions during the acid-base titrations do increase the confidence in the conclusions. However, more direct speciation methods for identifying mixed hydroxidosulfato complexes of iron(III) are necessary. For example, ir or Raman spectroscopy might be used to distinguish the SO_4^{2-} and OH^- bands of $FeOHSO_4$(aq) from those of the binary complexes, or nmr might be useful if exchange of the proton of the hydroxido ligand with water is sufficiently slow. From a simple chemical point of view a simple aqueous 1:1:1 species such as $FeOHSO_4$(aq) seems improbable because of the known bridging power of the bonded OH^- groups and the low repulsion between any neutral $FeOHSO_4$(aq) molecules, which must possess a strong facility to aggregate.

Table A-70: Species which were taken into account to obtain the "best fit" of the data (the formation constant values are in concentration units (molarities) for the solutions, and are appropriate for calculations involving small amounts of the species in 3 M $NaClO_4$(sln)).

Species	$\log_{10} \beta_{q,m,r}$ †	$\log_{10} {}^*\beta_{q,m,r}$ ‡	Source
HSO_4^-	1.01 ± 0.01		[2002CIA/TOM]
$Fe(SO_4)^+$	1.65 ± 0.02		[2002CIA/TOM2]
$Fe(SO_4)_2^-$	2.68 ± 0.02		[2002CIA/TOM2]
$FeHSO_4^{2+}$	2.4 ± 0.2		[2002CIA/TOM2]
$FeOH^{2+}$		– 3.05 ± 0.05	[1962SCH2]
$Fe(OH)_2^+$		– 6.3 ± 0.1	[1962SCH2]
$Fe_2(OH)_2^{4+}$		– 2.88 ± 0.02	[2001CIA/TOM3]
$Fe_3(OH)_4^{5+}$		– 6.14 ± 0.18	[2001CIA/TOM3]
$Fe_3(OH)_5^{4+}$		– 8.44 ± 0.09	[2001CIA/TOM3]
$FeOHSO_4$(aq)		– 0.49 ± 0.03	this paper

† For the reactions: $m\,Fe^{3+} + q\,H^+ + r\,SO_4^{2-} \rightleftharpoons Fe_mH_q(SO_4)_r^{(3m+q-2r)+}$.

‡ For the reactions: $m\,Fe^{3+} + q\,H_2O(l) + r\,SO_4^{2-} \rightleftharpoons Fe_m(OH)_q(SO_4)_r^{(3m-q-2r)+} + q\,H^+$.

[2002HEM/SEA]

In this review paper an attempt was made to evaluate and estimate chemical thermodynamic quantities for a number of iron-sulfate solids. For $Fe^{II}(Fe^{III})_2(SO_4)_4\cdot 14H_2O(s)$, $Fe^{II}(Fe^{III})_2(SO_4)_4\cdot 22H_2O(s)$ and $Fe^{II}(Fe^{III})_4(SO_4)_6(OH)_2\cdot 20H_2O(s)$ the estimated enthalpies of formation were – 2581.9, – 4692.2 and – 5288.2 kJ·mol^{-1}, respectively, and the corresponding estimated entropies were 282.2, 590.6 and 670.1 $J \cdot K^{-1} \cdot mol^{-1}$. These are probably reasonable estimates, but are not accepted in the set of selected data.

[2002JEN/BOD]

The solubility of siderite was measured at 15 °C from supersaturated solutions and from undersaturation using $FeCO_3(s)$ prepared in two different ways. The supersaturated solutions did not reach equilibrium even after several hundred days. $FeCO_3(s)$ that was not dried (or heated) had a solubility in 20 mM $NaHCO_3$ solution that was markedly greater than for the dried solid (as was suggested earlier by Ptacek [1992PTA])[1]. The quantities measured at equilibrium were the total alkalinity, the "pH" (as measured against standard buffer solutions) and total iron molarity.

The authors used bentonite as a seed for crystallization. However, they did not specify how much was added and how this addition might have influenced the measurements. The chemical system included Mn(II), Ca(II) and Fe(II) in solution together; yet the possible formation of solid solutions was not discussed.

Reanalysis of the results proved problematic. The analysis values for the 284-day sample on the "dry crystals" are inconsistent with those for the other "dry" samples, even though this would not be suggested from the authors' Figure 1 [2]. Our recalculated values for $\log_{10} K_{s,0}$ at 288.15 K (neglecting formation of iron(II)/carbonato or iron(II)/hydrogencarbonato complexes), are shown in the table.

	equilibration period/d	$\log_{10} K_{s,0}$
from "dry" crystals	10	− 10.65
	60	− 10.49
	110	− 10.61
	284	− 9.93
from "wet" crystals	30	− 9.87
	80	− 10.01
	80	− 9.90
	254	− 9.81
	364	− 10.12

These sparse results seem to be less reliable than those from other studies at higher (and/or constant) partial pressures of CO_2. Neglecting the 284-day measurement, the average value of $\log_{10} K_{s,0}$ for the "dry" crystals is -10.58, and for the "wet"

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[1] However, we note that, surprisingly, for $MnCO_3$ Jensen *et al.* found that the dried form appeared to be less stable than the undried form.

[2] Perhaps the listed iron concentration of "1.30 mg/l" is a typographical error for "0.30 mg/l".

crystals the average value of $\log_{10} K_{s,0}$ is -9.94. These are less negative than found from other studies, *e.g.*, [1992BRU/WER], [1976BAR/PER].

However, in all of the experiments the formation of $FeCO_3(aq)$ ($K^\circ_A = a_{FeCO_3(aq)} / a_{Fe^{2+}} a_{CO_3^{2-}}$) probably cannot be neglected, and the data are not sufficient in number or reliability to allow evaluation of values of both $\log_{10} K^\circ_{s,0}$ and the formation constant of $FeCO_3(aq)$. The authors, in a MINTEQA2 analysis [1991ALL/BRO], used estimated values from the literature ([1984FOU/CRI], [1981TUR/WHI]) for the formation constants of $FeCO_3(aq)$ ($\log_{10} K = 4.73$) and $FeHCO_3^+$ ($\log_{10} K = 2.17$) at 25 °C, then attempted to correct these to 15 °C [1984FOU/CRI]. They reported $\log_{10} K^\circ_{s,0}$ for the “dry” crystals to be -11.03, and for the “wet” crystals the average value of $\log_{10} K^\circ_{s,0}$ was -10.43.

Reasonable values for the solubility product are obtained using $FeCO_3(aq)$ formation constant values from 10^4 to 10^6 $kg \cdot mol^{-1}$ as discussed in Section X.1.2.1.2. Our recalculations using $10^{5.5}$ $kg \cdot mol^{-1}$ for the formation constant of $FeCO_3(aq)$ suggest values of $\log_{10} K^\circ_{s,0}$ that are less negative than those proposed by the authors by 0.1 to 0.2. The numerical results from this study are not used further in the present review.

[2002PRE/GAM]

These authors take into account all the available solubility data for $FeCO_3(cr)$ within an optimization routine, ChemSage, to obtain a consistent value for the enthalpy of formation of siderite. In the absence of ion-interaction parameters for Fe^{2+}, the Davies equation was used to predict the activity coefficients of the ions in solution.

A $\Delta_f H^\circ(FeCO_3, cr)$ value of $-(752.0 \pm 1.2)$ $kJ \cdot mol^{-1}$ was proposed and the existing solubility data were considered to be in very good agreement such that the previous discrepancies in reported values of $\Delta_f H^\circ(FeCO_3, cr)$ could be traced to unreliable auxiliary data for Fe(II).

This paper provides a useful critical review of the solubility data for siderite in aqueous media. No new data are presented.

[2002SIL/LIU]

The solubility of $FeCO_3(cr)$, synthesized in an aqueous solution of iron(II) sulfate heptahydrate and sodium hydrogen carbonate and aged at 323 K, was measured at 298.15 K as a function of NaCl (0.1 to 5.5 $mol \cdot kg^{-1}$) and hydrogen ion molalities with $p_{CO_2(g)}$ of 5 kPa. The uncertainty in $p_{CO_2(g)}$ is not stated, but is probably of the order of 10%. Some measurements were carried out at sufficiently low molalities of H^+ that complex formation between Fe^{2+} and carbonate species may have occurred.

The reported iron and hydrogen ion concentrations and $p_{CO_2(g)}$ values were reanalysed using CODATA values for $CO_2(g)$, $CO_2(aq)$, HCO_3^-, CO_3^{2-} and $H_2O(l)$ at 298.15 K. The solubility product values were corrected to $I = 0$ using the standard TDB SIT procedure. The average values for $\log_{10} {}^*K_{s,0}$ (A.204) obtained using the solutions

0.1 mol·kg^{-1} and 0.7 mol·kg^{-1} in NaCl(sln) are (7.03 ± 0.14) and (7.09 ± 0.04), respectively. However, for solutions 1.4 mol·kg^{-1}, 2.0 mol·kg^{-1}, and 2.5 mol·kg^{-1} in NaCl(sln), the average values for $\log_{10}{}^{*}K_{s,0}$ (A.204) are (7.83 ± 0.12), (7.78 ± 0.06), and (7.83 ± 0.14) (these uncertainties represent the 95% confidence limits, not including uncertainties in the auxiliary data).

$$\mathrm{FeCO_3(cr)} + 2\,\mathrm{H^+} \rightleftharpoons \mathrm{Fe^{2+}} + \mathrm{CO_2(g)} + \mathrm{H_2O(l)} \qquad \text{(A.204)}$$

Preis and Gamsjäger [2002PRE/GAM] also recalculated the values for the 1.4, 2.0 and 2.5 mol·kg^{-1} NaCl solutions using an SIT equation, and obtained a similar result ($\log_{10}{}^{*}K_{s,0}$ (A.204) = 7.77). Strangely enough, the results appear to bracket those from several other studies [1918SMI], [1969LAN], [1992GRE/TOM]. The reasons for the two different sets of results are not clear, although the authors invoked the possibility of inconsistencies in activity coefficient equations (unlikely at I = 0.1 mol·kg^{-1}), and association between $\mathrm{Fe^{2+}}$ and $\mathrm{CO_3^{2-}}$ (apparently inconsistent with the plots in the authors' Figure 1).

$\mathrm{NaHCO_3}$(sln) (amounts unstated) was added to the solutions before equilibrium was established with the flow of $\mathrm{CO_2}$(g). In essence, this process represents the addition of NaOH(sln) to the original solutions. Therefore, the sum of the calculated molalities of $\mathrm{HCO_3^-}$ and $\mathrm{OH^-}$ plus twice the molality of $\mathrm{CO_3^{2-}}$, would be expected to be greater than the molality of $\mathrm{H^+}$ plus twice the molality of $\mathrm{Fe^{2+}}$. However, for the lower acidity solutions, at each molality of NaCl(sln), there is a calculated excess of cations (by as much as 0.002 mol·kg^{-1}) without allowing for any $\mathrm{Na^+}$ ions from the added $\mathrm{NaHCO_3}$(sln). This suggests an error in the present calculations (likely in the interpretation of the reported results of the experiments), or a problem with the experiments themselves.

[2003DRO/NAV]

The enthalpy of formation of pure (stoichiometric) $((\mathrm{H_3O})\mathrm{Fe_3(SO_4)_2(OH)_6})$(cr) was measured by dissolution and decomposition in a sodium molybdate melt ($3\mathrm{Na_2O}\cdot4\mathrm{MoO_3}$) and reported as – 3741.6 kJ·mol^{-1}.

[2003LIU/PAP]

The solubility of "reagent grade hematite (Fischer Scientific)" was measured in 0.104 to 0.705 mol·kg^{-1} $\mathrm{H_2SO_4}$ solutions at 230, 250 and 270 °C (only four sulfuric acid concentrations per temperature) in a titanium autoclave. No mention was made of the purity, crystallinity or particle size of the solid phase. Data analysis was performed with the commercial OLI Systems code with the predominant species in solution being reported as: $\mathrm{Fe_2(SO_4)_3(aq)}$, $\mathrm{Fe(OH)_2(SO_4)^-}$, $\mathrm{FeSO_4^+}$, $\mathrm{FeHSO_4^{2+}}$ and $\mathrm{Fe^{3+}}$.

In view of the limited solubility data provided for such a complex system (*cf.* Section IX.1.2.1.3.6), together with the fact that an uncharacterized solid phase was used, no useful thermodynamic values can be extracted for this review.

[2003MAJ/GRE]

Enthalpies of formation of goethite (α-FeOOH), lepidocrocite (γ-FeOOH), and maghemite (γ-Fe_2O_3) were determined by a combination of acid dissolution (AD) and transposed temperature-drop (TTD) calorimetry measurements. The origin and characterization of the solid specimens is described in [2003MAJ/LAN]. Hematite for comparative measurements was 99.999% pure (metals basis) reagent with a crystallite size of 140 nm, corresponding to a calculated specific surface area of 8 $m^2 \cdot g^{-1}$, a BET measured surface area of 4 $m^2 \cdot g^{-1}$, and no measurable microstrain.

Heats of dissolution were measured in 5 M HCl(sln) at (340.00 ± 0.02) K, the quantities of acid, oxide and added water being controlled to achieve a constant final Fe^{3+} molality (23.2 to 23.5 $mmol \cdot kg^{-1}$). Transposed temperature-drop experiments were performed with ~15-mg pellets of hematite or goethite, dropped into an empty Pt crucible at 975 K. Similar experiments with maghemite and lepidocrocite did not give reproducible results.

The following measurements were reported and used to obtain $\Delta_f H_m^o$ (298.15 K) values for the three solids of interest, based on literature enthalpy data for α-Fe_2O_3 and H_2O and treating the initial state of excess water in the solids (except α-Fe_2O_3, which was rigorously anhydrous) as bulk liquid for the excess dilution (AD method) and evaporation (TTD method) correction terms of the enthalpy calculation.

$\Delta_{AD}H_m$ (Fe_2O_3, α, 340 K) = $-$(50.45 ± 1.17) $kJ \cdot mol^{-1}$ (5 measurements)

$\Delta_{AD}H_m$ (Fe_2O_3, γ, +0.116H_2O, 340 K) = $-$(68.73 ± 0.92) $kJ \cdot mol^{-1}$ (5 measurements)

$\Delta_{AD}H_m$ (FeOOH, α, +0.090H_2O, 340 K) = $-$(20.42 ± 0.32) $kJ \cdot mol^{-1}$ (4 measurements)

$\Delta_{AD}H_m$ (FeOOH, γ, +0.162H_2O, 340 K) = $-$(31.40 ± 0.72) $kJ \cdot mol^{-1}$ (4 measurements)

$[\Delta_{TTD}H_m]_{298K}^{975K}$ (Fe_2O_3, α) = (96.86 ± 0.45) $kJ \cdot mol^{-1}$ (21 measurements)

$[\Delta_{TTD}H_m]_{298K}^{975K}$ (FeOOH, α, +0.090H_2O, l) = (92.63 ± 0.79) $kJ \cdot mol^{-1}$ (12 measurements)

The $\Delta_{AD}H_m$ terms represent the heat of acid dissolution in 5 M HCl(sln) at 340 K for the nominal processes:

$$Fe_2O_3(cr) + xH_2O(l) + 6H^+(sln) \rightleftharpoons 2Fe^{3+}(sln) + (3 + x)H_2O(sln)$$

where x = 0 and 0.116 for physically bound water in the specimens of α-Fe_2O_3 and γ-Fe_2O_3, respectively; and

$$FeOOH(cr) + xH_2O(l) + 3H^+(sln) \rightleftharpoons Fe^{3+}(sln) + (2 + x)H_2O(sln)$$

where x = 0.090 and 0.162 for physically bound water in the specimens of α-FeOOH and γ-FeOOH, respectively.

The $[\Delta_{TTD}H_m]_{298K}^{975K}$ terms represent the heats of the temperature-drop processes:

(Fe_2O_3, α, 298.15 K) → (Fe_2O_3, α, 975 K) and (($FeOOH$, α, + $0.090H_2O$, l), 298.15 K) → 0.5(Fe_2O_3, α, 975 K) + 0.590(H_2O, g, 975 K).

The resulting $\Delta_f H_m^o$(298.15 K) value for γ-Fe_2O_3 is probably still the most accurate enthalpy determination for that phase, while the results for α-FeOOH and γ-FeOOH have been supplemented by more recent, surface-area-dependent studies [2005MAZ/NAV], [2007MAJ/MAZ]. Recalculation of the $\Delta_f H_m^o$ (298.15 K) values for α-FeOOH, γ-FeOOH, and γ-Fe_2O_3, for internal consistency within the current review, is discussed in Sections VII.2.9.1, VII.2.11.2, and VII.2.4.2, respectively.

The paper also includes a computational study on the p and T dependence of the phase relationships between α-FeOOH, α-Fe_2O_3, and water, which is beyond the scope of the current review.

[2003MAJ/LAN]

Heat capacities of goethite (α-FeOOH), lepidocrocite (γ-FeOOH), and maghemite (γ-Fe_2O_3) were measured from below liquid He temperature to the decomposition temperature, using a combination of adiabatic, semi-adiabatic, and differential-scanning calorimetry. The oxyhydroxides were synthetic materials with low impurity levels (< 160 ppm Al, 32 ppm Cl in goethite, 202 ppm Cl in lepidocrocite), prepared and purified on the basis of standard procedures [2000SCH/COR], and the maghemite was a high-purity, ordered (tetragonal) commercial specimen used in an earlier study [1998LAB/NAV]. Phase purity for all solids was verified by Rietfeld refinement of powder XRD data, and no amorphous impurities could be detected by oxalate extraction. Specific surface areas were measured by the BET method (18, 21, and 23 $m^2 \cdot g^{-1}$ for maghemite, goethite, and lepidocrocite), and excess water was analysed with an accuracy of ± 0.01 or better on a mole per mole basis.

Due to an oversight, data tables are not available as indicated in the journal, but J. Majzlan kindly provided the following original measurements:

- 133 $C_{p,m}^o$ values from 7.696 to 396.66 K for a maghemite specimen of composition $Fe_2O_3 \cdot 0.042H_2O$.
- 250 $C_{p,m}^o$ values from 0.7 to 396.15 K for a goethite specimen of composition $FeOOH \cdot 0.083H_2O$. These include 38 measurements to define a small anomaly below 2.1 K and 25 measurements between 357.08 and 396.15 K, around the Néel transition.
- 237 $C_{p,m}^o$ values from 5.707 to 387.01 K for a lepidocrocite specimen of composition $FeOOH \cdot 0.087H_2O$. These included 52 measurements between 49.2 and 109.16 K, around the Néel transition (near 68 K).

Heat-capacity data were corrected for excess water by using an empirical Debye-Einstein representation of $C_{p,m}^o$ for hexagonal ice, then fitted to obtain the following Maier-Kelley expressions.

$$[C^{\circ}_{p,\mathrm{m}}]^{760}_{273}\ (\mathrm{Fe_2O_3}, \gamma, T)/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = 106.8 + 0.06509(T/\mathrm{K}) - 1886000(\mathrm{K}/T)^2$$

$$[C^{\circ}_{p,\mathrm{m}}]^{375}_{273}\ (\mathrm{FeOOH}, \alpha, T)/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = 1.246 + 0.2332(T/\mathrm{K}) + 313900(\mathrm{K}/T)^2$$

$$[C^{\circ}_{p,\mathrm{m}}]^{390}_{273}\ (\mathrm{FeOOH}, \gamma, T)/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = 59.76 + 0.06052(T/\mathrm{K}) - 772900(\mathrm{K}/T)^2$$

The expression for γ-Fe_2O_3 is a bridging function spanning the temperature range from 400 to 700 K, within which data could not be obtained because of "unreasonable variations" in DSC measurements. The Curie temperature of maghemite is not well defined, but is above the normal temperature range for transformation to hematite (α-Fe_2O_3). The expression for α-FeOOH is limited by a C_p anomaly at 375 K (the Néel transition), with onset of dehydration near 400 K. Three other papers are cited, giving Néel temperatures from 330 to 403 K, probably reflecting variations in particle size and chemical purity. The Maier-Kelley expression for γ-FeOOH is limited by evolution of loosely bound water above 350 K and transformation to maghemite above ~ 400 K.

The following standard entropy and heat capacity values were obtained.

$$C^{\circ}_{p,\mathrm{m}}\ (\mathrm{Fe_2O_3}, \gamma, 298.15\ \mathrm{K}) = 104.69\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

$$S^{\circ}_{\mathrm{m}}\ (\mathrm{Fe_2O_3}, \gamma, 298.15\ \mathrm{K}) = (93.0 \pm 0.2)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

$$C^{\circ}_{p,\mathrm{m}}\ (\mathrm{FeOOH}, \alpha, 298.15\ \mathrm{K}) = 74.36\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

$$S^{\circ}_{\mathrm{m}}\ (\mathrm{FeOOH}, \alpha, 298.15\ \mathrm{K}) = (59.7 \pm 0.2)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

$$C^{\circ}_{p,\mathrm{m}}\ (\mathrm{FeOOH}, \gamma, 298.15\ \mathrm{K}) = 69.14\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

$$S^{\circ}_{\mathrm{m}}\ (\mathrm{FeOOH}, \gamma, 298.15\ \mathrm{K}) = (65.1 \pm 0.2)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

Rounded values for other temperatures are tabulated (up to 760 K for γ-Fe_2O_3, 375 K for α-FeOOH, and 390 K for γ-FeOOH). An additional configurational entropy term of 2.0 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ is calculated for the disordered, cubic form of γ-Fe_2O_3. The authors note good agreement on α-FeOOH with [1970KIN/WEL], which they consider to be the only reliable, previous source of low-temperature $C^{\circ}_{p,\mathrm{m}}$ data for any of these three phases.

An alternative fitting and simplified correction procedure, described in Sections VII.2.4.1, VII.2.9.2, and VII.2.11.1, gives very similar (albeit perhaps slightly less accurate) results while avoiding some minor inconsistencies between the above values and expressions and the authors' smoothed data tables.

[2003MAJ/NAV2]

Heat-capacity data for goethite (α-FeOOH, analysed composition $\mathrm{FeOOH\cdot 0.083H_2O}$) at 0.6 to 30 K are discussed in detail, complementing the measurements described in [2003MAJ/LAN]. Original data were kindly provided by J. Majzlan (pers. comm.). A weak, broad anomaly between about 0.7 and 1.5 K is attributed to "the ordering of a small amount of magnetic moments associated with the defects and interfaces in the α-FeOOH particles", and is therefore apparently not a bulk property of goethite. The associated entropy contribution is small, ~0.1 mJ·K^{-1}·mol^{-1}.

[2004MAJ/NAV]

A series of ferrihydrite specimens with varying degrees of crystallinity, from "2-line" to well-defined "6-line" types was prepared, and their enthalpies of formation were determined by comparing their heats of dissolution in 5 M HCl(sln) at 298 K with that of a well-characterized lepidocrocite (γ-FeOOH) specimen. Enthalpies are reported per mole of "FeOOH·xH$_2$O". A slight increase in stability of ferrihydrite with increasing crystallinity was observed, with a range of (3.2 ± 0.6) kJ·mol^{-1} in the heats of dissolution between the least and most crystalline specimens. When expressed as $\Delta_f H_m^o$ (FeOOH·xH$_2$O, s, 298.15 K), however, the differences appear much larger because of the variation in water content. The following table summarizes the heats of dissolution.

Designation	Type	x (H$_2$O/Fe$_2$O$_3$)	$\Delta_{sol}H_m^o$ /kJ·mol^{-1} (N)
fh0	2-line (Synthesis 1)	0.395	−(54.88 ± 0.45) (6)
fh2	2-line (Synthesis 2)	0.801	−(53.04 ± 0.86) (8)
fh6	Intermediate	0.593	−(52.94 ± 0.42) (5)
fh12	Intermediate	0.576	−(52.90 ± 0.32) (5)
fh24	6-line	0.520	−(51.70 ± 0.34) (5)

The authors argue that the entropy of ferrihydrite, expressed per mole of idealized formula Fe(OH)$_3$, should lie between those of a hypothetical, gibbsite-like crystalline Fe(OH)$_3$ (estimated at 122 J·K^{-1}·mol^{-1}) and [γ-FeOOH + H$_2$O(l)] (135 J·K^{-1}·mol^{-1}). On this basis, they estimate the following ranges of Gibbs energy values for the two classes of ferrihydrite:

$\Delta_r G_m^o$ ("Fe(OH)$_3$", s, 2-line, 298.15 K) = −(708.5 ± 2.0) to −(705.2 ± 2.0) kJ·mol^{-1}

$\Delta_r G_m^o$ ("Fe(OH)$_3$", s, 6-line, 298.15 K) = −(711.0 ± 2.0) to −(708.5 ± 2.0) kJ·mol^{-1}.

Strictly speaking these values refer to ferrihydrite-water mixtures, and should therefore be used with caution (especially when estimating values at temperatures other than 298.15 K), but they provide a convenient means of comparing solubility products between different ferrihydrites and other Fe(III) oxyhydroxide solids.

The revised value of $\Delta_f H_m^o$ (Fe$_2$O$_3$, ε, 298.15 K) = −(798.0 ± 6.6) kJ·mol^{-1}, given in this paper, is simply an adjustment of Trautmann's value [1966TRA] using a more current reference value for $\Delta_f H_m^o$ (Fe$_2$O$_3$, α, 298.15 K). A slight further adjustment is made in the current review for internal consistency. The authors estimate $\Delta_r G_m^o$ (Fe$_2$O$_3$, ε, 298.15 K) = −(798.0 ± 6.6) kJ·mol^{-1} by assuming the entropies of γ-Fe$_2$O$_3$ and ε-Fe$_2$O$_3$ to be the same.

The authors also reported heats of solution of two samples of schwertmannite (idealized formula $FeO(SO_4)_{0.125}(OH)_{0.75}$) in 5 M HCl(sln). Again the heats of dissolution were compared to that of a slightly hydrated lepidocrocite (γ-$FeOOH\cdot 0.162H_2O$) in 5 M HCl(sln), and heats of solution of MgO(cr) and $MgSO_4$(cr) in the same medium. The authors considered the heat of hydration of lepidocrocite to the 0.162 hydrate to be negligible (the excess water appears to have been treated as H_2O(l)). The values of $\Delta_f H^o_m$ (298.15 K) after recalculation using the reported heats of solution and auxiliary data consistent with those in the present review are:

$$\Delta_f H^o_m (FeO(SO_4)_{0.157}(OH)_{0.686}\cdot 0.972H_2O, \text{cr}, 298.15\ \text{K}) = -(884.1 \pm 2.0)\ \text{kJ}\cdot\text{mol}^{-1}.$$

and

$$\Delta_f H^o_m (FeO(SO_4)_{0.168}(OH)_{0.664}\cdot 1.226H_2O, \text{cr}, 298.15\ \text{K}) = -(960.6 \pm 2.0)\ \text{kJ}\cdot\text{mol}^{-1}.$$

The enthalpy of dissolution of $MgSO_4$ was reported as $-(51.84 \pm 0.99)$ kJ·mol^{-1}, considerably more positive than other values reported later by the same group, $-(53.42 \pm 0.53)$ kJ·mol^{-1} [2004MAJ/STE] and $-(53.50 \pm 0.48)$ kJ·mol^{-1} [2005MAJ/NAV], [2006MAJ/NAV]. If the latter value is used, the enthalpies of formation of the two schwertmannite samples are recalculated to be $-(884.4 \pm 2.0)$ and $-(960.9 \pm 2.0)$ kJ·mol^{-1}. In the absence of any explanation in the later papers, the value used in this review is based on the heat of dissolution of $MgSO_4$ as given in the original paper.

The authors also estimated the entropy of both schwertmannite samples, and calculated $-(518.0 \pm 2.0)$ kJ·mol^{-1} for $\Delta_f G^o_m$ ($FeO(SO_4)_{0.125}(OH)_{0.750}$, cr, 298.15 K). However, in the absence of experimental confirmation of the entropy, this estimate of the Gibbs energy is not used further in the present review.

[2004MAJ/STE]

Majzlan *et al.* synthesized and reported enthalpy of solution and heat-capacity measurements for a solid with the composition $(H_3O)_{0.91}Fe_{2.91}(SO_4)_2(OH)_{5.64}(H_2O)_{0.18}$, close to the ideal composition of hydronium jarosite. The heat-capacity measurements were carried out by semi-adiabatic calorimetry (0.545 to 30.66 K) and adiabatic calorimetry (12.77 to 394.69 K). Magnetic susceptibility measurements show a broad maximum at 16.5 K, which is attributed to a spin-glass freezing transition. However, the heat-capacity measurements plotted against temperature (and the first-derivative values) show only minor deviations from a smooth curve. There also appears to be a small anomaly at some temperature below 0.7 K, but any contribution to the entropy from this source should be within the experimental uncertainties. The entropy of the solid at 298.15 K was calculated by the authors as (438.9 ± 0.7) J·K^{-1}·mol^{-1}. The structural sites in the hydronium jarosite sample were not fully occupied, and a maximum configurational entropy of 15.2 J·K^{-1}·mol^{-1} was estimated by the authors using the procedure of Ulbrich and Waldbaum [1976ULB/WAL]. A simple function for $C^o_{p,\text{m}}$,

$(280.6 + 0.6149(T/\mathrm{K}) - 3199700(T/\mathrm{K})^{-2})$ J·K^{-1}·mol^{-1}, was fit by the authors to the experimentally determined values between 274.04 and 394.94 K.

The enthalpy of formation was determined as – (3694.5 ± 4.6) kJ·mol^{-1} by dissolution of $(H_3O)_{0.91}Fe_{2.91}(SO_4)_2(OH)_{5.64}(H_2O)_{0.18}$, α-$MgSO_4$, γ-FeOOH, MgO(cr) into 5 M HCl. The entropy value (neglecting the residual configurational entropy at 0 K) was then used with this to calculate – (3162.2 ± 4.6) kJ·mol^{-1} for $\Delta_f G_m((H_3O)_{0.91}Fe_{2.91}(SO_4)_2(OH)_{5.64}(H_2O)_{0.18})$.

From these measurements, a set of thermodynamic values was calculated for $(H_3O)Fe_3(SO_4)_2(OH)_6$(cr) at 298.15 K. For the entropy and heat capacity this was done by assuming that the entropy and heat capacity are zero for the reaction:

$$(H_3O)Fe_3(SO_4)_2(OH)_6(cr) + 0.062\,CaSO_4(cr) \rightleftharpoons$$
$$1.031(H_3O)_{0.91}Fe_{2.91}(SO_4)_2(OH)_{5.64}(H_2O)_{0.18}(cr) + 0.062\,CaO(cr).$$

Thus, (448.2 ± 0.7) J·K^{-1}·mol^{-1} was calculated for $S^o((H_3O)Fe_3(SO_4)_2(OH)_6$, cr) at 298.15 K and $(287.2 + 0.6281(T/\mathrm{K}) - 3286000(T/\mathrm{K})^{-2})$ for $C^o_{p,m}$/J·K^{-1}·mol^{-1} for temperatures between 273 and 400 K.

The Gibbs energy of formation of the end-member solid was calculated (by the original authors) to be – (3226.4 ± 4.6) kJ·mol^{-1} based on the value calculated for the non-stoichiometric solid, modelling of the solution formed by its dissolution, and comparison of the modelling results with equilibrium solution measurements of Posnjak and Merwin [1922POS/MER]. From this and the entropy the value of $(H_3O)Fe_3(SO_4)_2(OH)_6$(cr) at 298.15 K, $\Delta_f H^o_m((H_3O)Fe_3(SO_4)_2(OH)_6$, cr) at 298.15 K was reported as – (3770.2 ± 4.6) kJ·mol^{-1}.

Using auxiliary data that are consistent with those in present review (see the Appendix A entry for [2005MAJ/NAV]), the enthalpy of formation of $(H_3O)_{0.91}Fe_{2.91}(SO_4)_2(OH)_{5.64}(H_2O)_{0.18}$(cr), was recalculated to be –(3693.9 ± 6.5) kJ·mol^{-1}.

The value of the enthalpy of dissolution of $MgSO_4$(cr) was reported as – (53.42 ± 0.53) kJ·mol^{-1}, very slightly more positive than the value in later papers from the same group, – (53.50 ± 0.48) kJ·mol^{-1} [2005MAJ/NAV] [2006MAJ/NAV]. If the later value is used, the enthalpy of formation of $(H_3O)_{0.91}Fe_{2.91}(SO_4)_2(OH)_{5.64}(H_2O)_{0.18}$(cr), is recalculated to be – (3694.1 ± 6.4) kJ·mol^{-1}. In the absence of any explanation in the later papers, the value used in this review is based on the heat of dissolution of $MgSO_4$(cr) as given in the original paper.

[2004MOO/HAG]

The authors provided a very carefully selected and discussed set of osmotic coefficients for the system $FeCl_2$-H_2O. Experiments were done at (25.00 ± 0.01) °C in tantalum cups with equilibration times of 14 – 35 days. The unusual precaution was taken to use four pure reference solutions containing NaCl, KCl, $CaCl_2$ and H_2SO_4 for whose properties the following respective references were cited: [1985CLA/GLE], [1999ARC2], [1976RAR/HAB] and [1997RAR/CLE]. The authors recalculated osmotic coefficients from previous isopiestic and vapour-pressure studies using the equations for the osmotic coefficients for these standards. However, there appear to be errors in their treatment of vapour-pressure data from previous studies, and these errors have been corrected in the present review.

Since this system does not include other salts, it should be possible to derive from these data an independent estimate of $\log_{10}\beta_1^{\circ}(\mathrm{FeCl^+})$, $\varepsilon(\mathrm{Fe^{2+},Cl^-})$ and $\varepsilon(\mathrm{FeCl^+,Cl^-})$, and to close the gap of missing ε values. Previously there does not seem to have been any published attempt to evaluate osmotic data of electrolyte solutions under the assumption that complex formation takes place. Hence, we first have to establish the necessary formalism.

Evaluation of $FeCl_2$(sln) osmotic data

A series of chlorido-, hydroxido- and mixed species may form in aqueous solutions of $FeCl_2$. At sufficiently low pH values Fe^{2+}, Cl^-, $FeCl^+$, and probably $FeCl_2$(aq) (only in the upper concentration range of Cl^-) will be the dominant species. In the initial analysis; higher-order chlorido complexes $FeCl_3^-$, $FeCl_4^{2-}$ *etc.* as well as any sort of hydrolytic species will be neglected.

By adopting the above simple four-species model the speciation in solution is obtained by solving

$$\beta_2 m_{\mathrm{Cl^-}}{}^3 + \beta_1 m_{\mathrm{Cl^-}}{}^2 + m_{\mathrm{Cl^-}}(1 - m_{\mathrm{FeCl_2(sln)}}\beta_1) - 2m_{\mathrm{FeCl_2(sln)}} = 0, \quad \text{(A.205)}$$

with $m_{\mathrm{FeCl_2(sln)}}$ = total molality of $FeCl_2$ and

$$\beta_1 = m_{\mathrm{FeCl^+}} / (m_{\mathrm{Fe^{2+}}} m_{\mathrm{Cl^-}}) \text{ and}$$

$$\beta_2 = m_{\mathrm{FeCl_2(aq)}} / (m_{\mathrm{Fe^{2+}}} m_{\mathrm{Cl^-}}{}^2).$$

When combining Equation 12 from [2000GRE/WAN] and Equation IX.39 from [1997GRE/PLY2] we may obtain an SIT-compatible expression for the osmotic coefficient ϕ:

$$\phi = 1 - \frac{A_{DH}\ln(10)|z_+z_-|}{I_m 1.5^3}\left[1 + 1.5\sqrt{I_m} - 2(1 + 1.5\sqrt{I_m}) - \frac{1}{1 + 1.5\sqrt{I_m}}\right]$$

$$+ \frac{\ln(10)}{\sum\limits_k m_k}\left[\sum_{\text{cation}}\sum_{\text{anion}} \varepsilon(\text{cation,anion}) m_{\text{anion}} m_{\text{cation}}\right.$$

$$\sum_{\text{cation}}\sum_{\text{neutral}} \varepsilon(\text{cation,neutral}) m_{\text{neutral}} m_{\text{cation}} + \sum_{\text{cation}}\sum_{\text{neutral}} \varepsilon(\text{anion,neutral}) m_{\text{neutral}} m_{\text{anion}}$$

$$\left.\frac{1}{2}\sum_{\text{neutr.1}}\sum_{\text{neutr.2}}\varepsilon(\text{neutr.1},\text{neutr.2})m_{\text{neutr.1}}m_{\text{neutr.2}}\right] \qquad (\text{A.206})$$

A_{DH} is the usual Debye-Hückel parameter (0.509 $\text{kg}^{1/2}\cdot\text{mol}^{-1/2}$ at 25 °C).

Moog *et al.* calculated the osmotic coefficient with their Equation (1) according to

$$\phi = \frac{-1000\ln a_{\text{w}}}{18.0148(3m_{\text{FeCl}_2\text{(sln)}})}. \qquad (\text{A.207})$$

Since this formula does not include any model for the formation of FeCl_x^{2-x} complexes, the water activity ($\ln a_{\text{w}}$) is directly linked to the total concentration of the solute $m_{\text{FeCl}_2\text{(sln)}}$ (Table A-71).

Table A-71: Osmotic coefficients in the system $\text{FeCl}_2\text{-H}_2\text{O}$ at 25 °C from [2004MOO/HAG] (Table 1). Values of ln (a_{w}) are calculated according to Eq. (A.207) including full error propagation. Values marked with (*) have been corrected in the present review. Note that the last 9 systems (values shown in italics) have not been considered in the later evaluation (*i.e.*, systems where the final chloride concentration exceeds ~5 $\text{mol}\cdot\text{kg}^{-1}$).

$m_{\text{FeCl}_2\text{(sln)}}$	uncert. $m_{\text{FeCl}_2\text{(sln)}}$	ϕ meas.	uncert. ϕ meas.	Activity of water $\ln(a_{\text{w}})$	uncert. of $\ln(a_{\text{w}})$	Original reference
0.2392	0.0002	0.868	0.001	– 0.01122	0.00002	[2004MOO/HAG]
0.3132	0.0003	0.8755*	0.002	– 0.01482	0.00004	[1941STO/ROB]
0.3625	0.0004	0.8858	0.002	– 0.01735	0.00004	[1941STO/ROB]
0.3740	0.0007	0.87	0.03	– 0.01758	0.00061	[1989NIK/DIK]
0.4456	0.0006	0.914	0.002	– 0.02201	0.00006	[2004MOO/HAG]
0.553	0.001	0.92	0.02	– 0.02750	0.00060	[1989NIK/DIK]
0.5760	0.0006	0.9485	0.002	– 0.02953	0.00007	[1941STO/ROB]
0.6994	0.0005	0.976	0.001	– 0.03689	0.00005	[2004MOO/HAG]
0.7876	0.0008	0.9931	0.002	– 0.04227	0.00010	[1941STO/ROB]
0.9215	0.0008	1.045	0.002	– 0.05204	0.00011	[2004MOO/HAG]
0.9239	0.0006	1.047	0.002	– 0.05228	0.00011	[2004MOO/HAG]
0.9637	0.0008	1.058	0.002	– 0.05510	0.00011	[2004MOO/HAG]
0.9772	0.0008	1.063	0.002	– 0.05614	0.00012	[2004MOO/HAG]
1.056	0.001	1.0781	0.0020	– 0.06153	0.00013	[1941STO/ROB]
1.1068	0.0008	1.100	0.002	– 0.06580	0.00013	[2004MOO/HAG]
1.1560	0.0006	1.0895	0.0080	– 0.06807	0.00050	[1976SUS/GOR2]
1.1665	0.0008	1.119	0.002	– 0.07054	0.00014	[2004MOO/HAG]
1.264	0.001	1.102*	0.0080	– 0.075**28**	0.00055	[1956GRO]

(Continued on next page)

Table A-71 (continued)

$m_{\mathrm{FeCl_2(sln)}}$	uncert. $m_{\mathrm{FeCl_2(sln)}}$	ϕ meas.	uncert. ϕ meas.	Activity of water ln(a_w)	uncert. of ln(a_w)	Original reference
1.309	0.001	1.1512	0.0020	– 0.08144	0.00015	[1941STO/ROB]
1.368	0.001	1.181	0.002	– 0.08731	0.00016	[2004MOO/HAG]
1.413	0.001	1.194	0.002	– 0.09118	0.00017	[2004MOO/HAG]
1.565	0.001	1.234	0.002	– 0.10437	0.00018	[2004MOO/HAG]
1.6578	0.0008	1.2375	0.0060	– 0.11087	0.00054	[1976SUS/GOR2]
1.664	0.002	1.2699	0.0030	– 0.11420	0.00030	[1941STO/ROB]
1.723	0.002	1.2777	0.0030	– 0.11898	0.00031	[1941STO/ROB]
1.819	0.001	1.319	0.003	– 0.12967	0.00030	[2004MOO/HAG]
1.881	0.001	1.338	0.002	– 0.13602	0.00022	[2004MOO/HAG]
1.927	0.001	1.349	0.001	– 0.14049	0.00013	[2004MOO/HAG]
2.017	0.001	1.35**2***	0.005	– 0.147**38**	0.00055	[1956GRO]
2.050	0.002	1.3909	0.003	– 0.15410	0.00036	[1941STO/ROB]
2.218	0.002	1.44	0.002	– 0.17261	0.00029	[2004MOO/HAG]
2.266	0.001	1.448	0.002	– 0.17733	0.00026	[2004MOO/HAG]
2.399	0.001	1.489	0.003	– 0.19305	0.00040	[2004MOO/HAG]
2.550	0.001	1.504*	0.004	– 0.207**27**	0.00056	[1956GRO]
2.601	0.002	1.545	0.003	– 0.21718	0.00045	[2004MOO/HAG]
2.726	0.002	1.574	0.002	– 0.23189	0.00034	[2004MOO/HAG]
3.036	0.002	1.655	0.003	– 0.27319	0.00052	[2004MOO/HAG]
3.199	0.002	1.685	0.002	– 0.29132	0.00039	[2004MOO/HAG]
3.267	0.001	1.66**7***	0.004	– 0.294**33**	0.00071	[1956GRO]
3.664	*0.002*	*1.77*	*0.002*	– *0.35049*	*0.00044*	[2004MOO/HAG]
3.717	*0.003*	*1.784*	*0.003*	– *0.35838*	*0.00067*	[2004MOO/HAG]
4.044	*0.003*	*1.836*	*0.002*	– *0.40127*	*0.00053*	[2004MOO/HAG]
4.164	*0.001*	*1.8**29****	*0.003*	– *0.41**160***	*0.00068*	[1956GRO]
4.640	*0.003*	*1.907*	*0.002*	– *0.47821*	*0.00059*	[2004MOO/HAG]
4.810	*0.001*	*1.91**2****	*0.003*	– *0.497**03***	*0.00079*	[1956GRO]
4.971	*0.002*	*1.92*	*0.004*	– *0.51582*	*0.00109*	[1976SUS/GOR2]
5.087	*0.001*	*1.95**3****	*0.003*	– *0.53**693***	*0.00083*	[1956GRO]
5.088	*0.003*	*1.947*	*0.004*	– *0.53538*	*0.00114*	[2004MOO/HAG]

For the subsequent re-evaluation it's assumed that $FeCl^+$ is the only complex formed in solutions that are not too high in chloride concentration (below ~5 mol·kg^{-1}). This view is supported by the work of Zhao and Pan [2001ZHA/PAN] and particularly by [1987VOG/MCC], who studied Fe(II) chloride complexes (by spectroscopic methods) at high chloride concentrations. From their studies one might infer that higher-order octahedral as well as tetrahedral complexes are not formed in solutions with less than ~5 $\mathrm{mol{\cdot}kg^{-1}}$ chloride at ambient temperature. The formation of higher-order complexes becomes significant at elevated temperatures (*i.e.*, 49 °C [1987VOG/MCC]).

For the present evaluation this means that no uncharged complex (*i.e.*, $\mathrm{FeCl_2(aq)}$) needs to be considered and thus the last three terms of Eq. (A.206) become zero.

Equation (A.206) simplifies to

$$\begin{aligned}\phi-1 = &-\frac{A_{\mathrm{DH}}\ln(10)|z_+z_-|(t-2\ln t-1/t)}{1.5^3 I_{\mathrm{m}}}\\ &+\frac{\ln(10)}{\sum\limits_k m_k}\left[\varepsilon(\mathrm{Fe^{2+}},\mathrm{Cl^-})m_{\mathrm{Fe^{2+}}}m_{\mathrm{Cl^-}}+\varepsilon(\mathrm{FeCl^+},\mathrm{Cl^-})m_{\mathrm{FeCl^+}}m_{\mathrm{Cl^-}}\right]\end{aligned} \tag{A.208}$$

(with $t = 1 + 1.5\sqrt{I_{\mathrm{m}}}$ and $\sum\limits_{\mathrm{k}} m_{\mathrm{k}} = m_{\mathrm{Fe^{2+}}} + m_{\mathrm{FeCl^+}} + m_{\mathrm{Cl^-}} \equiv (3m_{\mathrm{FeCl_2\,(sln)}} - m_{\mathrm{FeCl^+}}))$

and Eq. (A.205) simplifies to

$$\beta_1\, m_{\mathrm{Cl^-}}{}^2 + m_{\mathrm{Cl^-}}\,(1 - m_{\mathrm{FeCl_2\,(sln)}}\,\beta_1) - 2\, m_{\mathrm{FeCl_2\,(\mathit{s}ln)}} = 0, \tag{A.209}$$

with $\beta_1 = m_{\mathrm{FeCl^+}} / (m_{\mathrm{Fe^{2+}}} m_{\mathrm{Cl^-}})$.

The ionic strength of the solution is given by

$$I_m = 3\, m_{\mathrm{FeCl_2\,(sln)}} - 2\, m_{\mathrm{FeCl^+}}\ ,$$

and the formation constant β_1 at the ionic strength I_m of interest is given by

$$\log_{10}\beta_1 = \log_{10}\beta_1^{\mathrm{o}} - \log_{10}\gamma_{\mathrm{FeCl^+}} + \log_{10}\gamma_{\mathrm{Fe^{2+}}} + \log_{10}\gamma_{\mathrm{Cl^-}}\ .$$

In the SIT formalism individual γ values are given by:

$$\log_{10}\gamma_{\mathrm{FeCl^+}} = -(A_{\mathrm{DH}}\sqrt{I_{\mathrm{m}}})/(1+1.5\sqrt{I_{\mathrm{m}}}) + \varepsilon(\mathrm{FeCl^+},\mathrm{Cl^-})m_{\mathrm{Cl^-}}$$

$$\log_{10}\gamma_{\mathrm{Fe^{2+}}} = -(4A_{\mathrm{DH}}\sqrt{I_{\mathrm{m}}})/(1+1.5\sqrt{I_{\mathrm{m}}}) + \varepsilon(\mathrm{Fe^{2+}},\mathrm{Cl^-})m_{\mathrm{Cl^-}}$$

$$\log_{10}\gamma_{\mathrm{Cl^-}} = -(A_{\mathrm{DH}}\sqrt{I_{\mathrm{m}}})/(1+1.5\sqrt{I_{\mathrm{m}}}) + \varepsilon(\mathrm{FeCl^+},\mathrm{Cl^-})m_{\mathrm{FeCl^+}} + \varepsilon(\mathrm{Fe^{2+}},\mathrm{Cl^-})m_{\mathrm{Fe^{2+}}}$$

We set $D = (\mathrm{A_{DH}}\sqrt{I_m})/(1+1.5\sqrt{I_m})$ and $\Delta\varepsilon = \varepsilon(\mathrm{FeCl^+},\mathrm{Cl^-}) - \varepsilon(\mathrm{Fe^{2+}},\mathrm{Cl^-})$ to obtain

$$\log_{10}\beta_1 = \log_{10}\beta_1^{\mathrm{o}} - 4D - 2(m_{\mathrm{FeCl_2\,(sln)}} - m_{\mathrm{FeCl^+}})\cdot\Delta\varepsilon + m_{\mathrm{FeCl_2\,(sln)}}\varepsilon(\mathrm{Fe^{2+}},\mathrm{Cl^-}) \tag{A.210}$$

Note that the above definition of $\Delta\varepsilon$ has its "historical" origin in the SIT evaluation as for example provided under Appendix A entry [1990HEI/SEW], where the regression of ($\log_{10}\beta_1$ + $4D$) *vs.* I_m produces the aforementioned difference. In principle, the subsequent paragraphs describe a non-linear least-squares fit extracting the three parameters $\log_{10}\beta_1^{\mathrm{o}}$, $\varepsilon(\mathrm{Fe^{2+}},\mathrm{Cl^-})$ and $\varepsilon(\mathrm{FeCl^+},\mathrm{Cl^-})$ from the measured water activity of $\mathrm{FeCl_2}$ solutions with variable concentration. Unfortunately, the non-linear procedure cannot be set up in a straight-forward manner, but requires nested iterations (*i.e.*, the ionic strength I_m depends on the parameters to be extracted). Hence, the following paragraphs, which are based on spread-sheet methods, offer just one possibility of how "best" parameters can be evaluated.

The osmotic coefficient ϕ as compiled in Table A-71 was evaluated by the authors according to Eq. (A.207) under the assumption that no complexes are formed, *i.e.*, by assuming that $\sum_{\mathrm{k}} m_{\mathrm{k}} = 3\,m_{\mathrm{FeCl_2\,(sln)}}$.

For further evaluations an effective ϕ_{eff} needs to be re-evaluated, using the actual sum of solutes for each data-point provided in Table A-71:

$$\phi_{\mathrm{eff}} = \frac{-1000\ln a_{\mathrm{w}}}{18.0153(m_{Fe^{2+}} + m_{\mathrm{FeCl^+}} + m_{\mathrm{Cl^-}})} \text{ or } \phi_{\mathrm{eff}} = \phi_{\mathrm{measured}}\frac{3m_{\mathrm{FeCl_2\,(sln)}}}{3m_{\mathrm{FeCl_2\,(sln)}} - m_{\mathrm{FeCl^+}}} \qquad \text{(A.211)}$$

Note that the correct molar mass of water is 18.0153 g·mol^{-1}, but the difference from the value 18.0148 g·mol^{-1} as used by Moog *et al.* is not significant. We rearrange Eq. (A.208) (now using the osmotic coefficient relevant for the case where the complex FeCl$^+$ is formed) to obtain:

$$\begin{aligned}\frac{(\phi_{\mathrm{eff}}-1)}{\ln 10} = {} & \frac{0.509|z_+z_-|}{1.5^3}\cdot\frac{(t-2\ln t-1/t)\sum_k m_k}{I_m} \\ & + \varepsilon(\mathrm{Fe^{2+},Cl^-})m_{\mathrm{Fe^{2+}}}m_{\mathrm{Cl^-}} + \varepsilon(\mathrm{FeCl^+,Cl^-})m_{\mathrm{FeCl^+}}m_{\mathrm{Cl^-}}\end{aligned}$$

and by further rearrangement

$$\begin{aligned}&\frac{(\phi_{\mathrm{eff}}-1)(3m_{\mathrm{FeCl_2\,(sln)}} - m_{\mathrm{FeCl^+}})}{\ln 10\cdot m_{\mathrm{FeCl_2\,(sln)}}} + \frac{0.509|z_+z_-|(t-2\ln t-1/t)(3m_{\mathrm{FeCl_2\,(sln)}} - m_{\mathrm{FeCl^+}})}{1.5^3\, m_{\mathrm{FeCl_2\,(s\,ln)}} I_m} \\ &-\Delta\varepsilon\left(2-\frac{m_{\mathrm{FeCl^+}}}{m_{\mathrm{FeCl_2\,(sln)}}}\right) = m_{\mathrm{Cl^-}}\,\varepsilon(\mathrm{Fe^{2+},Cl^-})\end{aligned} \qquad \text{(A.212)}$$

Equation (A.212) provides the tool to derive $\varepsilon(\mathrm{Fe^{2+},Cl^-})$ with the help of a linear regression, provided that $\Delta\varepsilon$ and $m_{\mathrm{FeCl^+}}$ are known. To derive $m_{\mathrm{FeCl^+}}$ in turn requires the evaluation of Eq. (A.210). This means that one has first to proceed through Eq. (A.210), then to calculate the speciation in solution and finally to perform the linear regression defined by Eq. (A.212).

A potential problem is encountered with the expression $|z_+\cdot z_-|$. The charges of the ions are clear if we have to deal with a completely dissociated system and we immediately understand that $z_- = -1$ in the present system where Cl$^-$ is the only anion. But what is z_+? In solution we have the doubly charged Fe^{2+} as well as the singly charged FeCl$^+$. A simple solution would be to take an "averaged" positive charge, leading to

$${}^{\mathrm{AV}}z_+ = (2\,m_{\mathrm{Fe^{2+}}} + m_{\mathrm{FeCl^+}})/(m_{\mathrm{Fe^{2+}}} + m_{\mathrm{FeCl^+}}). \qquad \text{(A.213)}$$

However, there is another possibility for defining z_+. For each individual solution we finally know the ionic strength I_m from molalities and charges of the involved species. Particularly, we also know the molality of each cationic solute, *i.e.*, $m_{\mathrm{Fe}^{2+}}$ and m_{FeCl^+}. We define the positive charge of a "cationic solute" in such a way that the known ionic strength is reproduced with its charge and the sum of all cationic solutes. This means that we define the existence of a single cationic solute with molality ($m_{\mathrm{Fe}^{2+}}$ + m_{FeCl^+}) and charge ${}^{\mathrm{I}}z_+$. With this definition we have to solve

$$½((+2)^2\, m_{\mathrm{Fe}^{2+}} + (+1)^2\, m_{\mathrm{FeCl}^+} + (-1)^2\, m_{\mathrm{Cl}^-}) = I_m = ½(({}^{\mathrm{I}}z_+)^2\, m_{\mathrm{FeCl_2(sln)}} + (-1)^2\, m_{\mathrm{Cl}^-})$$

to obtain

$${}^{\mathrm{I}}z_+ = \surd(4 - 3\, m_{\mathrm{FeCl}^+} /(m_{\mathrm{Fe}^{2+}} + m_{\mathrm{FeCl}^+})) \qquad \text{(A.214)}$$

Equation (A.214) seems more complicated than Eq. (A.213), but is certainly more consistent with Eq. (A.212) than is Eq. (A.213) because $|{}^{\mathrm{I}}z_+ \cdot z_-|$ is consistent with the ionic strength of the solution, but $|{}^{\mathrm{AV}}z_+ \cdot z_-|$ is not. Note that the actual difference between ${}^{\mathrm{I}}z_+$ and ${}^{\mathrm{AV}}z_+$ is small (less than 3%).

Selection of the "best fit"

The calculation was done in a stepwise fashion rather than as a global least-squares minimisation. Values of the three parameters $\log_{10} \beta^{\circ}$, $\Delta\varepsilon$, and $\varepsilon(\mathrm{Fe}^{2+},\mathrm{Cl}^-)_{\mathrm{INPUT}}$ have been pre-selected and Eq. (A.212) was evaluated for all experimental systems after the detailed speciation in solution had been calculated.

The linear regression "(A.212)" then produced an interaction coefficient $\varepsilon(\mathrm{Fe}^{2+},\mathrm{Cl}^-)_{\mathrm{OUTPUT}}$. The linear regression was of the form Y = m_{Cl^-} $\varepsilon(\mathrm{Fe}^{2+},\mathrm{Cl}^-)$, where Y is the left-hand-side of Eq. (A.212), and the value of $\varepsilon(\mathrm{Fe}^{2+},\mathrm{Cl}^-)$ was determined. This assumes that at a value of m_{Cl^-} equal to zero the value of the left hand side of Eq. (A.212) is zero. This process also was tested in each case by using an unconstrained fit, and the resulting intercept was calculated. For the selected combination of $\log_{10} \beta^{\circ}$ and $\Delta\varepsilon$ a solution was found when $\varepsilon(\mathrm{Fe}^{2+},\mathrm{Cl}^-)_{\mathrm{OUTPUT}}$ = $\varepsilon(\mathrm{Fe}^{2+},\mathrm{Cl}^-)_{\mathrm{INPUT}}$. Hence, $\varepsilon(\mathrm{Fe}^{2+},\mathrm{Cl}^-)_{\mathrm{INPUT}}$ has been varied until this condition was fulfilled.

The most important criterion for a good fit is how well the resulting parameters reproduce the actual observed quantity $\phi_{\mathrm{eff}}(m_{\mathrm{FeCl_2(sln)}})$. A sensible measure is therefore given by examining the sum of squares of the differences ϕ_{eff}(observed)-ϕ_{eff}(calculated), *i.e.* $\Sigma(\phi_{\mathrm{eff}}(\mathrm{obs}) - \phi_{\mathrm{eff}}(\mathrm{A.212}))^2$.

Analysis was performed in two steps. First, a series of $\log_{10} \beta^{\circ}$ and $\Delta\varepsilon$ values was explored to test for a global minimum for the sum of squares. In the calculation space defined by the ranges $-2.6 < \log_{10} \beta_1^{\circ} < 0$ and $0.1 > \Delta\varepsilon > -0.1$, a minimum sum of squares was found. Second, the minimal absolute value of the intercept for Eq. (A.212) was taken into account. The surface defined by the sum of squares in the minimization of the parameters is very "flat". Low sums of squares of differences were found in the region defined by values of $\log_{10} \beta_1^{\circ}$ from -2.60 to -1.72, $\varepsilon(\mathrm{Fe}^{2+},\mathrm{Cl}^-)$ from 0.167 to 0.169 $\mathrm{kg \cdot mol^{-1}}$ and $\varepsilon(\mathrm{FeCl}^+,\mathrm{Cl}^-)$ from 0.169 to 0.171 $\mathrm{kg \cdot mol^{-1}}$.

For the range of $\mathrm{FeCl_2}$ molalities < 3.3, a parameter set consisting of

$$\log_{10} \beta_1^{\circ} = -(2.05 \pm 0.15)$$

$$\varepsilon(\mathrm{Fe}^{2+},\mathrm{Cl}^-) = (0.17 \pm 0.01)\ \mathrm{kg \cdot mol^{-1}}$$

$$\varepsilon(\mathrm{FeCl}^+,\mathrm{Cl}^-) = (0.16 \pm 0.01)\ \mathrm{kg \cdot mol^{-1}}$$

seems to best cover the region where all criteria, *i.e.*, the sum of squares, the intercept and the coefficient of determination R^2, do not deviate too much from their “best” values. The evaluation of the slope $\varepsilon(\mathrm{Fe}^{2+},\mathrm{Cl}^-)$ according to Eq. (A.212) is demonstrated in Figure A-66, and the recalculation of experimental osmotic values from the “best” parameter set is shown in Figure A-67.

Figure A-66: Determination of $\varepsilon(\mathrm{Fe}^{2+},\mathrm{Cl}^-)$ from osmotic data in the $\mathrm{FeCl_2}$-$\mathrm{H_2O}$ system at 25 °C according to Eq. (A.212). Compositions producing chloride molalities above ~5 $\mathrm{mol \cdot kg^{-1}}$ were not considered. Parameters adopted were: $\log_{10} \beta_1^{\circ} = -2.05$, $\varepsilon(\mathrm{Fe}^{2+},\mathrm{Cl}^-) = 0.174\ \mathrm{kg \cdot mol^{-1}}$, $\varepsilon(\mathrm{FeCl}^+,\mathrm{Cl}^-) = 0.164\ \mathrm{kg \cdot mol^{-1}}$.

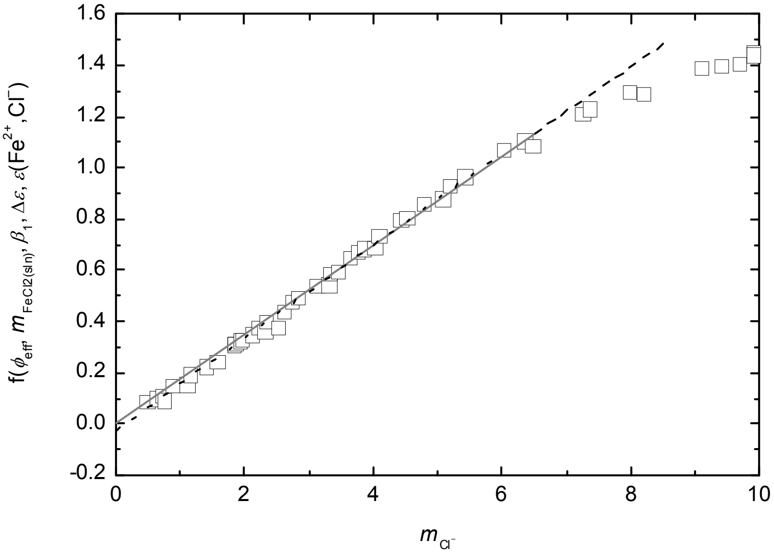
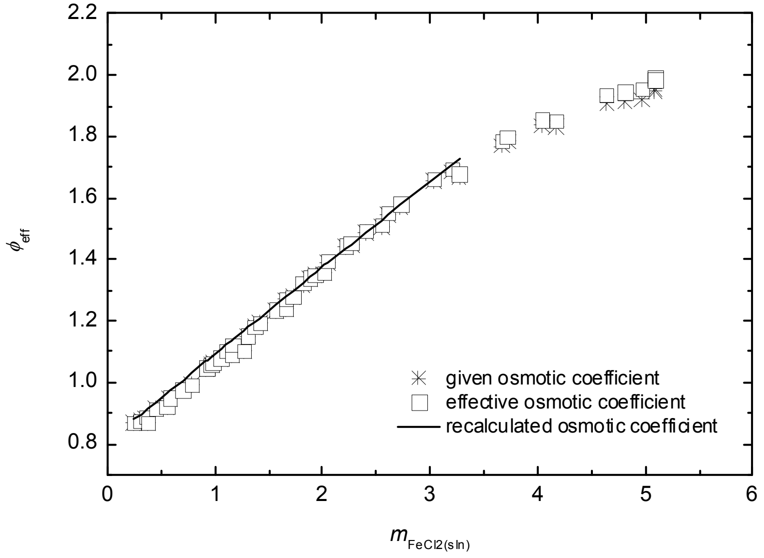


Figure A-67: Comparison of the relationship between the osmotic coefficient of iron(II) chloride (measured and calculated assuming $FeCl^+$ complex formation) and the molality of iron(II) chloride at 25 °C using the parameters defined in Figure A-66. The solid line represents the osmotic coefficients expressed using Eq. (A.212).



Individual activity coefficients were calculated according to their basic definition in the SIT approach, *i.e.*,

$$\log_{10}\gamma_j = -z^2D + \sum_k \varepsilon(j,k)\, m_k\,, \tag{A.215}$$

where D is the appropriate Debye-Hückel term and the sum extends over all counter-ions. The effective osmotic coefficients Eq. (A.211) and the γ_i values are provided in Table A-72 and plotted in Figure A-68.

Table A-72: Measured and calculated effective osmotic coefficients (Eq. (A.211)) and individual activity coefficients of ions according to Eq. (A.215).

$m_{FeCl_2(sln)}$	$\phi_{measured}$	$\phi_{effective}$	$\gamma_{Fe^{2+}}$	γ_{FeCl^+}	γ_{Cl^-}
0.23920	0.868	0.8682	0.2107	0.7739	0.7109
0.31320	0.8755	0.8756	0.2018	0.7976	0.7137
0.3625	0.8858	0.8861	0.1987	0.8167	0.7181
0.374	0.87	0.8703	0.1983	0.8214	0.7193
0.4456	0.914	0.9144	0.1969	0.8533	0.7285

(Continued on next page)

Table A-72 (continued)

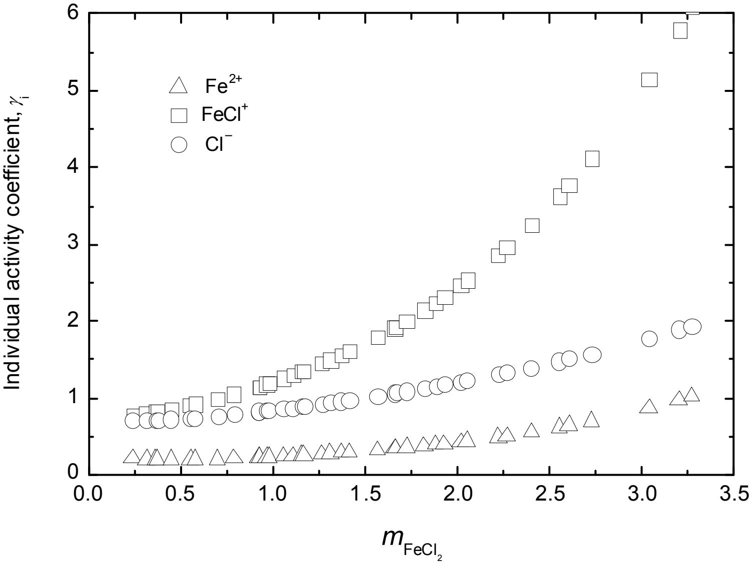
$m_{\mathrm{FeCl_2(sln)}}$	ϕ_{measured}	$\phi_{\mathrm{effective}}$	$\gamma_{\mathrm{Fe^{2+}}}$	$\gamma_{\mathrm{FeCl^+}}$	$\gamma_{\mathrm{Cl^-}}$
0.553	0.92	0.9205	0.1987	0.9078	0.7461
0.57600	0.9485	0.9490	0.1995	0.9204	0.7503
0.6994	0.976	0.9767	0.2061	0.9936	0.7754
0.7876	0.9931	0.9938	0.2126	1.0516	0.7954
0.9215	1.045	1.0459	0.2249	1.1487	0.8287
0.9239	1.047	1.0479	0.2252	1.1505	0.8293
0.9637	1.058	1.0590	0.2294	1.1816	0.8399
0.9772	1.063	1.0640	0.2308	1.1924	0.8435
1.056	1.0781	1.0792	0.2400	1.2578	0.8653
1.1068	1.100	1.1012	0.2463	1.3022	0.8800
1.156	1.0895	1.0908	0.2529	1.3470	0.8945
1.1665	1.119	1.1203	0.2543	1.3567	0.8977
1.264	1.102	1.1044	0.2684	1.4514	0.9279
1.309	1.1512	1.1527	0.2754	1.4976	0.9424
1.368	1.181	1.1827	0.2850	1.5606	0.9619
1.413	1.194	1.1958	0.2926	1.6106	0.9771
1.565	1.234	1.2361	0.3209	1.7927	1.0310
1.6578	1.2375	1.2398	0.3401	1.9145	1.0658
1.664	1.2699	1.2723	0.3414	1.9230	1.0682
1.723	1.2777	1.2802	0.3545	2.0053	1.0912
1.819	1.319	1.3218	0.3771	2.1473	1.1298
1.881	1.338	1.3410	0.3926	2.2446	1.1557
1.927	1.349	1.3521	0.4046	2.3196	1.1753
2.017	1.352	1.3574	0.4295	2.4741	1.2149
2.050	1.3909	1.3945	0.4390	2.5333	1.2297
2.218	1.44	1.4442	0.4917	2.8582	1.3088
2.266	1.448	1.4524	0.5080	2.9586	1.3324
2.399	1.489	1.4940	0.5564	3.2559	1.4004
2.550	1.504	1.5117	0.6177	3.6302	1.4822
2.601	1.545	1.5510	0.6400	3.7661	1.5110
2.726	1.574	1.5536	0.6985	4.1212	1.5841
3.036	1.655	1.6739	0.8691	5.1521	1.7823
3.199	1.685	1.6950	0.9756	5.7925	1.8968
3.267	1.667	1.6794	1.0239	6.0823	1.9468
3.664	*1.77*	*1.7843*	1.3588	8.0786	2.2676
3.717	*1.784*	*1.7989*	1.4111	8.3891	2.3143
4.044	*1.836*	*1.8548*	1.7810	10.5738	2.6256
4.164	*1.829*	*1.8512*	1.9393	11.5041	2.7503

(Continued on next page)

Table A-72 (continued)

$m_{\mathrm{FeCl_2\,(sln)}}$	ϕ_{measured}	$\phi_{\mathrm{effective}}$	$\gamma_{\mathrm{Fe^{2+}}}$	$\gamma_{\mathrm{FeCl^+}}$	$\gamma_{\mathrm{Cl^-}}$
4.64	*1.907*	*1.9350*	2.7116	16.0083	3.3070
4.81	*1.912*	*1.9450*	3.0521	17.9794	3.5323
4.971	*1.92*	*1.9541*	3.4109	20.0481	3.7599
5.087	*1.953*	*1.9920*	3.6931	21.6693	3.9329
5.088	*1.947*	*1.9839*	3.6957	21.6838	3.9344

Figure A-68: Individual ion activity coefficients according to Eq. (A.215).



In conclusion, the representation of the available osmotic data does not require consideration of a $FeCl^+$ complex. This is clearly demonstrated by the nearly insignificant formation constant value resulting from the evaluation. The result conflicts with results from a series of spectroscopic studies ([1987VOG/MCC], [1990HEI/SEW], [2001ZHA/PAN]) that confirmed the existence of the mono chlorido complex and also of higher-order complexes at elevated temperatures and chloride concentrations.

With $\varepsilon(\mathrm{Fe^{2+}},\mathrm{Cl^-}) = (0.17 \pm 0.01)\ \mathrm{kg\cdot mol^{-1}}$ the evaluation provides an interaction coefficient in an expected range, typical for a +2/–1 charge combination. The "quality" of this interaction coefficient is further corroborated by the fact that the present data set does not suffer from "mixed medium" effects; chloride is the only anion in the system. Notably, a much simpler treatment of the measured osmotic coefficients (see Eq. (VI.27)) in the linear range produces a nearly identical interaction coefficient and confirms the absence of the $FeCl^+$ complex at $FeCl_2(sln)$ molalities < 3 m at ambient temperatures with the sensitivity limits of the isopiestic data treatment methods.

Individual activity coefficients for Fe^{2+} and Cl^- show expected magnitudes and tendencies. When the molar ratio sum-of-ions/water exceeds about 6, there is insufficient water to fully hydrate the ions and a moderate increase in the γ_i values is to be expected (for $FeCl_2$ aqueous solutions this is the case for salt molalities above approximately 3 $mol\cdot kg^{-1}$). For the singly-charged ion $FeCl^+$ one would expect a behaviour similar to that of the singly-charged Cl^- ion, but as indicated in Table A-72, the activity coefficient γ_{FeCl^+} becomes very high with increasing molality of $FeCl_2(sln)$. It is not clear how an activity coefficient substantially exceeding unity should be interpreted. On page 355 Grenthe *et al.* [1997GRE/PLY2] state: *There is no unambiguous thermodynamic method to distinguish between complex formation / ion-pairing and other types of short-range interactions between species in solution when the extent of complex formation, is small or moderate.... It is up to the modeller to decide if he/she wishes to describe weak interactions ... in terms of complex formation or by Pitzer type of ion interactions.* Both the low formation constant and the strongly increasing γ_{FeCl^+} indicate that a model including complexes does not seem to be necessary for explaining the osmotic data for $FeCl_2(sln)$.

From the equation for $\phi(m)$ from Moog *et al.* [2004MOO/HAG], [2004RUM/HAG], the values 1.946, 2.540 and 0.586 for ϕ, $\gamma_\pm$, and a_w are calculated to apply at the saturation molality, 5.087 $mol\cdot kg^{-1}$. The authors' equation provides a good representation (within 2%) of the existing experimental data. Uncertainties in the values for m and ϕ (*i.e.*, a_w and, less directly, $\gamma_\pm$) are correlated.

The values of m, $\gamma_\pm$, and a_w at saturation can be used to calculate the Gibbs energy of dissolution of $FeCl_2\cdot 4H_2O(cr)$

$$FeCl_2\cdot 4H_2O(cr) \rightleftharpoons Fe^{2+} + 2\,Cl^- + 4\,H_2O(l). \qquad (A.216)$$

The primary contribution to the uncertainty in that Gibbs energy of dissolution (– 17.16 $kJ\cdot mol^{-1}$) is the uncertainty in the saturation molality (it might be as low as 4.95 m, but is unlikely to be greater than 5.15 m [1952SCH3]). In the present review, an uncertainty of ± 0.40 $kJ\cdot mol^{-1}$ is estimated based on recalculations assuming different values of m, $\gamma_\pm$ and a_w within the bounds discussed here.

[2004RUM/HAG]

Isopiestic measurements were performed on the following aqueous binary and ternary systems: $Fe_2(SO_4)_3$-H_2SO_4-H_2O, $FeCl_3$-H_2O, and $FeCl_3$-MCl_n-H_2O, where M = Na, K, Mg, and Ca at 25.00 °C. Loss of HCl from concentrated $FeCl_3$ solutions was evident but was monitored *in situ* by including cups containing unbuffered NaCl(sln) and $AgNO_3(sln)$ although an unknown quantity of HCl was lost by interaction with the chamber walls, limiting the maximum $FeCl_3$ concentration that could be studied to 1.7 $mol \cdot kg^{-1}$. No attempt was made to correct for the effect of hydrolysis on the speciation of Fe^{3+} and the authors speculate that the addition of HCl to minimize hydrolysis would exacerbate the problem of HCl volatility.

As in their companion study, [2004MOO/HAG], these investigators took the precaution of using four independent standard solutions of H_2SO_4, $CaCl_2$, NaCl and KCl. The reliability of their choice of osmotic coefficient data for these standard solutions is discussed in [2004MOO/HAG].

From the general equation which assumes that the interaction coefficient is a linear function of m_{NX}:

$$1-\phi=\frac{A\ln(10)|z_+z_-|}{I_m(Ba_j)^3}\left[1+Ba_j\sqrt{I_m}-2\ln(1+Ba_j\sqrt{I_m})-\frac{1}{(1+Ba_j\sqrt{I_m})}\right]$$
$$+\left(\frac{\nu_+\nu_-}{\nu_++\nu_-}\right)\ln(10)\varepsilon(\mathrm{N,X})m_{\mathrm{NX}}$$

It follows for $FeCl_3$ at 25.0 °C,

$$1-\phi=\frac{3.516}{I_m(3.375)}\left[1+1.5\sqrt{I_m}-2\ln(1+1.5\sqrt{I_m})-\frac{1}{(1+1.5\sqrt{I_m})}\right].$$
$$+1.727\varepsilon(\mathrm{Fe^{3+},X^-})m_{\mathrm{FeCl_3}}$$

Fits of the data in Figure A-70, where y represents the negative of the LHS of the above equation, are as follows: all points, unweighted gives a slope of (0.229 ± 0.002) (1σ); ignoring the two lowest concentrations, all remaining points (< 1.7 $mol \cdot kg^{-1}$) in an unweighted linear regression gives a slope of (0.232 ± 0.006), whereas all points with a $1/m^2$ weight gives (0.245 ± 0.012). The unweighted slope yields $\varepsilon(Fe^{3+}, Cl^-)$ = 0.133 $kg \cdot mol^{-1}$. Note that in the final fit adopted by this review, experimental uncertainties were assigned to the osmotic coefficients determined for these isopiestic measurements ranging from ± 0.007 at the lowest molality to ± 0.003 above 0.5 $mol \cdot kg^{-1}$ and these were used to provide the weighting factors.

Figures A-71 to A-73 illustrate the quality of the osmotic coefficient data for the three electrolytes used as isopiestic standards (H_2SO_4 [1976RAR/HAB], $CaCl_2$ [1997RAR/CLE], NaCl [1985CLA/GLE] and KCl [1999ARC2]) by Rumyantsev *et al.* from the sources given in these plots compared to those derived from tabulated water activities given as NEA auxiliary data. These three references provide the necessary equations for the osmotic coefficients based on analyses of data available at that time and are therefore preferred by this reviewer.

Figure A-69: Osmotic coefficients of iron(III) chloride as a function of molality at 25 °C.

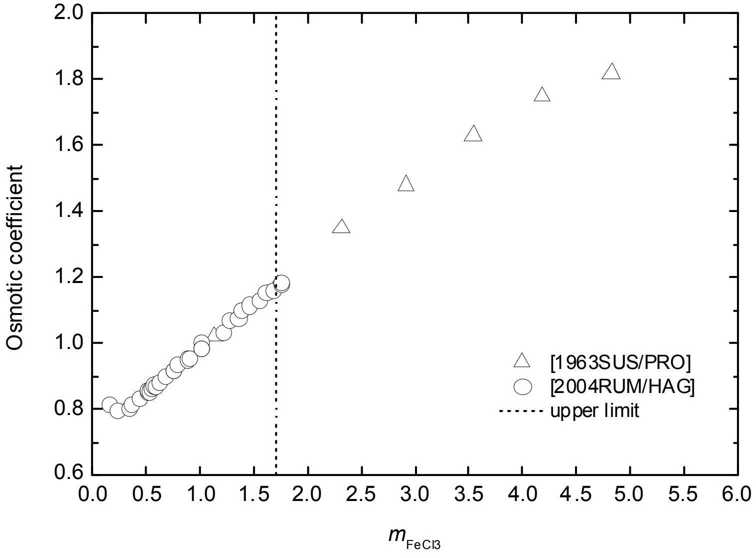


Figure A-70: Osmotic coefficient function (y) for iron(III) chloride at 25.0 °C.

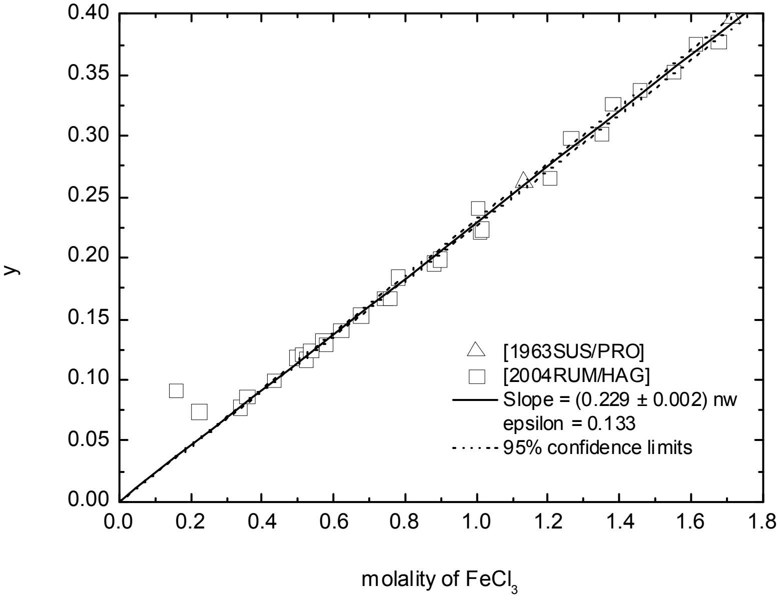


Figure A-71: Osmotic coefficients of sulfuric acid at 25.0 °C.

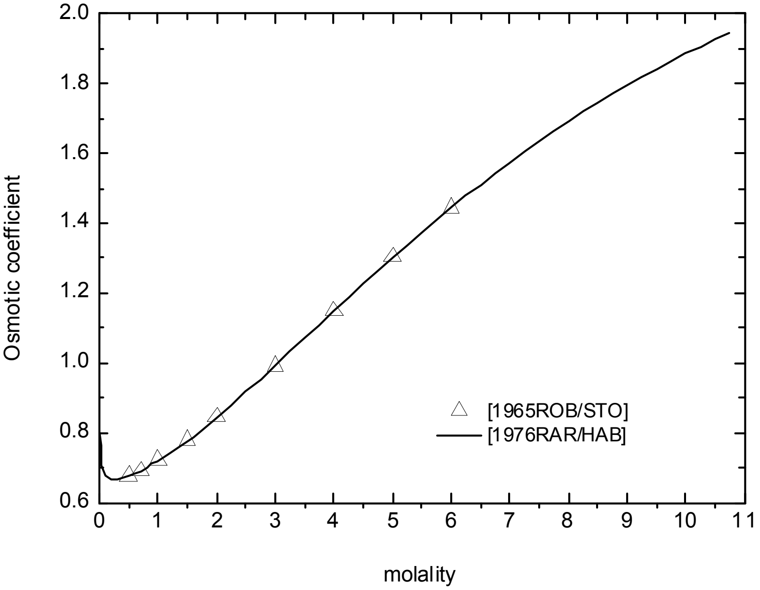


Figure A-72: Osmotic coefficients of calcium chloride at 25.0 °C.

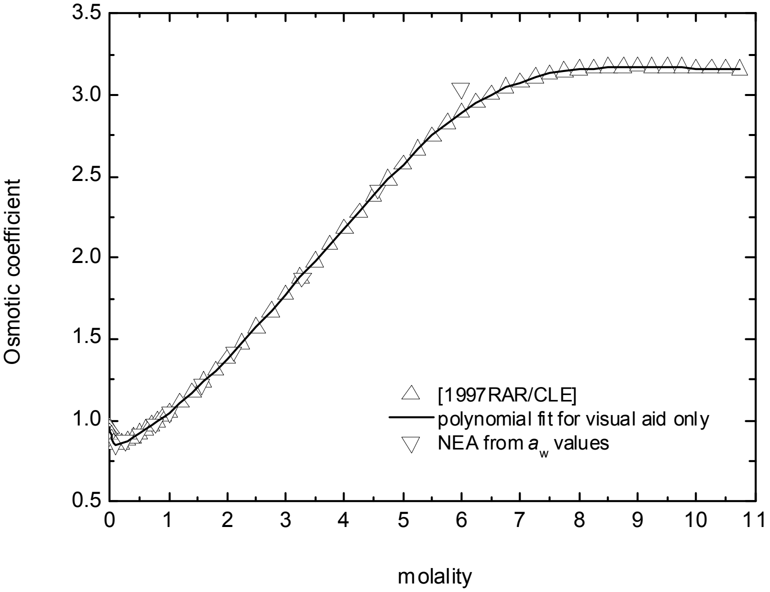
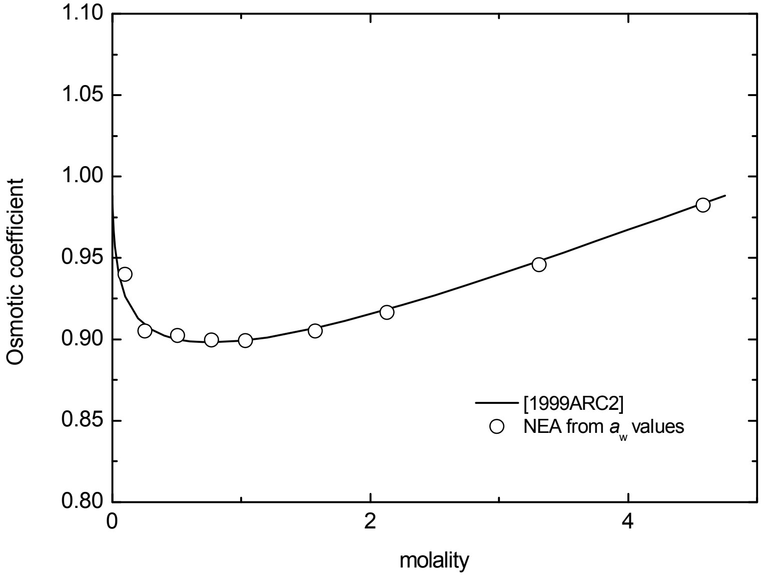


Figure A-73: Osmotic coefficients of potassium chloride at 25.0 °C.



[2004WES/ZIE]

This review chapter deals with the experimental techniques and data treatments currently used for determining the solubility of a wide range of metal oxides/hydroxides and spinels for which experimental results are available to high temperature. Empirical equations (at saturation water vapour pressures) extracted from the literature for the solubility of the crystalline $Fe(OH)_2$, Fe_3O_4, and Fe_2O_3 solids are given, corresponding to the equilibria:

$$Fe(OH)_2(cr) + (2 - y)H^+ \rightleftharpoons Fe(OH)_y^{2-y} + (2 - y)H_2O(l)$$

$\log_{10}{}^*K^\circ_{s,0} = -2.575 + 4021.9/T$ (valid from 273.15 to 423.15 K) taken from [1995ZIE/JON].

$$\tfrac{1}{3}\,Fe_3O_4(cr) + (2 - y)H^+ + \tfrac{1}{3}\,H_2(g) \rightleftharpoons Fe(OH)_y^{2-y} + \tfrac{1}{3}\,H_2O(l)$$

$\log_{10}{}^*K^\circ_{s,0} = -51.381 + 7114.02/T + 6.8581\ln(T)$ (valid from 298.15 to 573.15 K) [1995ZIE/JON]

$\log_{10}{}^*K^\circ_{s,1} = -56.881 + 6085.05/T + 6.8581\ln(T)$ (valid from 298.15 to 573.15 K) [1995ZIE/JON]

$\log_{10} K^\circ_{s,2} = -54.713 + 2031.8/T + 6.8581\ln(T)$ (valid from 298.15 to 573.15 K) [1995ZIE/JON]

$\log_{10}{}^{*}K^{\circ}_{s,3} = -59.498 - 118.03/T + 6.8581\ln(T)$ (valid from 298.15 to 573.15 K) [1995ZIE/JON]

$$\tfrac{1}{3}\,Fe_3O_4(cr) + (3-y)H^+ \rightleftharpoons Fe(OH)_y^{3-y} + \tfrac{1}{6}\,H_2(g) + (\tfrac{4}{3}-y)H_2O(l)$$

$\log_{10}{}^{*}K^{\circ}_{s,3} = -51.438 - 271.6/T + 6.8581\ln(T)$ (valid from 298.15 to 573.15 K) [1995ZIE/JON]

$\log_{10}{}^{*}K^{\circ}_{s,4} = -57.675 - 1274.5/T + 6.8581\ln(T)$ (valid from 298.15 to 573.15 K) [1995ZIE/JON]

A discussion of the original experimental results of [1995ZIE/JON] is given in the corresponding Appendix A entry. The solubility constants for hematite were derived by Wesolowski *et al.* by considering the electrochemical data of [1999SER/SUL] obtained from 278.15 to 363.15 K at 0.1 MPa for the redox equilibrium: $Fe^{3+} + \tfrac{1}{2}H_2(g) \rightleftharpoons Fe^{2+} + H^+$, for which $\log_{10}{}^{*}K^{\circ} = -15.599 + 3021.2/T + 3.2431\ln(T)$. They combined this expression with those for magnetite given above and the values of the thermodynamic properties of magnetite and hematite [1990HEM], and of water taken from SUPCRT92 [1992JOH/OEL] to give the following expressions for the temperature dependencies of the solubility constants for hematite according to the equilibria:

$$\tfrac{1}{2}Fe_2O_3(cr) + (3-y)H^+ \rightleftharpoons Fe(OH)_y^{3-y} + (1\tfrac{1}{2}-y)H_2O(l)$$

$\log_{10}{}^{*}K^{\circ}_{s,0} = 3.302 + 2905.3/T - 2.264\ln(T)$ (valid from 273.15 to 523.15 K)

$\log_{10}{}^{*}K^{\circ}_{s,1} = 8.822 + 599.7/T - 2.264\ln(T)$ (valid from 273.15 to 573.15 K)

$\log_{10}K^{\circ}_{s,3} = -1.817 - 2847.0/T$ (valid from 373.15 to 573.15 K)

$\log_{10}{}^{*}K^{\circ}_{s,4} = -8.054 - 3849.94/T$ (valid from 373.15 to 573.15 K)

The temperature dependencies of the solubility constants for the three iron oxide/hydroxide phases provided in this chapter are of value for comparison purposes only and are not adopted by this review. The thermodynamic quantities associated with the formation of Fe(s), $Fe(OH)_2(s)$, α-FeOOH, γ-FeOOH, $Fe_3O_4(s)$, α-Fe_2O_3, Fe^{2+}, $FeOH^+$, $Fe(OH)_2(aq)$, $Fe(OH)_3^-$, Fe^{3+}, $FeOH^{2+}$, $Fe(OH)_3(aq)$ and $Fe(OH)_4^-$ are also tabulated although the authors state that these suggested values do not necessarily correlate with the solubility constants shown above. All of the solubility expressions given in this paper are presented for comparative purposes only especially in light of the criticisms of constants derived for magnetite in [1995ZIE/JON].

[2005CAS/CRI]

This work dealt with the speciation of 0 to 1.3 m Fe(III) and Fe(II) solutions in 2.2 m H_2SO_4 solutions at 25 and 50 °C.

Conductivity, pH measurements, Raman spectra and density measurements as well as a literature data review were used to assign formulae to the Fe(III) species present in these acidic solutions.

$Fe(HSO_4)SO_4(aq)$

The existence of the soluble aqueous complex $Fe(HSO_4)SO_4(aq)$ is claimed in this paper. This was based on the presence of a Raman emission band that can be attributed to the $M–OSO_3H$ stretch in the $242-282$ cm^{-1} region.

The pH decrease associated with the Fe(III) concentration upon the dissolution of the solid $Fe(HSO_4)SO_4$ (rhomboclase) in water was attributed to the reaction:

$$Fe(HSO_4)SO_4(aq) \rightleftharpoons Fe^{3+} + H^{+} + 2\,SO_4^{2-}$$

Finally the authors concluded that the Fe(II) species Fe^{2+} and $FeSO_4$, and the Fe(III) species Fe^{3+}, $FeSO_4^{+}$, $Fe(SO_4)_2^{-}$, and $Fe(HSO_4)SO_4(aq)$ are present in acidic sulfate solutions.

The authors tried to obtain quantitative results by adjusting the conductivity of the solutions to a model containing the species quoted above and their molar diffusivities.

They did not give formation constants except for $Fe(HSO_4)SO_4(aq)$, and that was based on rhomboclase solubility: $K^{\circ} = a_{Fe(HSO_4)SO_4(aq)} / (a_{SO_4^{2-}}{}^{2} a_{H^+} a_{Fe^{3+}}) = 10^{8.1}$ at 25 °C and 10^{10} at 50 °C.

The equilibrium constant for the reaction: $Fe^{3+} + SO_4^{2-} + HSO_4^{-} \rightleftharpoons Fe(HSO_4)SO_4(aq)$ was estimated to be (380 ± 50) M^{-2} by Lister and Rivington [1955LIS/RIV2], whereas for the equivalent reaction the results of Casas *et al.* [2005CAS/CRI] would give a value of $\approx 10^{6}$ M^{-2}. The ionic strengths relevant to these two estimates are different, but still this is a major discrepancy, and we consider the result from Casas *et al.* only as qualitative information limited to the speciation.

An extended Debye-Hückel relationship was used to calculate the activities of the ions.

This work presents speciation and formation constant results obtained using a suspect method of investigation; interpretation of conductivity data for these solutions is ambiguous because the conductivity depends on many parameters.

The pH measurements of highly acidic solutions at various ionic strengths are not suitable for quantitative work because of the many unknown junction potentials. So the existence of the new species $Fe(HSO_4)SO_4(aq)$, claimed in this paper, remains based mostly on the Raman data.

No quantitative information from this paper was used to determine the recommended thermodynamic constants of Fe^{3+} sulfate complexes. The use of Raman spectroscopy is interesting in assessing the presence of a species difficult to detect by other techniques—here it is the stretching of the $M–OSO_3H$ bond at around 250 cm^{-1} which, if the assignment is correct, could be used in further investigations. Other species, such as mixed hydroxidosulfato complexes, which are difficult to detect with methods such as potentiometry, might also be characterized using Raman spectroscopy.

[2005GRI]

This thesis describes work that was carried out under the direction of Bruno and Duro who had co-authored a previous paper [2000BRU/DUR] on complexation of iron(III) with carbonate. New solubility measurements were done for ferrihydrite and hematite, and characterization of the solid surfaces was carried out. Co-precipitation from U(VI)-Fe(III) mixtures in the presence of carbonates was also investigated. Rate constants were measured for the dissolution of hematite and ferrihydrite in the presence of carbonates. In contrast to the earlier solubility study [1992BRU/STU] a useful comparison was done of the analytical concentrations of iron in filtrates obtained when 0.02 µm and 0.45 µm filters were used.

Although the "pH" calibration was described, Grivé seems to have assumed a straight-line Nernstian relationship, but her Figure 101 shows curvature. The make and model of the electrodes were not reported. The author seems to have used the term "pH" to mean $-\log_{10} c_{\mathrm{H}^+}$. The solution ionic strength and analysis results were noted as being in units of "$\mathrm{mol{\cdot}L^{-1}}$". It can only be assumed, based Section 6.3 of the thesis, that a factor of 1.0265 $\mathrm{dm^3}$ solution per kg H_2O [2003GUI/FAN] was used to convert amount concentrations to molalities so that the TDB [2003GUI/FAN] SIT coefficients could be used.

The solubility measurements under various CO_2 pressures give convincing evidence for a neutral Fe(III)-carbonate species, likely $\mathrm{FeCO_3OH(aq)}$, and an anionic species, likely $\mathrm{Fe(CO_3)_3^{3-}}$. Uncertainty about the nature of the saturating solids, however, makes it difficult to determine accurate stability constants.

Grivé checked the reversibility of the dissolution-precipitation cycle of "dry-stored" hematite under an N_2 atmosphere, and a value of $\log_{10} {}^*K = c_{\mathrm{Fe}^{3+}} / c_{\mathrm{H}^+}{}^3 = (0.48 \pm 0.50)$ was found[1].

The value of $\log_{10} K_s = -(0.01 \pm 0.50)$ at $I = 0$ for dry-stored hematite (Table 8, p. 89 of thesis) is a reasonable value. This corresponds to $\log_{10} K_s = -(42.01 \pm 0.50)$ for the reaction:

$$\tfrac{1}{2}\,\alpha\text{-}\mathrm{Fe_2O_3} + 1\tfrac{1}{2}\,\mathrm{H_2O(l)} \rightleftharpoons \mathrm{Fe^{3+}} + 3\,\mathrm{OH^-}.$$

The acid solubility measurements (Figure 46, p. 90) show some systematic deviations from the calculated solubility line. This might be interpreted in terms of a slightly higher $\log_{10} {}^*K_s$ value (~0.2 at $I = 0$), but with failure to achieve saturation in

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[1] The author reported the value (0.48 ± 0.50) for both "$\log_{10} K_s^{0.5}$" and "$\log_{10} K_s$" ($\log_{10} {}^*K_s$) for hematite. From the value − 1.88 listed in the author's Table 9 for $\log_{10} K_s$ as based on the US NBS compilation [1969WAG/EVA], it appears that Grivé's value always refers to $c_{\mathrm{Fe}^{3+}} / c_{\mathrm{H}^+}{}^3$, not $c_{\mathrm{Fe}^{3+}}{}^2 / c_{\mathrm{H}^+}{}^6$.

the most acidic solutions (pH < 2). Between pH values of 2 and 1, the solubility increases with the cube of a_{H^+}, whereas the dissolution kinetics likely have a lower-order dependence on a_{H^+}, hence increasingly longer equilibration times can be expected for increasingly acidic conditions. Alternatively, solubility may be less affected by fine particulates for the most acidic conditions examined. The ESEM images (thesis Figure 16) show a significant amount of very fine (a few nm) particulates in all of the solids, none of which shows a well-defined particle morphology. There does not seem to be any information on the surface area:volume ratios for the solubility measurements; if low, this could also contribute to slow equilibration.

Unfortunately, this "dry-stored" solid is too insoluble to allow detection of any carbonate-containing iron(III) species in acidic to neutral solutions, though the increased solubilities under CO_2 shown in the thesis Figure 48 ("pH" values > 7) correspond to formation of an anionic complex.

Data for the "suspension hematite" material (thesis Figure 49) are difficult to interpret. Since this material was apparently titrated from an initial storage pH of ~2, it is likely that the solubilities measured at near-neutral pH values correspond to a freshly precipitated iron, perhaps a ferrihydrite, rather than hematite. The solubility of this material seems to have evolved with time in the course of the experiments (as might be expected for a fresh precipitate). Note that this does not imply conversion of hematite to ferrihydrite, but rather the precipitation of ferrihydrite, perhaps as a surface coating on the hematite particles (also see similar comments by Hummel [2000HUM] with respect to the work of Bruno *et al.* [1992BRU/STU]). The value of $\log_{10} {}^*K_\mathrm{s} = (2.27 \pm 0.45)$ at $I = 0$ for hematite suspension (Table 10, p. 96 of thesis) corresponds to $\log_{10} K_\mathrm{s} = -(39.73 \pm 0.45)$ for the hematite solubility reaction above. This is much higher than expected for hematite, but one log unit lower than expected (about −38.7) for freshly precipitated ferrihydrite.

The iron(III) concentrations in solutions of aqueous sodium perchlorate at metastable equilibrium with ferrihydrite under N_2/CO_2 gas mixtures were determined. An attempt was made to confirm the reversibility of the dissolution-precipitation equilibrium in experiments that lasted 90 days. From these measurements the solubility product constant (based on the solutions that passed through a 0.02 μm filter) was calculated at ionic strengths of 0.5 M and zero. The calculations took into account the values of the formation constants of: FeOH^{2+}, $\mathrm{Fe(OH)}_2^+$, $\mathrm{Fe}_2(\mathrm{OH})_2^{4+}$ as found in Baes and Mesmer [1976BAE/MES] and using the SIT model. Values of $\log_{10} {}^*K_\mathrm{s} = (2.17 \pm 0.41)$ at $I_\mathrm{c} = 0.5$ and $\log_{10} {}^*K_\mathrm{s} = (1.19 \pm 0.41)$ at $I = 0$ were reported.

The value of $\log_{10} {}^*K_\mathrm{s} = (2.27 \pm 0.45)$ at $I = 0$ for ferrihydrite based on the solutions that passed through a 0.02 μm filter (identical to the value reported for the "suspension hematite") corresponds to $\log_{10} K_\mathrm{s} = -(39.73 \pm 0.45)$ for the simplified reaction

$$\text{“Fe(OH)}_3\text{(s)”} \rightleftharpoons \mathrm{Fe}^{3+} + 3\,\mathrm{OH}^-.$$

This is one log unit lower than expected (about −38.7) for 2-line ferrihydrite. It is perhaps more in line with a poorly crystalline goethite (α-FeOOH) or lepidocrocite (γ-FeOOH) than a true ferrihydrite specimen. The diffractogram (Figure 14, p. 48), while consistent with 2-line ferrihydrite, has such low signal-to-noise that the possible presence of other poorly crystallized phases cannot be ruled out. The anionic complex was assumed to have a stoichiometric metal:carbonate ratio of 3.0, though the actual slope of the solubility curve was possibly affected by changes in ionic strength.

Solubility data for "ferrihydrite" gave the best evidence for both of the Fe(III) carbonate complexes. The solubility of ferrihydrite in contact with gas-phase CO_2 was measured for three partial pressures 98, 30.1 and 1 kPa (0.97, 0.297 and 0.01 atm.), at a nominal ionic strength of 0.5 M ($NaClO_4$) and 25 °C. The Fe(III) concentrations values between pH 4 and 7 were constant, but the apparent constant solubility value depended strongly on the pore size of the filter used for the solid liquid separation before the analysis for iron. The measured Fe(III) concentrations decreased by one order of magnitude when a 0.45 μm filter was replaced by a 0.02 μm filter. That showed the presence of colloids. At "pH" values greater than 7 the solubility increased strongly with increasing pH. The shape of the ferrihydrite solubility curve *vs.* pH is similar to that observed by Bruno *et al.* for their "hematite" system [1992BRU/STU], but the plateau attributable to the predominance of the neutral solution species, $FeCO_3OH(aq)$, which is formed from the solid without any change in charge, is more pronounced.

The variation of the ferrihydrite and hematite solubility as a function of the pH is shown in Figure A-74.

The ionic strength for each Fe(III) solubility sample was not discussed in detail in the thesis. The only information tabulated in the thesis is the initial $NaClO_4$ concentration, the pH and the p_{CO_2} in the final samples. For solutions with a low initial pH, $HClO_4$ in 0.5 M $NaClO_4$ was added to a 0.5 M $NaClO_4$ solution. To increase the pH an $NaHCO_3$ solution was added. It seems to have been intended that the Na^+ concentration would remain approximately constant and the ionic strength close to 0.5 M (±10%). This likely was true for solutions in which the HCO_3^- and CO_3^{2-} concentrations were low. However that assumption cannot be accepted for the samples with pH values higher than 7.7 under 30.1 kPa CO_2, because for those the equilibrium between the carbonate species can only occur for Na^+ concentrations greater than 0.5 M. The author provided no indication as to how such solutions were prepared (*cf.* thesis Table 3).

The solubility data were interpreted in terms of two carbonate species, $FeCO_3OH$ and $Fe(CO_3)_3^{3-}$. The formation constants (at 25 °C)

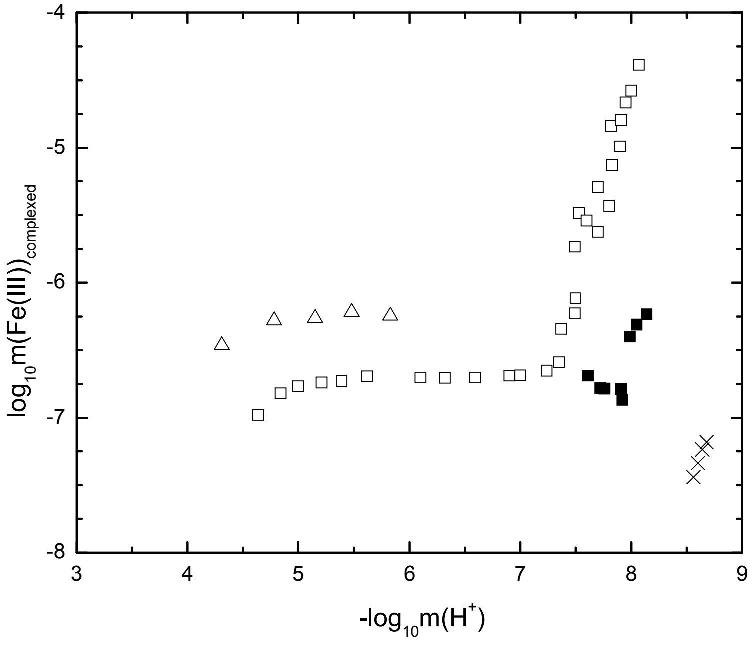
$$\log_{10}{}^*\beta^{\circ}_{1,1,1} = a_{FeCO_3OH(aq)}a_{H^+} / (a_{Fe^{3+}}a_{CO_3^{2-}}) = 10^{(10.76 \pm 0.38)}$$

and

$$\log_{10}\beta^{\circ}_{3,1} = a_{Fe(CO_3)_3^{3-}} / (a_{Fe^{3+}}a_{CO_3^{2-}}{}^3) = 10^{(24.24 \pm 0.42)}$$

were reported (but no values were reported explicitly for I =0.5 M ($NaClO_4$)).

Figure A-74: Solubility of ferrihydrite in contact with CO_2 × (p_{CO_2} = 1 kPa), □ (p_{CO_2} = 30.1 kPa), Δ (p_{CO_2} = 98 kPa); solubility of hematite in contact with CO_2 ■ (p_{CO_2} = 30.1 kPa).



The value of $\log_{10} \beta^{\circ}_{3,1}$ was compared to known formation constants for other trivalent-ion tricarbonates using an electrostatic model (attributed by Grivé to Neck) that attempted to predict the stabilities of metal ion-carbonate complexes.

In the present review the values of the formation constants for the complexes were recalculated from the data in the thesis (Tables 28-30, 32) using the solubility product values reported in the thesis for the solids "ferrihydrite" and "dry-stored hematite". Hydrolysis constant values for iron(III) and constants for the carbonate equilibria were taken from the present review. The calculated molalities of the carbonate complexes for five low-pH solutions were found to be negative, and therefore those five results were not used. Three calculations sets were considered, (a) one with all the data from these tables ($\log_{10} {}^{*}\beta^{\circ}_{1,1,1}$ = (8.81 ± 0.02), $\log_{10} \beta^{\circ}_{3,1}$ = (22.48 ± 0.04)), (b) one with the hematite results omitted ($\log_{10} {}^{*}\beta^{\circ}_{1,1,1}$ = (8.80 ± 0.04) $\log_{10} \beta^{\circ}_{3,1}$ = (22.48 ± 0.04)), and (c) one in which solutions with recalculated ionic strengths greater than 0.07 m were omitted ($\log_{10} {}^{*}\beta^{\circ}_{1,1,1}$ = (8.81 ± 0.02), $\log_{10} \beta^{\circ}_{3,1}$ = (22.28 ± 0.05)). Thus the hematite results are completely consistent with the "ferrihydrite" results, and the value for $\beta_{1,3}$ appears to be slightly smaller when derived at approximately constant ionic strength.

In all these calculations it was assumed that each solid phase remained the same in the pH range 4 to 8 as it was in contact with solutions at lower pH values (where the solubility product was determined). Also, no account was made for reported sorption of carbonate on the "ferrihydrite" or for colloids smaller than 0.02 μm. The kinetics of approach to equilibrium can be slow, and even though this aspect was investigated, very slow processes still might have been masked by faster ones. The anionic complex was assumed to have an Fe:carbonate ratio of 1.00:3.00. Attempts to fit a straight line to the high "pH" data (without any allowance for variation in the ionic strengths) gave a slope between 2.7 and 2.8.

If the values calculated using the data for $0.7 > I_m > 0.513$ m are considered to be values for ~0.6 m, values of ${}^*\beta^{\circ}_{1,1,1}$ and $\beta^{\circ}_{3,1}$ can be obtained by applying the appropriate SIT formula (Appendix B). The Debye Hückel coefficient D has the value 0.1824. The values and sources of the required interaction coefficients are $\varepsilon(\mathrm{Fe}^{3+},\mathrm{ClO}_4^-) = (0.73 \pm 0.04)\ \mathrm{kg{\cdot}mol^{-1}}$ (from the present review, Section VI.4.1), $\varepsilon(\mathrm{H}^+,\mathrm{ClO}_4^-) = (0.14 \pm 0.02)\ \mathrm{kg{\cdot}mol^{-1}}$ and $\varepsilon(\mathrm{Na}^+,\mathrm{CO}_3^{2-}) = -(0.08 \pm 0.03)\ \mathrm{kg{\cdot}mol^{-1}}$ (Appendix B). The value of $\varepsilon(\mathrm{Na}^+,\mathrm{Fe(CO_3)_3^{3-}})$ is unknown, and by analogy we used the value of $\varepsilon(\mathrm{Na}^+,\mathrm{Am(CO_3)_3^{3-}}) = -(0.23 \pm 0.07)\ \mathrm{kg{\cdot}mol^{-1}}$ from the NEA-TDB Tables. For the neutral species $\mathrm{FeCO_3OH(aq)}$ the value of the interaction coefficient with any ion is assumed to be zero.

From this, $\log_{10}{}^*\beta^{\circ}_{1,1,1} = (10.69 \pm 0.04)$ and $\log_{10}\beta^{\circ}_{3,1} = (24.0 \pm 0.1)$. However, the statistical uncertainties given by the data treatment are small compared to the other major uncertainties pointed out above. Therefore the estimated uncertainties have been increased substantially to ±2.0:

$$\log_{10}{}^*\beta^{\circ}_{1,1,1} = (10.7 \pm 2.0) \text{ and } \log_{10}\beta^{\circ}_{3,1} = (24.0 \pm 2.0).$$

These values are very close to those reported by Grivé [2005GRI], and are probably the best current values for Fe(III) carbonate complexes. Only improvements in the speciation and characterization of the solid(s) and the solutions can confirm and improve the precision of the stability constants.

[2005LAN]

This synopsis deals only with Chapter 5, on heat-capacity measurements of akaganéite, β-FeOOH. The thesis also includes sections on instrument development and heat-capacity measurements for U metal, $\mathrm{TiB_2}$, and LiF. Starting material was synthetic akaganéite with the composition $\mathrm{FeOOH{\cdot}0.620H_2O{\cdot}0.0096HCl}$. Here, "HCl" denotes partial occupancy of akaganéite tunnel sites by $\mathrm{Cl^-}$, with an equivalent quantity of $\mathrm{H^+}$ as protonated sites in the FeOOH framework and/or $\mathrm{H_3O^+}$ in tunnel sites. The water content is distributed in an undetermined fashion between tunnel and surface sites.

Two series of C_p data were obtained on a 1.0-g pelletized sample. Slight dehydration during sample preparation resulted in the ratio H_2O:FeOOH = 0.551 for the first series of measurements (144 values at 18.221 to 310.27 K). Rehydration in air yielded H_2O:FeOOH = 0.652 for the second series (103 values at 12.943 to 321.15 K). Data below 20 K in the second series were influenced by He adsorption.

Differences between the two data sets indicated that the adsorbed water makes a gradual transition from ice-like heat-capacity values below 150 K to water-like values near 273 K. This has important implications for the heat capacities and entropies of other Fe oxides and oxyhydroxides, as discussed in Section VII.2.1.

Based on the heat-capacity data, Lang obtained the following entropy values.

$$\Delta_0^{298.15\mathrm{K}} S_\mathrm{m}^\circ \,(\text{“}\beta\text{-FeOOH}\cdot 0.551\mathrm{H_2O}\text{”}) = (79.94 \pm 0.20)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

$$\Delta_0^{298.15\mathrm{K}} S_\mathrm{m}^\circ \,(\text{“}\beta\text{-FeOOH}\cdot 0.652\mathrm{H_2O}\text{”}) = (85.33 \pm 0.21)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

These values exclude a configurational contribution of 0.339 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ calculated by Lang for the Cl^- ions; no corresponding contribution for H_2O was estimated. Lang also attempted to derive an entropy for anhydrous akaganéite, obtaining the value:

$$\Delta_0^{298.15\mathrm{K}} S_\mathrm{m}^\circ \,(\text{“bare }\beta\text{-FeOOH”}) = (53.8 \pm 3.3)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

The C_p data show little indication of the magnetic transition (nominal Néel temperature ~290 K), apparently because of the small particle size (rods, 25 to 80 nm diameter, 400 to 500 nm long). A slight inflection near 310 K for “β-FeOOH·0.652H_2O” may correspond to the onset of magnetic ordering (*i.e.*, upper tail of the magnetic transition).

Recalculation of $\Delta_0^{298.15\mathrm{K}} S_\mathrm{m}^\circ$ (“β-FeOOH·0.551H_2O”, cr) by curve-fitting procedures similar to those used for other oxides and oxyhydroxides yielded $\Delta_0^{298.15\mathrm{K}} S_\mathrm{m}^\circ$ (“β-FeOOH·0.551H_2O”, cr) = (79.60 ± 0.61) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$. The small difference from Lang's value of (79.94 ± 0.20) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ lies almost entirely in the low-temperature treatments. The scatter in the data is relatively large, and both Lang's Debye extrapolation for $T < 30$ K and the fitted power-expression for $T < 40$ K in the recalculation involve rather long extrapolations from 18 to 0 K.

The molar masses cited by Lang for the molar heat capacities do not include the Cl content (0.34 wt.-%), implying that all the values given above may be too low by a corresponding proportion.

Because of the various uncertainties outlined above, the following value (excluding configurational contributions) is recommended as representative of synthetic akaganéite:

$$\Delta_0^{298.15\mathrm{K}} S_\mathrm{m}^\circ \,(\beta\text{-FeOOH}\cdot 0.551\mathrm{H_2O}\cdot 0.0096\mathrm{HCl, cr}) = (79.9 \pm 1.0)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

A separate fitting procedure, using the 16 data points between 289.75 and 310.27 K (8 points either side of 298.15 K) yielded:

$$C^{\circ}_{p,\mathrm{m}}\ (\text{“}\beta\text{-FeOOH}\cdot 0.551\mathrm{H_2O}\text{”, cr, 298.15 K}) = (91.18 \pm 0.20)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}},$$

in good agreement with Lang's value of 91.24 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$. Correction for the Cl content leads to the following recommended value.

$$C^{\circ}_{p,\mathrm{m}}\ (\beta\text{-FeOOH}\cdot 0.551\mathrm{H_2O}\cdot 0.0096\mathrm{HCl}\text{, cr, 298.15 K}) = (91.50 \pm 0.20)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

[2005LUT/RIC]

Techniques such as UV-visible spectrophotometry, NMR, EPR, electrochemistry, laser ablation FT mass spectrometry, anion chromatography and electrophoresis were applied to the solutions containing bisulfide (controlled by $H_2S(g)$) and Cu(II), Zn(II), Pb(II), Ag(I) or Fe(II). The authors claimed that metal sulfide clusters are formed in these solutions and these clusters constitute a major fraction of the dissolved metal load in anoxic oceanic, sedimentary, freshwater and deep ocean vent environments. A cluster is defined as a quantum-sized particle or complex, which contains a discrete number of atoms in a molecule or ion that is small enough to behave as a dissolved species. Although the authors presented much supporting evidence, and the theoretical discussion is persuasive, this review considers that the experimental evidence is not yet sufficient to prove the existence of "polynuclear" molecular units in equilibrium with other species in the solution. This review considers the existence of a metal cluster to be probable, but still not well established.

[2005MAJ/MYN]

The interaction between sulfate moieties ($\mathrm{SO_4^{2-}}$, $\mathrm{HSO_4^-}$) 0.015 $\mathrm{mol\cdot kg^{-1}}$ and iron(III) 0.01, 0.02 and 0.05 $\mathrm{mol\cdot kg^{-1}}$ (as well as Fe(II)) was investigated at pH values of 1, 2 and 3 using two techniques: infrared spectroscopy (attenuated total reflectance mode) and sulfur K-edge XANES (X-ray absorption spectroscopy near edge structure).

The infrared spectra clearly showed interaction of ($\mathrm{SO_4^{2-}}$, $\mathrm{HSO_4^-}$) with $\mathrm{Fe^{3+}}$ at pH 1 and 2. No quantitative result can be drawn from these spectra, and $\mathrm{FeSO_4^+}$ and $\mathrm{FeHSO_4^{2+}}$ cannot be distinguished.

X-ray absorption spectroscopy can distinguish $\mathrm{HSO_4^-}$ from $\mathrm{SO_4^{2-}}$. The maximum of absorption occurs at 2479.6 eV for $\mathrm{SO_4^{2-}}$ and 2480 eV for $\mathrm{HSO_4^-}$. Weak features appear at ~2.0 eV below the S-absorption edge. These features at pH values of 1 and 2 have been compared to those in Fe(III) solids containing sulfate and for which the structures have been solved—jarosite (in which the bonded sulfate is tridentate), copiapite (with bidentate sulfate) and roemerite (with monodentate sulfate). The position of the pre-edge of the solutions is closer to that in roemerite, and this indicates that the sulfate is monodentate.

However, the authors tried to interpret the pre-edge absorption of X-rays quantitatively, and estimated that the amount of monodentate sulfate is only (10 ± 10)%

of the total sulfate. That is in contradiction to the infrared results, which show that most of the sulfate is bonded to Fe^{3+}. The infrared results are in agreement with the stability of the sulfatoiron(III) complexes accepted in the present review.

To explain the infrared/XANES discrepancy the authors proposed that the infrared behaviour is due to the occurrence of one or several sulfate species in which sulfate is bonded to iron through hydrogen bonding. These species could be oligomers, precursors of the poorly crystalline iron sulfate solids which precipitate in acid-mine drainage waters.

We consider this interpretation to be highly improbable because the change in the infrared absorption of sulfate induced by such weak hydrogen bonding would be surely a minor change compared with direct bonding of sulfate to iron. The existence of oligomers of hydrated iron(III) in acidic solution has not been found by previous investigators.

The aim of this research can be compared to that of Sapieszko *et al.* [1977SAP/PAT] who tried to identify mixed hydroxidosulfatoiron(III) complexes in aqueous solutions as the precursors to the precipitation of mixed hydroxide-sulfate solid compounds. They used UV-visible spectrophotometry. They were not able to identify such species in spite of their extensive experimental data. At pH 1.7 for a solution initially 0.18 M in $Fe(NO_3)_3$ and 0.53 M in Na_2SO_4, from which $Fe_3(SO_4)_2(OH)_5(s)$ precipitates, no mixed complexes were detected. They suggested the reaction:

$$FeOH^{2+}(sln) + 2\,FeSO_4^+ + 6\,H_2O(sln) \rightleftharpoons Fe_3(SO_4)_2(OH)_5{\cdot}2H_2O(s) + 4\,H^+(sln).$$

The two species, $FeOH^{2+}$ (1.07×10^{-3} M) and $FeSO_4^+$ (0.158 M), were present in the initial solution .

So, following [1977SAP/PAT], we do not consider the existence of such complexes in solution to be proven, and do not accept the proposal in the paper for pre-existence of soluble precursors of sulfate in the precipitation of the mixed hydroxide-sulfate solid compounds. Most of the arguments developed are based on semi-quantitative interpretation of X-ray absorption data. In view of the spectra shown in Figure 5 of the original paper, it seems very difficult to draw the conclusion that only 10% of the sulfate is directly bonded to Fe^{3+}. The problem of unambiguous identification of mixed hydroxidosulfatoiron(III) complexes in aqueous solutions needs further investigation. The choice of a proper method of speciation remains the key.

The authors made only a very few comments on the behaviour of $Fe(II) - SO_4^{2-}$ solutions. In their Figure 1, the authors attributed a very weak band at around 980 cm^{-1} to ionic strength effects. In their discussion they concluded that sulfate and Fe(II) either associate in outer-sphere complexes, or do not associate at all. This last conclusion, however, is contradicted by the shoulder at 1200 cm^{-1} observed at pH 2 (again in the authors' Figure 1). Unfortunately this was not discussed at all. The present review believes that the disappearance of this shoulder with increasing Fe(II) concentrations indicates replacement of the proton by Fe^{2+} ion in the species HSO_4^-. At pH 1, when 90% of the sulfate is protonated, this shoulder stays, even when increasing concentrations of Fe(II) are added to the system. Such behaviour clearly indicates the presence of association of Fe^{2+} with the sulfate (though it may be weak).

The key information from this paper is the recognition of the monodentate character of the bond between SO_4^{2-} and Fe^{3+} at room temperature in the aqueous complex $FeSO_4^+$.

[2005MAJ/NAV]

Majzlan *et al.* [2005MAJ/NAV] reported heat-capacity measurements for anhydrous monoclinic $Fe_2(SO_4)_3$ using adiabatic calorimetry from 20 to 394 K and semi-adiabatic calorimetry from 0.5 to 38 K. There is a thermal anomaly at 30 K. The two sets of measurements from 20 to 35 K are in reasonable agreement, though the semi-adiabatic calorimetry had better resolution in the region of the anomaly. From 1 to 6 K, the plot of C_p / T against T^2 is approximately linear, and would extrapolate to a value of zero at 0 K; there is slight curvature to the plot below 1 K, but the value of C_p at 1 K and below is so small that the effect on the estimated value of S_m^o (298.15 K) is negligible. The results are in reasonable agreement with those of Pankratz and Weller [1969PAN/WEL], though the measured values of C_p are less than those in [1969PAN/WEL] between 50 and 100 K, by 8% at 53 K. At higher temperatures, the differences become less, and the Majzlan *et al.* [2005MAJ/NAV] values are systematically slightly greater than those of Pankratz and Weller [1969PAN/WEL] for temperatures above 200 K. A value of (305.62 ± 0.62) $J \cdot K^{-1} \cdot mol^{-1}$ is reported for S_m^o ($Fe_2(SO_4)_3$, cr, 298.15 K).

The authors also measured the enthalpies of solution of monoclinic iron(III) sulfate, γ-FeOOH, H_2O(l), MgO(cr) and α-$MgSO_4$ at 25 °C into a 5 M HCl solution. From these results, earlier measurements of the heats of solution of α-$MgSO_4$, MgO, water and $H_2SO_4 \cdot 6H_2O$(l) into 4.36 m HCl solutions [1980KO/DAU], and literature values for the enthalpies of formation of MgO(cr), H_2O(l) [1989COX/WAG], $H_2SO_4 \cdot 6H_2O$(l) [1982WAG/EVA], [1989COX/WAG] and γ-FeOOH from the present review, a value of $-(2584.17 \pm 6.07)$ $kJ \cdot mol^{-1}$ is recalculated for the enthalpy of formation of monoclinic $Fe_2(SO_4)_3$(cr) at 298.15 K.

[2005MAZ/NAV]

The authors measured $\Delta_f H_m^o$ for synthetic goethite as a function of particle size (2 - 75 nm, corresponding to BET surface areas (SA) of 30 - 273 $m^2 \cdot g^{-1}$) by high-temperature drop-solution calorimetry (in a $3Na_2O \cdot 4MoO_3$ melt at 701 °C) and, for the most fine-grained specimens (2 - 9 nm) also by acid-dissolution calorimetry (5.00 M HCl at 25 °C). Lattice parameters and particle size were determined by Rietveld XRD analysis; excess water content was also measured ($FeOOH \cdot xH_2O$, $0.076 \leq x \leq 0.818$, increasing monotonically with SA). Coarse-grained goethite dissolved too slowly in

HCl for accurate calorimetry, therefore lepidocrocite (γ-FeOOH) was used for comparative measurements. The enthalpy of excess water was approximated as bulk $H_2O(l)$ with zero enthalpy of adsorption.

The authors obtained $\Delta_f H^\circ_m$ (FeOOH, α, 298.15 K) = −(561.5 ± 1.5) $kJ{\cdot}mol^{-1}$ for coarse-grained material (*i.e.*, extrapolated to zero surface area) from drop-solution calorimetry and −(563.9 ± 1.6) $kJ{\cdot}mol^{-1}$ from acid-dissolution calorimetry. The authors favoured the former value; comparable literature values include −(560.7 ± 1.2) $kJ{\cdot}mol^{-1}$ for goethite with surface area (SA) = 21 $m^2{\cdot}g^{-1}$ [2003MAJ/GRE], −(559.4 ± 1.3) $kJ{\cdot}mol^{-1}$ for natural goethite, corrected for impurities [1965BAR], and an extrapolated value of − (562.9 ± 1.5) $kJ{\cdot}mol^{-1}$ for a fictive, zero-SA material from reinterpretation of the SA-dependent measurements of [1966FER] by [1994DIA/KHO]. This hypothetical, zero-SA state would be approximated by macrocrystalline material, which is difficult to obtain. These results are discussed further in Section VII.2.9.1.

The obtained surface-enthalpy values were (0.60 ± 0.10) $J{\cdot}m^{-2}$ from drop-solution calorimetry and (0.86 ± 0.30) $J{\cdot}m^{-2}$ from acid-dissolution calorimetry; the authors preferred the former, more precise value. Though lower than previously reported values of 1.25 to 1.55 $J{\cdot}m^{-2}$ ([1966FER], [1994DIA/KHO], and references therein), this still amounts to about 15 $kJ{\cdot}mol^{-1}$ for the finest-grained material (2 nm, 273 $m^2{\cdot}g^{-1}$). The current value appears to be more reliable than earlier estimates, because the various goethite specimens were prepared by all-aqueous methods, rather than precipitation followed by dry-heat treatment (see synopsis of [1966FER]). Nevertheless, the finer-grained materials in particular may well have an internal disorder contribution to the excess-enthalpy term. Also, the degree of hydration to which the surface energy refers is unclear, and different surface properties of different crystallographic faces can not be addressed.

[2005RIC/MOR]

This paper reviews the research work which has been done on acid volatile sulfides or AVS, which is the name for the environmentally distributed materials which release H_2S if treated with acid. Although AVS is not equivalent to FeS(aq) and/or solid FeS, AVS minerals are closely related to mackinawite and greigite. Concerning the topic, the papers on the dissolved iron(II)-S(–II) species, characteristics of FeS clusters, structures, compositions and solubilities of iron monosulfide (mackinawite, greigite and pyrite) were reviewed, and the review is of value for reference.

[2005WOL/CHA]

To describe the experimentally determined surface properties of synthetic FeS produced by reacting aqueous Fe(II) (prepared by dissolution of $Fe(NH_4)_2(SO_4)_2{\cdot}4H_2O(cr)$) with aqueous sulfide (prepared by dissolution of $Na_2S{\cdot}9H_2O(cr)$), the solubility of FeS in the neutral pH range (6.5 – 8) was measured at I = 0.05 ~ 0.1 M and 23 °C. The logarithm (base 10) of the total dissolved Fe(II) varied from – 4.07 at pH 6.55 to – 4.78 at pH 7.8 with a slope of about – 0.5, which tends to level off toward zero with increasing pH. The solubility of FeS was assumed to be described by the reaction, $FeS(s) + 2H^+ \rightleftharpoons Fe^{2+} + H_2S(aq)$ for which $^*K_s^{app} = a_{Fe^{2+}} a_{H_2S(aq)} / a^2_{H^+}$ was the apparent solubility constant at zero ionic strength. Side reactions such as, $H_2S(aq) \rightleftharpoons HS^- + H^+$ with $K_1 = 10^{-6.98}$, $FeS(s) + H^+ \rightleftharpoons FeSH^+$ with $\beta_1 = 10^{(2.05\pm0.50)}$ [1996LUT/RIC] and $FeS(s) + H_2S(sq) \rightleftharpoons Fe(SH)_2(aq)$ with $\beta_2 = 10^{-(3.43\pm0.1)}$ [1999DAV/PHI] were considered. By assuming $Fe_T = [Fe^{2+}] + [FeSH^+] + [Fe(SH)_2(aq)] + [FeS(s)]$, $S_T = [HS^-] + [H_2S(aq)] + [FeSH^+] + 2[Fe(SH)_2(aq)] + [FeS(s)]$ and $Fe_T = S_T$, $^*K_s^{app}$ was obtained to be $^*K_s^{app} = 10^{(4.87\pm0.27)}$. However, in the discussion, the authors concluded that, judging from the slope of $\log_{10} Fe_T$ *vs*. pH which tended to level off towards zero with increasing pH, there might have been an effect from the pH-independent reaction, $FeS(s) \rightleftharpoons FeS(aq)$, where the size of the aqueous cluster complex was too small to allow removal by filtration through the 0.2 µm filter discs used. Therefore, since the value reported for $^*K_s^{app}$ does not refer to the corresponding reaction, this review does not use the numerical result in this paper.

[2006GIC/FRO]

A nanocomposite sample of ε-Fe_2O_3 and amorphous SiO_2 was studied by a combination of X-ray and neutron diffraction, Mössbauer spectroscopy, and magnetic and heat-capacity measurements at 10-300 K in order to characterize the previously known but incompletely understood second-order phase transition sequence between 80 and 150 K. The substance is described as a collinear ferrimagnet above 150 K, while magnetic ordering below 80 K is characterized by a square-wave incommensurate structure. The C_p measurements show a broad anomaly near 130 K, but they are depicted in arbitrary units and obviously include a large contribution from the SiO_2 component of the material, therefore no data can be extracted for the current review.

[2006LIU/ETS]

This paper is a report of a new determination of the formation constants for all of the Fe(III) chloride complexes at 25, 60 and 90 °C and for I = 0 to 11.6 m. UV-visible spectrophotometry plus XANES and EXAFS spectroscopy were used. These two last techniques gave some insight as to the geometry of the complexes.

Using results from very highly concentrated chloride solutions, an extended Debye-Hückel equation[1] for ionic activity coefficients, and an estimated Setchénow coefficient for $FeCl_3(aq)$ the authors were able to propose a complete set of formation constants for: $FeCl_2^+$, $FeCl_3(aq)$, and $FeCl_4^-$ (for 25 °C, $\log_{10} \beta^\circ_{2,1} = (1.87 \pm 0.25)$, $\log_{10} \beta^\circ_{3,1} = (0.77 \pm 0.25)$, $\log_{10} \beta^\circ_{4,1} = -(1.26 \pm 0.45)$). These β° values are fairly consistent with previous determinations, but they have lower uncertainties.

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[1] The formulation incorporated Kielland distance parameters [1937KIE] as well linear and quadratic terms in ionic strength.

XANES and EXAFS reinforced the interpretation of the UV-visible spectroscopic data. The structural shift O_h=>T_d symmetry with the increase of the Cl^- number was investigated. It was confirmed that adding high concentrations of Cl^- ions to octahedral $Fe^{3+}\cdot6H_2O$ results in formation of tetrahedral $FeCl_4^-$ species. The boundary species is $FeCl_3(aq)$, which adopts several geometries, $FeCl_3(H_2O)_3$ (O_h), $FeCl_3(H_2O)_2$ trigonal bipyramidal and $FeCl_3(H_2O)(T_d)$.

This paper comes after many others on the same subject, but the method of data interpretation and the volume of experimental work permit description of the Fe(III)-chloride system over a larger range of Cl^- concentrations at several temperatures. As already mentioned in the paper of Byrne and Kester [1981BYR/KES], the mathematical treatment for the interpretation of the spectrophotometric data now is more efficient than was possible for early studies, and speciation of multi-component solutions has become possible. The method used here (PCA, principal components analysis), determines the minimum number of parameters necessary to optimize the fit of the experimental data. This allows some previous assumptions found in the literature, such as a large variation of the molar absorption coefficients as a function of the ionic strength or the temperature, to be discarded.

In this paper, devoted mainly to the higher-order chloride complexes, the problem of the relative stability of the inner- and outer-sphere monochlorido species has not been addressed because of the limited data at low chloride concentrations.

The stability of the chloride complexes increases with increasing temperature, and an extrapolation to 300 °C was carried out by the authors, who applied the equation of Anderson *et al.* [1991AND/CAS],

$$\ln K = -\,[p_1 + p_2/(T/\mathrm{K}) + (p_3 \ln \rho_\mathrm{w})(T/\mathrm{K})^{-1}]$$

where p_1, p_2 and p_3 are parameters which are calculated from the experimental values of K as a function of the temperature, where ρ_w is a number, equal to the value of the density of water at the temperature T (in kelvin), when that density is expressed in units of $\mathrm{g\cdot cm^{-3}}$.

In this paper the stability constant of $FeCl^{2+}$ has not been re-determined and, where needed, the value of Tagirov *et al.* [2000TAG/DIA] was used. The SIT value for $\log_{10} K_1^\circ$ (1.51 ± 0.10) is the same (see main text), so no new number has been introduced to calculate the values of $\log_{10} {K'}_1^\circ$, (in this Appendix A entry these refer to $\log_{10} K_1$ values for $I = 0$, at temperatures other than 298.15°K).

The application of the Anderson equation to the work of Tagirov *et al.* [2000TAG/DIA], which contain $\log_{10} {K'}_1^\circ$ values, leads to $\log_{10} {K'}_1^\circ = 2.57$ at 100 °C and $\log_{10} {K'}_1^\circ = 5.91$ at 300 °C. These values with the other high-temperature stability constants determined in this work led to the prediction that the solubility of hematite at 300 °C is much higher than previously estimated, and that $FeCl_4^-$ becomes the predominant chloride species for $a_{\mathrm{Cl}^-} = 5\ \mathrm{mol\cdot kg^{-1}}$.

The derivation of $\Delta_r H_m^o$ from these data has been attempted by applying the van't Hoff relation to the experimental values of K_n^o as a function of temperature

$$d \ln K_n^o / d(1/T) = - \Delta_r H_m^o / R$$

The three points available for each complex do not fall on straight lines. This could mean that $\Delta_r H_m^o$ varies with the temperature even in the moderately narrow range of temperatures investigated (25 to 90 °C). Other authors [1989BRU/PET], [2000TAG/DIA] who measured the formation constant of $FeCl^{2+}$ over a wider temperature limits clearly found that $\Delta_r H_m^o$ varies even over this narrow range.

Because of the small number of points, three for each complex, only a linear fit has been carried out and the stepwise $\Delta_r H_m^o$ values ($\Delta_2 H^\circ = (19.35 \pm 7.30)$ kJ·mol^{-1}, $\Delta_3 H^\circ = (14.8 \pm 7.3)$ kJ·mol^{-1}, $\Delta_4 H^\circ = (7.5 \pm 1.5)$ J·K^{-1}·mol^{-1}) resulting from these calculations must be taken with caution. However it seems well established that the formation heats of the Fe^{3+} higher-order chloride complexes are endothermic and that an increase in temperature stabilizes these complexes with regard to the lower-order complexes.

So the results of this work, which brought out new, useful qualitative information about Fe^{3+}-chloride associates, cannot be used easily in an SIT-consistent analysis for at least two reasons. First, the high ionic strengths used are beyond the domain of validity of the SIT model. Second, ion-interaction coefficients for the triflate ion, the anion of the added salt, do not appear in the present set of TDB tables. Another source of inconsistency with an SIT analysis is the use by the authors of SUPCRT values for HCl and LiCl ion-pair formation, as the SIT model incorporates such interactions into the activity coefficients.

[2006MAJ/NAV]

The authors measured the heats of solution of $Fe_2(SO_4)_3\cdot5.03H_2O(cr)$, and solids with the compositions $(H_3O)_{1.34}Fe(SO_4)_{2.17}\cdot3.06H_2O$, $Fe_{4.78}(SO_4)_6(OH)_{2.34}\cdot20.71H_2O$ and $Fe_{1.55}Al_{0.45}(SO_4)_3\cdot9.65H_2O$ at 25 °C into a 5 M HCl solution. Using previous measurements of the enthalpies of solution of γ-FeOOH [2003MAJ/GRE], $H_2O(l)$, MgO(cr) and α-$MgSO_4$ under similar conditions [2005MAJ/NAV], measurements of the heats of solution of α-$MgSO_4$, MgO, water and $H_2SO_4\cdot6H_2O(l)$ into 4.36 m HCl solutions [1980KO/DAU], literature values for the enthalpies of formation of MgO(cr), $H_2O(l)$ [1989COX/WAG], $H_2SO_4\cdot6H_2O(l)$ [1982WAG/EVA], [1989COX/WAG], and for γ-FeOOH from the present review (Section VII.2.11.2), a value of $-(4115.50 \pm 5.71)$ kJ·mol^{-1} is recalculated for the enthalpy of formation of $Fe_2(SO_4)_3\cdot5.03H_2O(cr)$ at 298.15 K. If the enthalpy contribution of the last 0.03 moles of hydration is estimated to contribute (9.0 ± 0.2) kJ·mol^{-1} to the overall enthalpy of formation, the value of $\Delta_f H_m^o$ ($Fe_2(SO_4)_3\cdot5H_2O$, cr, 298.15 K) is $-(4106.5 \pm 5.7)$ kJ·mol^{-1}. The uncertainty reported in the weight%-loss analyses of the sample used for the experiments ((67.44 ± 0.10)%) suggest that the stoichiometry with respect to water content was between $Fe_2(SO_4)_3\cdot4.94H_2O$ and $Fe_2(SO_4)_3\cdot5.11H_2O$. This introduces a further uncertainty of 0.7 to 1.3 $kJ\cdot mol^{-1}$ in the value of the enthalpy of formation of the stoichionetric pentahydrate, and the adjusted value of $\Delta_f H_m^o$ ($Fe_2(SO_4)_3\cdot5H_2O$, cr, 298.15 K) is $-(4106.5 \pm 5.9)$ $kJ\cdot mol^{-1}$. Similar recalculations lead to values of $-(3201.22 \pm 3.56)$ $kJ\cdot mol^{-1}$ and $-(12046.2 \pm 12.6)$ $kJ\cdot mol^{-1}$ for $\Delta_f H_m^o$ ($(H_3O)_{1.34}Fe(SO_4)_{2.17}\cdot3.06H_2O$, cr, 298.15 K) and $\Delta_f H_m^o$ ($Fe_{4.78}(SO_4)_6(OH)_{2.34}\cdot20.71H_2O$, cr, 298.15 K), respectively.

[2006MAZ/DEO]

A series of 14 akaganéite samples was prepared by hydrolysis of aqueous $FeCl_3$ solutions under various conditions, sometimes adding urotropin (hexamethylenetetramine or 1,3,5,7-tetraazaadamantane) to control particle size. Surface areas, measured by the BET method after conditioning at 333 K, ranged from 33.5 to 279.7 $m^2\cdot g^{-1}$; higher surface areas were measured on some specimens after conditioning at 423 K. The dialysed products contained no detectable organic material and minimal quantities of Cl^- (Cl/Fe molar ratio ≤ 0.0054) but substantial quantities of excess water (H_2O/FeOOH molar ratios between 0.54 and 0.82). The compositions are thus markedly different from natural and freshly precipitated akaganéites, which typically contain significant quantities of chloride.

By heating at 423 K, the authors showed that tunnel sites within the akaganéite structure were about 80% occupied by H_2O, relative to the nominal H_2O/FeOOH molar ratio of 0.25 for well-crystallized material. The adsorption enthalpy for tunnel water was indistinguishable from zero relative to H_2O(l). Sorption-calorimetry measurements showed, however, that about 40% of the excess water was "chemisorbed" with a mean adsorption enthalpy of $-(15.0 \pm 1.1)$ $kJ\cdot mol^{-1}$, again relative to H_2O(l). Maximum measured adsorption enthalpies, based on the first dose of H_2O on dried surfaces in the calorimetry runs, were around -60 $kJ\cdot mol^{-1}$.

Dissolution-calorimetry measurements were made with ~5 mg samples in 5 M HCl at 298 and 343 K. Dissolution of several of the coarser-grained akaganéite samples was too slow to measure the heat of dissolution at 298 K. Reference materials were lepidocrocite (γ-FeOOH) for 298 K runs and both goethite (α-FeOOH) and hematite (α-Fe_2O_3) at 70 °C.

Based on the calorimetric measurements, the authors derived an extrapolated (fictive) zero-surface-area value of $\Delta_f H_m^o$ (FeOOH, β, 298.15 K) = $-(554.7 \pm 1.9)$ $kJ\cdot mol^{-1}$, *i.e.*, ignoring the tunnel water, which was thermodynamically indistinguishable from H_2O(l). This zero-surface-area state would be approximated by macrocrystalline material, which is not available. For internal consistency with the current review, this value should be adjusted to $-(555.1 \pm 2.4)$ $kJ\cdot mol^{-1}$. The effective surface enthalpy was evaluated as (0.44 ± 0.04) $J\cdot m^{-2}$ for H_2O-free surfaces, relaxing to (0.34 ± 0.04) $J\cdot m^{-2}$ upon adsorption of H_2O.

While the thermochemical calculations are sound, some aspects of the results are troubling. Correlation of the excess H_2O with surface area (their Figure 1) leads to an extrapolated H_2O/FeOOH molar ratio of about 0.4 – 0.5 at zero surface area, or about twice the values inferred from partial drying tests (~ 0.2) or crystallographic considerations (maximum 0.25). Some of the correlations appear to have been unduly influenced by anomalous behaviour of the specimen with the highest surface area (see their Figures 5 to 7). When dissolution enthalpies are correlated with surface area (their Figure 5), markedly different extrapolated values at zero surface area are obtained for the raw heats of dissolution and the values corrected for chemisorption of water, the corrected values being about 3 $\mathrm{kJ \cdot mol^{-1}}$ more negative. Transposed temperature-drop measurements between 298 and 343 K point to values for $C^{\circ}_{p,\mathrm{m}}$ (FeOOH, β) nearly twice as high as those for α-FeOOH and γ-FeOOH. The excess H_2O is not sufficient to account for this difference, which is difficult to explain unless there is a large magnetic contribution to $C^{\circ}_{p,\mathrm{m}}$ (FeOOH, β) in this temperature range, *e.g.*, from the Néel transition near 295 K (see Section VII.2.10).

Considering only the 343 K dissolution data for the five most coarse-grained specimens, and adjusting for the enthalpy of α-FeOOH selected in this review, we obtain $\Delta_{\mathrm{f}} H^{\circ}_{\mathrm{m}}$ (FeOOH, β, 298.15 K) = $-(551.5 \pm 2.2)$ $\mathrm{kJ \cdot mol^{-1}}$ for dry akaganéite and $-(555.1 \pm 2.2)$ $\mathrm{kJ \cdot mol^{-1}}$ for a material with chemisorbed water. For some purposes, such as calculations of solubility or other thermochemical cycles involving akaganéite, it may be appropriate to use one or the other of these values, since they are representative of the most crystalline form of akaganéite that is normally available.

[2006OHF/RIC]

Direct observation using high-resolution transmission electron microscopy (HRTEM) was carried out on a precipitated iron(II) monosulfide. The precipitate was prepared by the reaction between aqueous $(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$ and aqueous $Na_2S\cdot 9H_2O$ in an O_2-free N_2 atmosphere. The FeS suspension was retained on the 0.45-μm filter paper which was then re-suspended in ethanol and scooped onto a Cu micro-grid by a thin acetate film. HRTEM examination of the precipitated FeS aggregates and freeze-dried FeS showed that both consisted of irregularly aggregated, thin tabular flake-like nanoparticles displaying a continuum of particle sizes from 2 to 5.7 nm in thickness and from 3 to 10.8 nm in length. Selective Area Electron Diffraction (SAED) patterns obtained from the FeS aggregates displayed Debye-rings with d-spacings similar to that of crystalline mackinawite synthesized by the reaction of metallic iron with aqueous sulfide, and which showed irregularly shaped single crystals with dimensions of approximately 0.8 μm. This paper confirmed that the direct product of the reaction between Fe(II) and S(–II) is the nanoparticulate mackinawite precipitate. The result of the paper can be accepted as complementary information for the review.

[2006PRZ]

A copy of this e-mail correspondence is stored in the NEA TDB bibliography file. There are further explanations of the experiments and data analyses in [1992PRZ/WIS] and [1993PRZ/WIS].

[2006RIC]

The solubility of synthetic nanoparticulate mackinawite, FeS(mk), in aqueous solution was measured at 23 °C from pH 3 – 10. Aliquots of deoxygenated NaOH were added to the solution of $Fe(NH_4)_2(SO_4)_2\cdot H_2O$ with H_2S gas passing through the solution. After the rate of change in pH decreased so that $d(pH)/dt < 0.02$ per hour (this required between 2 and 6 hours), the solution was sampled and filtered using a 0.45 μm filter. The pH, $c_{S(-II)_{total}}$ and $c_{Fe(II)_{total}}$ in the solution were measured. In more acidic solutions, $\log_{10} c_{Fe(II)_{total}}$ was inversely proportional (with a slope of –2) to pH and in more alkaline regions, $c_{Fe(II)_{total}}$ appeared to be independent of pH and p_{H_2S}. The results (ionic strength from 0.1 to 0.65) were modelled using the Davies equation and the Setchenow equation. The pH-dependent dissolution reaction was described by

$$\mathrm{FeS(mk)} + 2\,\mathrm{H}^+ \rightleftharpoons \mathrm{Fe}^{2+} + \mathrm{H_2S(aq)} \qquad (A.217)$$

and $\log_{10} {}^{*}K_s(A.217) = (3.5 \pm 0.25)$ ($n = 84$, 1σ). The contribution to the difference in the $\log_{10}K$ value for this reaction ($\Delta z^2 = 2$) from use of the Davies equation instead of the SIT equation in this ionic strength range, is estimated to be at most ±0.2. The pH-independent dissolution reaction was described by

$$\mathrm{FeS(mk)} = \mathrm{FeS(aq,\ polymeric)}, \qquad (A.218)$$

where FeS(aq) was claimed to be a monomeric representation of the aqueous cluster complex, Fe_xS_x, and $\log_{10} K_s(A.218) = -(5.7 \pm 0.27)$. The analytical detection limit for Fe(II) was confirmed to be two orders of magnitudes below the measured $c_{Fe(II)_{total}}$. The value of $c_{S(-II)_{total}}$ was compared with $c_{S(-II)_{total}}$ calculated using $\log_{10} K = -1.02$ and $\log_{10} K = -6.98$ for the conversion of $H_2S(g)$ to $H_2S(aq)$ and for the first deprotonation constant of $H_2S(aq)$, respectively. The filtration system was also examined. The author claimed that the use of a 0.1 M NaCl supporting electrolyte in these experiments caused sufficient flocculation of the FeS particles that they were quantitatively retained on a 0.45 μm filter. Successive filtrations down to 0.02 μm revealed no significant trend, and standard precipitates were quantitatively retained. Although this study seems to have been carried out very carefully, the result that $c_{Fe(II)_{total}}$ in the alkaline region was independent of pH and p_{H_2S} is different from that of Davison *et al.* [1999DAV/PHI] where $c_{Fe(II)_{total}}$ in alkaline region depended on p_{H_2S}. The former claims the reaction to be FeS(mk) = FeS(cluster) where FeS(cluster) means a quantum-sized particle or complex which contains a discrete number of atoms in a molecule or ion that is small enough to behave as a dissolved species. The latter claims the reaction to be FeS(mk) + $H_2S(aq)$ = $Fe(HS)_2(aq)$. The value of $c_{Fe(II)_{total}}$ is expected to be independent of pH in both reactions, but it is independent of the partial pressure of $H_2S(g)$ in the former, while it depends on the partial pressure of $H_2S(g)$ in the latter. In these studies, the speciation in the solution phase and the surface or ageing property of the FeS(mk) still remain unclear. So far, this review cannot find any experimental fault in either one of these papers. Thus, this review accepts the solubility constant as $\log_{10}{}^*K_s(\text{A.217}) = (3.5 \pm 0.3)$ (2σ) but suspends judgment on the selection of a value for the intrinsic solubility and the speciation in the higher pH region.

[2006TRO/BOU]

The authors used a solid-solution model to calculate values for the Gibbs energies of formation for the "green rusts" containing sulfate, carbonate and chloride for Fe(III):(Fe + $\text{Mg})_{\text{total}}$ ratios from ¼ to ⅓. The standard chemical potentials for the anion-containing fictive Fe(III) end-members are based on electronegativity values for the anions relative to hydroxide. The values look fairly reasonable, but the sources of the anion values (and the details of the calculation of the values for the Fe(III) end members) are not given. Neglecting water of hydration and using the authors' parameter values, $\Delta_f G^\circ_m$ values (for approximately 298 K?) are -3790, -12006 and -2129 $\text{kJ}\cdot\text{mol}^{-1}$ for $(\text{Fe}^{\text{III}})_2(\text{Fe}^{\text{II}})_4(\text{OH})_{12}\text{SO}_4$, $(\text{Fe}^{\text{III}})_6(\text{Fe}^{\text{II}})_{12}(\text{OH})_{36}(\text{HCO}_3)_4(\text{CO}_3)$ and $\text{Fe}^{\text{III}}(\text{Fe}^{\text{II}})_3(\text{OH})_8\text{Cl}$, respectively.

[2007DAC/GEI]

Dachs *et al.* [2007DAC/GEI] reported extensive heat-capacity measurements for $Fe_2SiO_4(cr)$ using heat-pulse calorimetry with 20 to 48 mg samples between 5 and 302 K. They reported (151.4 ± 0.1) $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and (130.6 ± 0.2) $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for S°_m (298.15 K) and $C^\circ_{p,m}$ (298.15 K), respectively, and these values are in reasonable agreement with those of Robie and Finch [1982ROB/FIN] (though the agreement is not within the combined uncertainty limits assigned by the authors). The main objective of the paper was to determine the properties of Mg_2SiO_4/Fe_2SiO_4 solid solutions, and the authors note that their measurement technique is not as accurate as low-temperature adiabatic calorimetry, especially near the Néel temperature, and that the measured C_p values between 100 and 300 K may be 1 to 2% low. The values from this paper were not used in the present review, but provide an excellent demonstration of changes in heat capacity and entropy of the solid solutions as a function of composition.

[2007HUN/BEN]

The hydrothermal reactions between a nanocrystalline mackinawite suspension and a polysulfide solution in a sealed silica ampoule at the temperatures 100 to 200 °C were monitored *in situ* and in real time using synchrotron-based energy-dispersive X-ray diffraction. A full diffraction pattern was collected as a function of energy simultaneously on three detectors set at 2θ angles of 2.92°, 5.44°, and 8.32° and the rate of formation and disappearance of the peaks during the reaction, and the changes in morphology of the solid phases as observed with high-resolution microscopy, were used to derive kinetic parameters and to determine the mechanisms of the reaction. It was shown that greigite (Fe_3S_4) is formed as an intermediate in the hydrothermal (100 –

200 °C) transformation of mackinawite (FeS) to pyrite (FeS_2) using zero-valent sulfur as an oxidant. The transformations of mackinawite to greigite and greigite to pyrite under non-sulfur limiting conditions obey zero-order kinetics indicating a solid-state mechanism. The result indicated that the reaction time for transformation of mackinawite to pyrite is eight days at 10 °C, and twelve days at 4 °C. The presence of oxygen was carefully avoided, and the experiment, analysis and discussion were done adequately. The result of the paper can be accepted as qualitative information for the present review.

[2007MAJ/MAZ]

A series of four lepidocrocite (γ-FeOOH) samples was studied at 25 °C by a combination of acid-dissolution calorimetry in 5 M HCl and water-adsorption calorimetry. The measured range of surface areas (BET method) was (42.5 ± 0.7) to (103.3 ± 0.4) $m^2 \cdot g^{-1}$. In a previous study [2003MAJ/GRE], a value of $\Delta_f H_m^o$ (FeOOH, γ, 298.15 K) = $-(549.4 \pm 1.4)$ $kJ \cdot mol^{-1}$ was obtained for the material with the lowest surface area; this value is adjusted slightly in the current review (Section VII.2.11.2). This substance served as the reference material for the current heat-of-dissolution measurements.

About 40% of adsorbed water was shown to be chemisorbed, with a mean enthalpy of adsorption of $-(21.8 \pm 2.6)$ $kJ \cdot mol^{-1}$ relative to H_2O(l). The authors describe the predominance of the {010} growth/cleavage planes in lepidocrocite surface chemistry; note, however, that edges of these planes may be important in some specific anion or ligand sorption processes.

Based on the calorimetric measurements, the authors derived a zero-surface-area value of $\Delta_f H_m^o$ (FeOOH, γ, 298.15 K) = $-(552.0 \pm 1.6)$ $kJ \cdot mol^{-1}$. The effective surface enthalpy was evaluated as (0.62 ± 0.14) $J \cdot m^{-2}$ for H_2O-free surfaces, relaxing to (0.40 ± 0.16) $J \cdot m^{-2}$ for a hydrated surface. These values should be used for thermodynamic calculations on γ-FeOOH of known specific surface area. The earlier value is still appropriate for cycles involving relatively well-crystallized "bulk" γ-FeOOH, perhaps with uncertainty limits adjusted to reflect uncertainties in particle size.

[2007STE]

This is potentially, the most comprehensive study of the hydrolysis of iron(III) in that potentiometric, UV-visible spectrophotometric and solubility measurements were employed at (25.0 ± 0.1) °C to a molar ionic strength of 3 ($NaClO_4$). Unfortunately, no raw experimental results were provided.

1. The potentiometric measurements utilized a glass electrode with Fe(III) concentrations of 9.97×10^{-4} to 0.0307 M over the pH_c range 1.66 – 2.80 at ionic strengths of 0.1, 0.5, 1.0 and 3.0. Calibration of the electrodes was carried out correctly before each titration on a molarity basis with a Nernst slope of (59.9 ± 0.6) (2σ). The

titrant contained $NaHCO_3$ which mitigates the localized high pH when the titrant is added and thereby also reduces the premature precipitation of iron(III) hydroxide, but introduces the possibility of carbonate complexation and subsequent precipitation of iron(III) carbonate solids.

2. The spectra of 118 solutions with Fe(III) concentrations of 3.48×10^{-6} to 9.53×10^{-4} M were measured over the pH_c range 1.54 – 5.10 (low iron concentrations were employed to mitigate the formation of higher-order iron(III) species). Solutions were also pumped directly from the potentiometric cell through a quartz cell for spectral analysis. The Fe^{3+} ion is reported to exhibit peaks at λ_{max} = 240 nm (ε = 380 - 420 $m^2 \cdot mol^{-1}$); $FeOH^+$: λ_{max} = 205 nm (ε = 460 - 480 $m^2 \cdot mol^{-1}$) and λ_{max} = 297 nm (ε = 200 - 210 $m^2 \cdot mol^{-1}$); $Fe(OH)_2^+$: λ_{max} = 242 nm (ε = 430 $m^2 \cdot mol^{-1}$) and $\lambda_{shoulder}$ = 339 nm (ε = 180 $m^2 \cdot mol^{-1}$).

The author tabulated his combined results from (1) and (2) (Table A-73) presumably with uncertainties derived from the statistical fits:

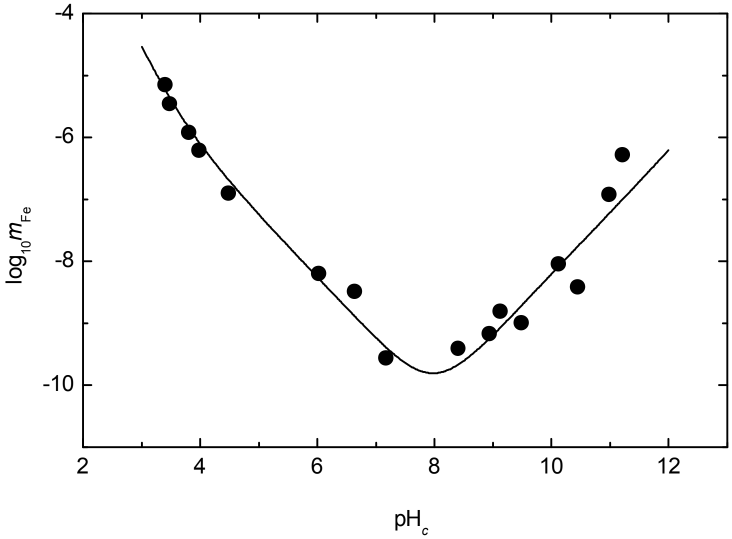
Table A-73: Summary of the logarithms of the molal hydrolysis constants at 25 °C.

I	$-\log_{10}{}^*\beta_{1,1}$ potentiometry	$-\log_{10}{}^*\beta_{1,1}$ spectrometry
0.101	2.54 ± 0.02	2.57 ± 0.04
0.512	2.69 ± 0.01	2.67 ± 0.03
1.076	2.75 ± 0.03	2.73 ± 0.02
3.493	2.79 ± 0.03	2.75 ± 0.02
		$-\log_{10}{}^*\beta_{2,1}$
0.101		6.34 ± 0.13
0.512		6.78 ± 0.03
1.076		6.94 ± 0.02
	$-\log_{10}{}^*\beta_{2,2}$	
0.101	2.93 ± 0.01	
0.512	2.89 ± 0.01	
1.076	2.87 ± 0.01	
3.493	2.74 ± 0.01	

3. The solubility of 2-line ferrihydrite (*i.e.*, poorly crystalline with only two broad lines in the XRD) was measured at 0.01 M ($NaClO_4$) ionic strength. The solid was characterized before and after the experiments by XRD and ir spectroscopy (no change was observed with time), and the solutions were filtered through a 0.02 µm filter. Equilibrium was reached within two to three weeks in alkaline and neutral solutions, but required one to two months in acidic solutions. The pH of the filtered solutions was measured with a glass electrode calibrated with commercial pH buffers. The pH was adjusted with $NaHCO_3$ and allowance was made for the presence of $Fe(OH)CO_3(aq)$

according to [2000BRU/DUR]. The author states that the presence of this complex was significant in the near-neutral pH region, but did not affect the solubility corresponding to the formation of $Fe(OH)_3(aq)$ and $Fe(OH)_4^-$. These "corrected" results are only shown in a plot of $\log_{10} m_{Fe(III)_{total}}$ *vs.* pH_c. These individual solubility data were obtained by digitizing Figure 3 in this paper (reproduced below in Figure A-75) and, because 2-line ferrihydrite is not a stable crystalline phase, these data are only considered here for comparison purposes. Also, ferrihydrite is represented as $Fe(OH)_3$ (s) in this paper. However, as the ionic strength is so low (0.01 M), the water activity can be ignored given the accuracy of such measurements. The solubility profile in Figure A-75 (solid curve) was based on the following solubility constants deduced from this paper: $\log_{10} {}^*\beta_{s,0} = 3.5$, $\log_{10} {}^*\beta_{s,1} = 1.3$, $\log_{10} {}^*\beta_{s,2} = -2.3$, $\log_{10} \beta_{s,3} = \leq -10.8$ and $\log_{10} {}^*\beta_{s,4} = -18.2$. The solubility constants led to the following hydrolysis constants: $\log_{10} {}^*\beta^{o}_{1,1} = -2.0$, $\log_{10} {}^*\beta^{o}_{2,1} = -5.5$, $\log_{10} {}^*\beta^{o}_{3,1} = \leq -14.0$, and $\log_{10} {}^*\beta^{o}_{4,1} = -21.5$. The value of $\log_{10} {}^*\beta^{o}_{1,1}$ is within reasonable agreement with that obtained from other techniques, *viz.*, between – 2.09 and – 2.15, especially considering how few solubility data points are available at low pH_c, and the inherent unreliability of solubility measurements of metastable solid phases. However, the value of $\log_{10} {}^*\beta^{o}_{2,1}$ is one unit smaller than the combined data from [1953HED2] and [1990SAL/VAS] that are considered in this review as being the most reliable values available. This discrepancy is perhaps surprising because according to Figure A-75, $Fe(OH)_2^+$ is dominant over a relatively wide range of pH_c , *viz.*, 3.5 to 6.5.

Figure A-75: Solubility dependence of ferrihydrite *vs.* pH_c at 25 °C.



According to Figure A-75, the value of $\log_{10}\beta_{s,3} = -10.80$ indicates that the $Fe(OH)_3(aq)$ species would give a minor contribution to the solubility minimum and cannot therefore be considered as being at all reliable. The value of $\log_{10}{}^{*}\beta^{\circ}_{4,1} = -21.5$ can only be considered as provisional given the paucity of comparable data in the literature and the problems mentioned above associated with using a poorly crystalline solid phase. On the other hand, the kinetics of dissolution of metal hydroxides and oxides are faster in basic solutions and according to Figure A-75, the $Fe(OH)_4^-$ is dominant over a wide range of pH_c. Moreover, the author claims that the presence of carbonate (bicarbonate) did not affect the solubility of ferrihydrite in this region.

The combined potentiometric and spectrophotometric values for $\log_{10}{}^{*}\beta_{1,1}$ appear quite reliable and consistent with previous results. However, the spectrophotometric $\log_{10}{}^{*}\beta_{2,1}$ values are significantly lower than the results of two previous studies, but they are internally consistent with the solubility result. As no explanation can be offered for this discrepancy, it suggests that the uncertainty in the accepted $\log_{10}{}^{*}\beta_{2,1}$ values should be increased until further experiments are reported. The value of $\log_{10}{}^{*}\beta^{\circ}_{4,1} = -21.5$ is of interest but cannot be considered as reliable without confirmation. Due to the insolubility and slow dissolution kinetics of crystalline iron(III) oxide/hydroxide phases, it is possible that the latter constant may only be obtained in the future by extrapolation of high-temperature solubility data.

Appendix B

Ionic strength corrections[1]

Thermodynamic data always refer to a selected standard state. The definition given by IUPAC [1982LAF] is adopted in this review as outlined in Section II.3.1. According to this definition, the standard state for a solute B in a solution is a hypothetical solution, at the standard state pressure, in which $m_B = m^\circ = 1\ \text{mol·kg}^{-1}$, and in which the activity coefficient γ_B is unity. However, for many reactions, measurements cannot be made accurately (or at all) in dilute solutions from which the necessary extrapolation to the standard state would be simple. This is invariably the case for reactions involving ions of high charge. Precise thermodynamic information for these systems can only be obtained in the presence of an inert electrolyte of sufficiently high concentration that ensures activity factors are reasonably constant throughout the measurements. This appendix describes and illustrates the method used in this review for the extrapolation of experimental equilibrium data to zero ionic strength.

The activity factors of all the species participating in reactions in high ionic strength media must be estimated in order to reduce the thermodynamic data obtained from the experiment to the state $I = 0$. Two alternative methods can be used to describe the ionic medium dependence of equilibrium constants:

- One method takes into account the individual characteristics of the ionic media by using a medium dependent expression for the activity coefficients of the species involved in the equilibrium reactions. The medium dependence is described by virial or ion interaction coefficients as used in the Pitzer equations [1973PIT] and in the specific ion interaction treatment.
- The other method uses an extended Debye-Hückel expression in which the activity coefficients of reactants and products depend only on the ionic charge and the ionic strength, but it accounts for the medium specific properties by introducing ion pairing between the medium ions and the species involved in the equilibrium reactions. Earlier, this approach has been used extensively in

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[1] This appendix contains much of the text of the TDB-2 Guideline written by Grenthe and Wanner [2000GRE/WAN], earlier versions of which have been printed in the previous NEA TDB reviews. The equations presented here are an essential part of the review procedure and are required to use the selected thermodynamic values. Parts of Section B.1.1 and the contents of Tables B-4, B-5, B-6 and B-7 have been revised by Rand *et al.* [2008RAN/FUG] and in the present review.

marine chemistry, *cf.* Refs. [1979JOH/PYT], [1979MIL], [1979PYT], [1979WHI2].

The activity factor estimates are thus based on the use of Debye-Hückel type equations. The "extended" Debye-Hückel equations are either in the form of specific ion interaction methods or the Davies equation [1962DAV]. However, the Davies equation should in general not be used at ionic strengths larger than 0.1 $\text{mol}\cdot\text{kg}^{-1}$. The method preferred in the NEA Thermochemical Database review is a medium-dependent expression for the activity coefficients, which is the specific ion interaction treatment in the form of the Brønsted-Guggenheim-Scatchard approach. Other forms of specific ion interaction methods (the Pitzer and Brewer "B-method" [1961LEW/RAN] and the Pitzer virial coefficient method [1979PIT]) are described in the NEA Guidelines for the extrapolation to zero ionic strength [2000GRE/WAN].

The specific ion interaction methods are reliable for intercomparison of experimental data in a given concentration range. In many cases this includes data at rather low ionic strengths, I = 0.01 to 0.1 M, *cf.* Figure B-1, while in other cases, notably for cations of high charge ($\geq +4$ and ≤ -4), the lowest available ionic strength is often 0.2 M or higher, see for example Figures V.12 and V.13 in [1992GRE/FUG]. It is reasonable to assume that the extrapolated equilibrium constants at $I = 0$ are more precise in the former than in the latter cases. The extrapolation error is composed of two parts, one due to experimental errors, and the other due to model errors. The model errors seem to be rather small for many systems, less than 0.1 in $\log_{10} K^{\circ}$. For reactions involving ions of high charge, which may be extensively hydrolysed, one cannot perform experiments at low ionic strengths. Hence, it is impossible to estimate the extrapolation error. This is true for all methods used to estimate activity corrections. Systematic model errors of this type are not included in the uncertainties assigned to the selected data in this review.

B.1 The specific ion interaction equations

B.1.1 Background

The Debye-Hückel term, which is the dominant term in the expression for the activity coefficients in dilute solution, accounts for electrostatic, non-specific long-range interactions. At higher concentrations, short range, non-electrostatic interactions have to be taken into account. This is usually done by adding ionic strength dependent terms to the Debye-Hückel expression. This method was first outlined by Brønsted [1922BRO], [1922BRO2] and elaborated by Scatchard [1936SCA] and Guggenheim [1966GUG]. Biedermann [1975BIE] highlighted its practical value, especially for the estimation of ionic medium effects on equilibrium constants. The two basic assumptions in the specific ion interaction treatment are described below.

- **Assumption 1:** The activity coefficient γ_j of an ion j of charge z_j in the solution of ionic strength I_m may be described by Eq. (B.1):

$$\log_{10}\gamma_j = -z_j^2 D + \sum_k \varepsilon(j,k,I_m)\, m_k \qquad \text{(B.1)}$$

D is the Debye-Hückel term:

$$D = \frac{A\sqrt{I_m}}{1 + B a_j \sqrt{I_m}} \qquad \text{(B.2)}$$

A and B are constants which are temperature and pressure dependent, a_j is an ion size parameter ("distance of closest approach") for the hydrated ion j, and I_m is the molal ionic strength:

$$I_m = \frac{1}{2}\sum_i m_i z_i^2$$

The Debye-Hückel limiting slope, A, has a value of (0.509 ± 0.001) $\text{kg}^{\frac{1}{2}}\cdot\text{mol}^{-\frac{1}{2}}$ at 298.15 K and 1 bar, (*cf.* Section B.1.2). The term Ba_j in the denominator of Eq. (B.2) (where a_j is an "effective" ion size parameter and B is a constant determined by the temperature and the physical properties of water) has been assigned an empirical value of 1.5 $\text{kg}^{\frac{1}{2}}\cdot\text{mol}^{-\frac{1}{2}}$ (Eq. (B.2a)). The value 1.5 was proposed by Scatchard [1976SCA] to minimise the ionic strength dependence of $\varepsilon(j,k)$ for a number of electrolytes, and it was found to be particularly appropriate between I_m = 0.5 and 3.5 m. A constant value of Ba_j for all species simplifies modelling of both binary and multicomponent aqueous electrolyte systems, and makes it easier to give a consistent description of mean activity coefficient both in binary and multicomponent solutions ([1959ROB/STO], pp.435-441). Thus,

$$D = \frac{A I_m^{\frac{1}{2}}}{1 + 1.5 I_m^{\frac{1}{2}}} \qquad \text{(B.2a)}$$

It should be mentioned that some authors have proposed different values for Ba_j ranging from Ba_j = 1.0 [1935GUG] to Ba_j = 1.6 [1962VAS]. However, the parameter Ba_j is empirical and as such is correlated to the value of $\varepsilon(j,k,I_m)$. Hence, this variety of values for Ba_j does not represent an uncertainty range, but rather indicates that several different sets of Ba_j and $\varepsilon(j,k,I_m)$ may describe equally well the experimental mean activity coefficients of a given electrolyte. The ion interaction coefficients at 298.15 K listed in Table B-4, Table B-5, Table B-6 and Table B-7 have thus to be used with Ba_j = 1.5 $\text{kg}^{\frac{1}{2}}\cdot\text{mol}^{-\frac{1}{2}}$.

The summation in Eq. (B.1) extends over all ions k present in solution. Their molality is denoted by m_k, and the specific ion interaction parameters, $\varepsilon(j,k,I_m)$, in general depend only slightly on the ionic strength. The concentrations of the ions of the ionic medium are often very much larger than those of the reacting species. Hence, the ionic medium ions will make the main contribution to the value of $\log_{10}\gamma_j$ for the reacting ions. This fact often makes it possible to simplify the summation $\sum_k \varepsilon(j,k,I_m) m_k$, so that only ion interaction coefficients between the participating ionic species and the ionic medium ions are included, as shown in Eqs. (B.5) to (B.9).

- **Assumption 2:** The ion interaction coefficients, $\varepsilon(j,k,I_m)$ are zero for ions of the same charge sign and for uncharged species. The rationale behind this is that ε, which describes specific short-range interactions, must be small for ions of the same charge since they are usually far from one another due to electrostatic repulsion. This holds to a lesser extent also for uncharged species, but in some cases the experimental data allow determination of interaction coefficients for uncharged species with electroneutral combinations of ions, *cf.* Table B-7.

Equation (B.1) will allow fairly accurate estimates of the activity coefficients in mixtures of electrolytes if the ion interaction coefficients are known. Ion interaction coefficients for simple ions can be obtained from tabulated data of mean activity coefficients of strong electrolytes or from the corresponding osmotic coefficients. Ion interaction coefficients for complexes can either be estimated from the charge and size of the ion or determined experimentally from the variation of the equilibrium constant with the ionic strength.

Ion interaction coefficients are not strictly constant but may vary slightly with the ionic strength. The extent of this variation depends on the charge type and is small for 1:1, 1:2 and 2:1 electrolytes for molalities less than 3.5 m. The concentration dependence of the ion interaction coefficients can thus often be neglected. This point was emphasised by Guggenheim [1966GUG], who has presented a considerable amount of experimental material supporting this approach. The concentration dependence is larger for electrolytes of higher charge. In order to reproduce accurately their activity coefficient data, concentration dependent ion interaction coefficients have to be used, *cf.* Lewis *et al.* [1961LEW/RAN], Baes and Mesmer [1976BAE/MES], or Ciavatta [1980CIA].

For cases where the uncertainties in the epsilon values collected in Table B-4 and Table B-5 are $\pm\,0.03$ kg·mol^{-1} or greater, Ciavatta [1980CIA] proposed the use of Eq. (B.3)

$$\varepsilon = \varepsilon_1 + \varepsilon_2 \log_{10} I_m \tag{B.3}$$

However, even if the value of ε calculated in this way describes the variation with ionic strength slightly better than a constant value, this equation has no theoretical basis; ε_2 is a fitting parameter and the term $\varepsilon_2 \log_{10} I_m$ goes to minus infinity at the limiting value $I_m = 0$. This expression for the composition dependence of ε should be avoided, even though the term $\varepsilon\cdot m = (\varepsilon_1 + \varepsilon_2\log_{10} I_m)\cdot m$ (in the calculation of activity coefficients) is zero at $I_m = 0$. There may be cases where reviewers will still want to use Eq. (B.3) to describe the ionic strength variation of the interaction parameters, but the rationale behind this should then be described. However, as discussed by Rand *et al.* [2008RAN/FUG] (*cf.* Section IX.1.3.3) the one- and two-epsilon models usually will provide similar calculated results for values of $\log_{10} K^{\circ}$. As the two-epsilon model has been used in the current and previous volumes, the relevant parameters have been retained and augmented in Table B-6.

By using a more elaborate virial expansion, Pitzer and co-workers [1973PIT], [1973PIT/MAY], [1974PIT/KIM], [1974PIT/MAY], [1975PIT], [1976PIT/SIL], [1978PIT/PET], [1979PIT] have managed to describe measured activity coefficients of a large number of electrolytes with high precision over a large concentration range. Pitzer's model generally contains three parameters as compared to one in the specific ion interaction treatment. The use of the treatment requires the knowledge of all these parameters. The derivation of Pitzer coefficients for many complexes, such as those of the actinides would require a very large amount of additional experimental work, since few data of this type are currently available.

The way in which the activity coefficient corrections are performed in this review according to the specific ion interaction treatment is illustrated below for a general case of a complex formation reaction. Charges on all species except the hydrogen ions are omitted for brevity.

$$m\,\mathrm{M} + q\,\mathrm{L} + n\,\mathrm{H_2O(l)} \rightleftharpoons \mathrm{M}_m\mathrm{L}_q(\mathrm{OH})_n + n\,\mathrm{H}^+$$

The formation constant of $\mathrm{M}_m\mathrm{L}_q(\mathrm{OH})_n$, ${}^*\beta_{q,n,m}$, determined in an ionic medium (1:1 salt NX) of the ionic strength I_m, is related to the corresponding value at zero ionic strength, ${}^*\beta^{\circ}_{q,n,m}$ by Eq. (B.4).

$$\begin{aligned}\log_{10} {}^*\beta_{q,n,m} = \log_{10} {}^*\beta^{\circ}_{q,n,m} + m\log_{10}\gamma_{\mathrm{M}} + q\log_{10}\gamma_{\mathrm{L}} + n\log_{10} a_{\mathrm{H_2O}} \\ -\log_{10}\gamma_{q,n,m} - n\log_{10}\gamma_{\mathrm{H^+}}\end{aligned} \quad \text{(B.4)}$$

The subscript (q,n,m) denotes the complex ion, $\mathrm{M}_m\mathrm{L}_q(\mathrm{OH})_n$. If the concentrations of N and X are much greater than the concentrations of M, L, $\mathrm{M}_m\mathrm{L}_q(\mathrm{OH})_n$ and H^+, only the molalities m_{N} and m_{X} have to be taken into account for the calculation of the term, $\sum_k \varepsilon(j,k,I_m)m_k$ in Eq. (B.1). For example, for the activity coefficient of the metal cation M, γ_{M}, Eq. (B.5) is obtained at 298.15 K and 1 bar.

$$\log_{10}\gamma_{\mathrm{M}} = \frac{-z_{\mathrm{M}}^2\, 0.509\sqrt{I_m}}{1 + 1.5\sqrt{I_m}} + \varepsilon(\mathrm{M,X},I_m)m_{\mathrm{X}} \quad \text{(B.5)}$$

Under these conditions, $I_m \approx m_{\mathrm{X}} = m_{\mathrm{N}}$ Substituting the $\log_{10}\gamma_j$ values in Eq. (B.4) with the corresponding forms of Eq. (B.5) and rearranging leads to:

$$\log_{10} {}^*\beta_{q,n,m} - \Delta z^2 D - n\log_{10} a_{\mathrm{H_2O}} = \log_{10} {}^*\beta^{\circ}_{q,n,m} - \Delta\varepsilon I_m \quad \text{(B.6)}$$

where, at 298.15 K and 1 bar:

$$\Delta z^2 = (m\,z_{\mathrm{M}} - q\,z_{\mathrm{L}} - n)^2 + n - m z_{\mathrm{M}}^2 - q\,z_{\mathrm{L}}^2 \quad \text{(B.7)}$$

$$D = \frac{0.509\sqrt{I_m}}{1 + 1.5\sqrt{I_m}} \qquad \text{(B.8)}$$

$$\Delta\varepsilon = \varepsilon(q,n,m,\text{N or X}) + n\,\varepsilon(\text{H, X}) - q\,\varepsilon(\text{N, L}) - m\,\varepsilon(\text{M, X}) \qquad \text{(B.9)}$$

Here $(m\,z_{\text{M}} - q\,z_{\text{L}} - n)$, z_{M} and z_{L} are the charges of the complex, $\text{M}_m\text{L}_q(\text{OH})_n$, 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, $a_{\text{H}_2\text{O}}$. The activity of water in an electrolyte mixture can be calculated as:

$$\log_{10} a_{\text{H}_2\text{O}} = \frac{-\phi_m \sum\limits_k m_k}{\ln(10)\, M^{-1}_{\text{H}_2\text{O}}} \qquad \text{(B.10)}$$

where ϕ_m is the osmotic coefficient of the mixture, $M_{\text{H}_2\text{O}}$ is the molar mass of H_2O, and the summation extends over all solute species k with molality m_k present in the solution. In the presence of an ionic medium NX as the dominant species, Eq. (B.10) can be simplified by neglecting the contributions of all minor species, *i.e.*, the reacting ions. Hence, for a 1:1 electrolyte of ionic strength $I_m \approx m_{\text{NX}}$, Eq. (B.10) becomes:

$$\log_{10} a_{\text{H}_2\text{O}} = \frac{-2\,m_{\text{NX}}\,\phi_m}{\ln(10)\, M^{-1}_{\text{H}_2\text{O}}} \qquad \text{(B.11)}$$

Alternatively, water activities can be taken from Table B-1. These have been calculated for the most common ionic media at various concentrations applying Pitzer’s ion interaction model and the interaction parameters given in [1991PIT]. Data in *italics* have been calculated for concentrations beyond the validity of the parameter set applied. These data are therefore extrapolations and should be used with care.

Values of osmotic coefficients for single electrolytes have been compiled by various authors, *e.g.*, Robinson and Stokes [1959ROB/STO]. The activity of water can also be calculated from the known activity coefficients of the dissolved species. In the presence of an ionic medium, $\text{N}_{\nu_+}\text{X}_{\nu_-}$, of a concentration much larger than those of the reacting ions, the osmotic coefficient can be calculated according to Eq. (B.12) (*cf.* Eqs. (23-39), (23-40) and (A4-2) in [1961LEW/RAN]).

$$\begin{aligned} 1-\phi_m = {} & \frac{A\ln(10)\left|z_+z_-\right|}{I_m(B\,a_j)^3}\left[1+B\,a_j\sqrt{I_m} - 2\ln(1+B\,a_j\sqrt{I_m}) - \frac{1}{1+B\,a_j\sqrt{I_m}}\right] \\ & - \ln(10)\ \varepsilon(\text{N,X})\,m_{\text{NX}}\left(\frac{\nu_+\nu_-}{\nu_+ + \nu_-}\right) \end{aligned} \qquad \text{(B.12)}$$

with the general term Ba_j = 1.5 $\text{kg}^{½}\cdot\text{mol}^{-½}$, which is mainly used in NEA reviews (*cf.*, Section B.1.2), rather than the implied Ba_j = 1.0 $\text{kg}^{½}\cdot\text{mol}^{-½}$ in the expressions in Lewis and Randall, and ν_+ and ν_- are the number of cations and anions in the salt formula ($\nu_+z_+ = \left|\nu_-z_-\right|$) and in this case:

$$I_m = \frac{1}{2}\left|z_+ z_-\right| m_{\mathrm{NX}}(\nu_+ + \nu_-)\,.$$

Table B-1: Water activities $a_{\mathrm{H_2O}}$ for the most common ionic media at various concentrations applying Pitzer's ion interaction approach and the interaction parameters given in [1991PIT] and using density conversions from Table II-5. 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 $a_{\mathrm{H_2O}}$ at 298.15 K								
c (M)	$HClO_4$	$NaClO_4$	$LiClO_4$	NH_4ClO_4	$Ba(ClO_4)_2$	HCl	NaCl	LiCl
0.100	0.9966	0.9966	0.9966	0.9967	0.9953	0.9966	0.9966	0.9966
0.250	0.9914	0.9917	0.9912	0.9920	0.9879	0.9914	0.9917	0.9915
0.500	0.9821	0.9833	0.9817	0.9844	0.9740	0.9823	0.9833	0.9826
0.750	0.9720	0.9747	0.9713	0.9769	0.9576	0.9726	0.9748	0.9731
1.000	0.9609	0.9660	0.9602	0.9694	0.9387	0.9620	0.9661	0.9631
1.500	0.9357	0.9476	0.9341	0.9542	0.8929	0.9386	0.9479	0.9412
2.000	0.9056	0.9279	0.9037		*0.8383*	0.9115	0.9284	0.9167
3.000	0.8285	0.8840	0.8280		*0.7226*	0.8459	0.8850	0.8589
4.000	0.7260	0.8331	*0.7309*			0.7643	0.8352	0.7991
5.000	*0.5982*	*0.7744*				0.6677	0.7782	0.7079
6.000	*0.4513*	*0.7075*				*0.5592*		*0.6169*
c (M)	KCl	NH_4Cl	$MgCl_2$	$CaCl_2$	NaBr	HNO_3	$NaNO_3$	$LiNO_3$
0.100	0.9966	0.9966	0.9953	0.9954	0.9966	0.9966	0.9967	0.9966
0.250	0.9918	0.9918	0.9880	0.9882	0.9916	0.9915	0.9919	0.9915
0.500	0.9836	0.9836	0.9744	0.9753	0.9830	0.9827	0.9841	0.9827
0.750	0.9754	0.9753	0.9585	0.9605	0.9742	0.9736	0.9764	0.9733
1.000	0.9671	0.9669	0.9399	0.9436	0.9650	0.9641	0.9688	0.9635
1.500	0.9500	0.9494	0.8939	0.9024	0.9455	0.9439	0.9536	0.9422
2.000	0.9320	0.9311	0.8358	0.8507	0.9241	0.9221	0.9385	0.9188
3.000	0.8933	0.8918	0.6866	0.7168	0.8753	0.8737	0.9079	0.8657
4.000	0.8503	0.8491	0.5083	0.5511	*0.8174*	0.8196	0.8766	0.8052
5.000		*0.8037*		*0.3738*	*0.7499*	0.7612	0.8446	0.7390
6.000					*0.6728*	*0.7006*	*0.8120*	*0.6696*
0.500	0.9843	0.9813	0.9814	0.9805	0.9789	0.9828		

(Continued on next page)

Table B-1 (continued)

	Water activities a_{H_2O} at 298.15 K					
c (M)	NH_4NO_3	Na_2SO_4	$(NH_4)_2SO_4$	Na_2CO_3	K_2CO_3	NaSCN
0.750	0.9768	0.9732	0.9728	0.9720	0.9683	0.9736
1.000	0.9694	0.9653	0.9640	0.9637	0.9570	0.9641
1.500	0.9548	0.9491	0.9455	0.9467	0.9316	0.9438
2.000	0.9403		0.9247	0.9283	0.9014	0.9215
3.000	0.9115		0.8735		0.8235	0.8708
4.000	0.8829		0.8050		0.7195	*0.8115*
5.000	*0.8545*				*0.5887*	*0.7436*
6.000	*0.8266*					*0.6685*

The activity of water is obtained by inserting Eq. (B.12) into Eq. (B.11). It should be mentioned that in mixed electrolytes with several components at high concentrations, it might be necessary to use Pitzer's equation to calculate the activity of water. On the other hand, a_{H_2O} is nearly constant in most experimental studies of equilibria in dilute aqueous solutions, where an ionic medium is used in large excess with respect to the reactants. The medium electrolyte thus determines the osmotic coefficient of the solvent.

In natural waters the situation is similar; the ionic strength of most surface waters is so low that the activity of $H_2O(l)$ can be set equal to unity. A correction may be necessary in the case of seawater, where a sufficiently good approximation for the osmotic coefficient may be obtained by considering NaCl as the dominant electrolyte.

In more complex solutions of high ionic strengths with more than one electrolyte at significant concentrations, *e.g.*, (Na^+, Mg^{2+}, Ca^{2+}) (Cl^-, SO_4^{2-}), Pitzer's equation (*cf.* [2000GRE/WAN]) may be used to estimate the osmotic coefficient; the necessary interaction coefficients are known for most systems of geochemical interest.

Note that in all ion interaction approaches, the equation for the mean activity coefficients can be split up to give equations for conventional single ion activity coefficients in mixtures, *e.g.*, Eq. (B.1). The latter are strictly valid only when used in combinations which yield electroneutrality. Thus, while estimating medium effects on standard potentials, a combination of redox equilibria with, $H^+ + e^- \rightleftharpoons \frac{1}{2}H_2(g)$, is necessary (*cf.* Example B.3).

B.1.2 Ionic strength corrections at temperatures other than 25 °C (298.15 K)

Values of the Debye-Hückel parameter A in Eqs. (B.2), (B.2a) and (B.12) are listed in Table B-2 for several temperatures at a pressure of 1 bar below 100 °C and at the steam saturated pressure for $t \geq 100$ °C. The values in Table B-2 can be calculated from the static dielectric constant and the density of water as a function of temperature and pressure, as discussed in various references [1974HEL/KIR], [1979BRA/PIT], [1981HEL/KIR], [1984ANA/ATK], [1990ARC/WAN], [2009PAT/HRU]. The values in Table B-2 are those from Helgeson *et al.* [1981HEL/KIR]. More recent expressions for the density and dielectric constant (*e.g.*, those of Archer and Wang [1990ARC/WAN] or Pátek *et al.* [2009PAT/HRU]) would generate very slightly different values, but the Table B-2 values should be used to provide consistent TDB activity coefficient expressions.

Table B-2: Values of the Debye-Hückel constant A as a function of temperature at a pressure of 1 bar below 100 °C and at the steam saturated pressure for $t \geq 100$ °C. The uncertainty in the A parameter is estimated by this review to be $\pm$ 0.001 $\text{kg}^{½}\cdot\text{mol}^{-½}$ at 25 °C, and $\pm$ 0.006 $\text{kg}^{½}\cdot\text{mol}^{-½}$ at 300 °C.

t/°C	p/bar	A/ $\text{kg}^{½}\cdot\text{mol}^{-½}$
0	1.00	0.491
5	1.00	0.494
10	1.00	0.498
15	1.00	0.501
20	1.00	0.505
25	1.00	0.509
30	1.00	0.514
35	1.00	0.518
40	1.00	0.523
50	1.00	0.534
75	1.00	0.564
100	1.013	0.600
125	2.32	0.642
150	4.76	0.690
175	8.92	0.745
200	15.5	0.810
250	39.7	0.979
300	85.8	1.256

In this review the term Ba_j, in the denominator of the Debye-Hückel term, D of Eq. (B.2), has been assigned a value of 1.5 $\text{kg}^{½}\cdot\text{mol}^{-½}$ (Eq. (B.2a)), and is kept constant at all temperatures. Due to the variation of B with temperature, this implies a temperature dependence for ion-size parameters. Assuming the ion size is in reality constant, it becomes obvious that this simplification introduces an error in D, which increases with temperature and ionic strength. However, this error is less than $\pm 0.01\ \text{kg}^{½}\cdot\text{mol}^{-½}$ at $t \leq 100$ °C and $I < 6$ m, and less than $\pm 0.006\ \text{kg}^{½}\cdot\text{mol}^{-½}$ at $t \leq 50$ °C and $I \leq 4$ m.

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. Nevertheless, as long as a consistent approach is followed, values of $\varepsilon(j,k,I_m)$ absorb the choice of Ba_j, and for moderate temperature intervals (between 0 and 200 °C) the choice $Ba_j = 1.5\ \text{kg}^{½}\cdot\text{mol}^{-½}$ is simple and is recommended by this review.

The variation of $\varepsilon(j,k,I_m)$ with temperature is discussed by Lewis *et al.* [1961LEW/RAN], Millero [1979MIL], Helgeson *et al.* [1981HEL/KIR], [1990OEL/HEL], Giffaut *et al.* [1993GIF/VIT2] and Grenthe and Plyasunov [1997GRE/PLY]. The absolute values for the reported ion interaction parameters differ in these studies due to the fact that the Debye-Hückel term used by these authors is not exactly the same. Nevertheless, common to all these studies is the fact that values of $(\partial\varepsilon/\partial T)_p$ are usually $\leq 0.005\ \text{kg}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ 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 $\leq 0.13\ \text{kg}\cdot\text{mol}^{-1}$. It is clear that in order to reduce the uncertainties in solubility calculations at $t \neq 25$ °C, studies on the variation of $\varepsilon(j,k,I_m)$ values with temperature should be undertaken.

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_{HCl}:

$$\begin{aligned} 2\log_{10}\gamma_{\pm,\text{HCl}} &= \log_{10}\gamma_{\text{H}^+} + \log_{10}\gamma_{\text{Cl}^-} \\ &= -D + \varepsilon(\text{H}^+,\text{Cl}^-)\,m_{\text{Cl}^-} - D + \varepsilon(\text{H}^+,\text{Cl}^-)\,m_{\text{H}^+} \\ \log_{10}\gamma_{\pm,\text{HCl}} &= -D + \varepsilon(\text{H}^+,\text{Cl}^-)\,m_{\text{HCl}} \end{aligned}$$

By plotting $(\log_{10}\gamma_{\pm,\text{HCl}} + D)$ *versus* m_{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:

$$UO_2^{2+} + Cl^- \rightleftharpoons UO_2Cl^+ \quad (B.13)$$

The following formula is deduced from Eq. (B.6) for the extrapolation to $I = 0$:

$$\log_{10} \beta_1 + 4D = \log_{10} \beta_1^{o} - \Delta\varepsilon\, I_m \quad (B.14)$$

Table B-3: The preparation of the experimental equilibrium constants for the extrapolation to $I = 0$ with the specific ion interaction method at 25 °C and 1 bar, according to Reaction (B.13). The linear regression of this set of data is shown in Figure B-1.

I_m	$\log_{10} \beta_1$ (exp) (a)	$\log_{10} \beta_{1,m}$ (b)	$\log_{10} \beta_{1,m} + 4D$
0.10	– 0.17 ± 0.10	– 0.174	0.264 ± 0.100
0.20	– 0.25 ± 0.10	– 0.254	0.292 ± 0.100
0.26	– 0.35 ± 0.04	– 0.357	0.230 ± 0.040
0.31	– 0.39 ± 0.04	– 0.397	0.220 ± 0.040
0.41	– 0.41 ± 0.04	– 0.420	0.246 ± 0.040
0.51	– 0.32 ± 0.10	– 0.331	0.371 ± 0.100
0.57	– 0.42 ± 0.04	– 0.432	0.288 ± 0.040
0.67	– 0.34 ± 0.04	– 0.354	0.395 ± 0.040
0.89	– 0.42 ± 0.04	– 0.438	0.357 ± 0.040
1.05	– 0.31 ± 0.10	– 0.331	0.491 ± 0.100
1.05	– 0.277 ± 0.260	– 0.298	0.525 ± 0.260
1.61	– 0.24 ± 0.10	– 0.272	0.618 ± 0.100
2.21	– 0.15 ± 0.10	– 0.193	0.744 ± 0.100
2.21	– 0.12 ± 0.10	– 0.163	0.774 ± 0.100
2.82	– 0.06 ± 0.10	– 0.112	0.860 ± 0.100
3.50	0.04 ± 0.10	– 0.027	0.974 ± 0.100

(a) Equilibrium constants for Reaction (B.13) in aqueous $NaClO_4$ solutions, with assigned uncertainties, corrected to 25 °C where necessary. For details of the data, see Section V.4.2.1.2 of [1992GRE/FUG].

(b) Equilibrium constants were converted from molarity to molality basis as described in Section II.2

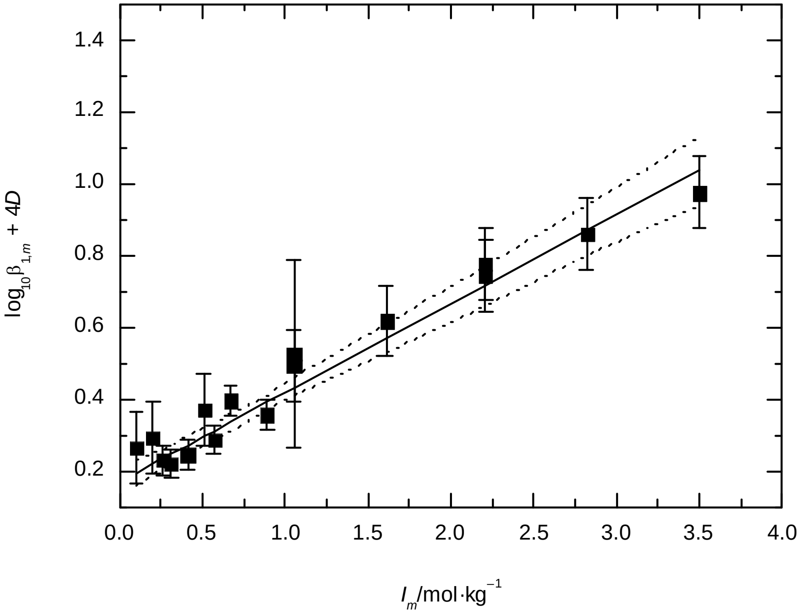
The linear regression is done as described in Appendix C. The following results are obtained:

$$\log_{10} \beta_1^\circ = (0.170 \pm 0.021)$$

$$\Delta\varepsilon(\text{B.13}) = -(0.248 \pm 0.022)\ \text{kg·mol}^{-1}.$$

The experimental data are depicted in Figure B-1, where the area enclosed by the dotted lines represents the uncertainty range that is obtained by using the results in $\log_{10} \beta_1^\circ$ and $\Delta\varepsilon$ and correcting back to $I \neq 0$.

Figure B-1: Plot of $\log_{10} \beta_1 + 4D$ *versus* I_m for Reaction (B.13), at 25 °C and 1 bar. The straight line shows the result of the weighted linear regression, and the dotted lines represent the uncertainty range obtained by propagating the resulting uncertainties at $I = 0$ back to $I = 4$ m.



Example B.3:

When using the specific ion interaction treatment, the relationship between the redox potential of the couple, UO_2^{2+}/U^{4+}, in a perchlorate 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:

$$\text{Pt} \mid H_2(g) \mid H^+ \vdots\vdots\ UO_2^{2+}, U^{4+} \mid \text{Pt}$$

is:

$$\mathrm{UO_2^{2+} + H_2(g) + 2\,H^+ \rightleftharpoons U^{4+} + 2\,H_2O(l)}. \tag{B.15}$$

For this reaction

$$\log_{10} K^{\mathrm{o}} = \log_{10}\left(\frac{a_{\mathrm{U^{4+}}} \cdot a^2_{\mathrm{H_2O}}}{a_{\mathrm{UO_2^{2+}}} \cdot a^2_{\mathrm{H^+}} \cdot f_{\mathrm{H_2}}}\right).$$

$$\begin{aligned}\log_{10} K^{\mathrm{o}} = {} & \log_{10} K + \log_{10}\gamma_{\mathrm{U^{4+}}} - \log_{10}\gamma_{\mathrm{UO_2^{2+}}} - 2\log_{10}\gamma_{\mathrm{H^+}} - \log_{10}\gamma_{f,\mathrm{H_2}} \\ & + 2\log_{10} a_{\mathrm{H_2O}}\end{aligned},$$

$f_{\mathrm{H_2}} \approx p_{\mathrm{H_2}}$ at reasonably low partial pressure of $H_2(g)$, $a_{\mathrm{H_2O}} \approx 1$ (which is a reasonable approximation for $I_m \le 3$), and

$$\begin{aligned}\log_{10}\gamma_{\mathrm{U^{4+}}} &= -16\,D + \varepsilon(\mathrm{U^{4+}, ClO_4^-})\,m_{\mathrm{ClO_4^-}} \\ \log_{10}\gamma_{\mathrm{UO_2^{2+}}} &= -4\,D + \varepsilon(\mathrm{UO_2^{2+}, ClO_4^-})\,m_{\mathrm{ClO_4^-}} \\ \log_{10}\gamma_{\mathrm{H^+}} &= -D + \varepsilon(\mathrm{H^+, ClO_4^-})\,m_{\mathrm{ClO_4^-}}\end{aligned}$$

Hence,

$$\begin{aligned}\log_{10} K^{\mathrm{o}} = {} & \log_{10} K - 10\,D \\ & + (\varepsilon(\mathrm{U^{4+}, ClO_4^-}) - \varepsilon(\mathrm{UO_2^{2+}, ClO_4^-}) - 2\,\varepsilon(\mathrm{H^+, ClO_4^-}))\,m_{\mathrm{ClO_4^-}}\end{aligned} \tag{B.16}$$

The relationship between the equilibrium constant and the redox potential is:

$$\ln K = \frac{nF}{RT}\,E \tag{B.17}$$

$$\ln K^{\mathrm{o}} = \frac{nF}{RT}\,E^{\mathrm{o}}. \tag{B.18}$$

E is the redox potential in a medium of ionic strength I, E^{o} is the corresponding standard potential at $I = 0$, and n is the number of transferred electrons in the reaction considered. Combining Eqs. (B.16), (B.17) and (B.18) and rearranging them leads to Eq. (B.19):

$$E - 10D\left(\frac{RT\ln(10)}{nF}\right) = E^{\mathrm{o}} - \Delta\varepsilon\, m_{\mathrm{ClO_4^-}}\left(\frac{RT\ln(10)}{nF}\right) \tag{B.19}$$

For $n = 2$ in the present example and $T = 298.15$ K, Eq. (B.19) becomes:

$$E/\mathrm{mV} - 295.8\;D = E^{\mathrm{o}}/\mathrm{mV} - 29.58\,\Delta\varepsilon m_{\mathrm{ClO_4^-}}$$

where

$$\Delta\varepsilon = \varepsilon(\mathrm{U^{4+}, ClO_4^-}) - \varepsilon(\mathrm{UO_2^{2+}, ClO_4^-}) - 2\varepsilon(\mathrm{H^+, ClO_4^-}).$$

B.1.4 On the magnitude of ion interaction coefficients

Ciavatta [1980CIA] made a compilation of ion interaction coefficients for a large number of electrolytes. Similar data for complex formation reactions of various kinds were reported by Spahiu [1983SPA] and Ferri *et al.* [1983FER/GRE]. These and some other data for 25 °C and 1 bar have been collected and are listed in Section B.3.

It is obvious from the data in these tables that the charge of an ion is of great importance for determining the magnitude of the ion interaction coefficient. Ions of the same charge type have similar ion interaction coefficients with a given counter-ion. Based on the tabulated data, Grenthe *et al.* [1992GRE/FUG] proposed that it is possible to estimate, with an error of at most ± 0.1 kg·mol^{-1} in ε, ion interaction coefficients for cases where there are insufficient experimental data for an extrapolation to $I = 0$. The error that is made by this approximation is estimated to be ± 0.1 kg·mol^{-1} in $\Delta\varepsilon$ in most cases, based on comparison with $\Delta\varepsilon$ values of various reactions of the same charge type.

B.2 Ion interaction coefficients *versus* equilibrium constants for ion pairs

It can be shown that the virial type of activity coefficient equations and the ionic pairing model are equivalent provided that the ionic pairing is weak. In these cases the distinction between complex formation and activity coefficient variations is difficult or even arbitrary unless independent experimental evidence for complex formation is available, *e.g.*, from spectroscopic data, as is the case for the weak uranium(VI) chloride complexes. It should be noted that the ion interaction coefficients evaluated and tabulated by Ciavatta [1980CIA] were obtained from experimental mean activity coefficient data without taking into account complex formation. However, it is known that many of the metal ions listed by Ciavatta form weak complexes with chloride and nitrate ion. This fact is reflected by ion interaction coefficients that are smaller than those for the non-complexing perchlorate ion, *cf.* Table B-4. This review takes chloride and nitrate complex formation into account when these ions are part of the ionic medium and uses the value of the ion interaction coefficient, $\varepsilon(\mathrm{M}^{n+},\mathrm{ClO}_4^-)$, as a substitute for $\varepsilon(\mathrm{M}^{n+},\mathrm{Cl}^-)$ and $\varepsilon(\mathrm{M}^{n+},\mathrm{NO}_3^-)$. In this way, the medium dependence of the activity coefficients is described with a combination of a specific ion interaction model and an ion pairing model. It is evident that the use of NEA recommended data with ionic strength correction models that differ from those used in the evaluation procedure can lead to inconsistencies in the results of the speciation calculations.

It should be mentioned that complex formation may also occur between highly charged complexes and the counterion of the ionic medium. An example is the stabilisation of the complex ion, $\mathrm{UO}_2(\mathrm{CO}_3)_3^{5-}$, at high ionic strength, see for example Section V.7.1.2.1.d (p. 322) in the uranium review [1992GRE/FUG].

B.3 Tables of ion interaction coefficients

Table B-4, Table B-5, Table B-6 and Table B-7 contain the selected specific ion interaction coefficients used in this review, according to the specific ion interaction treatment described. Table B-4 contains cation interaction coefficients with Cl^-, ClO_4^- and NO_3^-, Table B-5 anion interaction coefficients with Li^+, Na^+ (or NH_4^+) and K^+, and Table B-7 neutral species – electroneutral combination of ions. The coefficients have the units of $kg{\cdot}mol^{-1}$ and are valid for 298.15 K and 1 bar. The species are ordered by charge and appear, within each charge class, in the standard order of arrangement, *cf.* Section II.1.8.

It should be noted that ion interaction coefficients tabulated in Table B-4, Table B-5 and Table B-6 may also involve ion pairing effects, as described in Section B.2. In direct comparisons of ion interaction coefficients, or when estimates are made by analogy, this aspect must be taken into account.

Table B-4: Ion interaction coefficients $\varepsilon(j,k)$ ($kg{\cdot}mol^{-1}$) for cations j with k = Cl^-, ClO_4^- and NO_3^- at 298.15 K. The uncertainties represent the 95% confidence level. The ion interaction coefficients marked with † can be described more accurately with an ionic strength dependent function, listed in Table B-6. The coefficients $\varepsilon(M^{n+}, Cl^-)$ and $\varepsilon(M^{n+}, NO_3^-)$ reported by Ciavatta [1980CIA] were evaluated without taking chloride and nitrate complexation into account, as discussed in Section B.2.

j	k	$\varepsilon(j,k)$	Comments
H^+	Cl^-	0.12 ± 0.01	Reported by Ciavatta [1980CIA].
	ClO_4^-	0.14 ± 0.02	
	NO_3^-	0.07 ± 0.01	
NH_4^+	Cl^-	-0.01 ± 0.01	Reported by Ciavatta [1980CIA].
	ClO_4^-	$-0.08 \pm 0.04^{\dagger}$	
	NO_3^-	$-0.06 \pm 0.03^{\dagger}$	
H_2gly^+	Cl^-	-0.06 ± 0.02	Reported by Ciavatta [1988CIA].
	ClO_4^-	—	
	NO_3^-	—	
H_5edta^+	Cl^-	-0.23 ± 0.15	See Section VIII.3.7 of [2005HUM/AND].
	ClO_4^-	-0.23 ± 0.15	
	NO_3^-	-0.23 ± 0.15	
$SnOH^+$	Cl^-	—	
	ClO_4^-	-0.07 ± 0.13	See Section VII.1.1 of [2012GAM/GAJ].
	NO_3^-	—	
SnF^+	Cl^-	—	
	ClO_4^-	0.14 ± 0.10	See Section VIII.3.1.1 of [2012GAM/GAJ].
	NO_3^-	—	

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Table B-4 (continued)

j	*k*	$\varepsilon(j,k)$	Comments
$SnCl^+$	Cl^-	—	
	ClO_4^-	0.08 ± 0.07	See Section VIII.3.2.1 of [2012GAM/GAJ].
	NO_3^-	—	
$SnBr^+$	Cl^-	—	
	ClO_4^-	0.15 ± 0.07	See Section VIII.3.3.1 of [2012GAM/GAJ].
	NO_3^-	—	
$SnNO_3^+$	Cl^-	—	
	ClO_4^-	0.17 ± 0.09	See Section X.1.1 of [2012GAM/GAJ].
	NO_3^-	—	
$SnSCN^+$	Cl^-	—	
	ClO_4^-	0.17 ± 0.29	See Section XI.1.1 of [2012GAM/GAJ].
	NO_3^-	—	
Tl^+	Cl^-	—	
	ClO_4^-	$-0.21 \pm 0.06^\dagger$	
	NO_3^-	—	
$ZnHCO_3^+$	Cl^-	0.2	Taken from Ferri *et al.* [1985FER/GRE].
	ClO_4^-	—	
	NO_3^-	—	
$CdCl^+$	Cl^-	—	
	ClO_4^-	0.25 ± 0.02	Reported by Ciavatta [1980CIA].
	NO_3^-	—	
CdI^+	Cl^-	—	
	ClO_4^-	0.27 ± 0.02	Reported by Ciavatta [1980CIA].
	NO_3^-	—	
$CdSCN^+$	Cl^-	—	
	ClO_4^-	0.31 ± 0.02	Reported by Ciavatta [1980CIA].
	NO_3^-	—	
$HgCl^+$	Cl^-	—	
	ClO_4^-	0.19 ± 0.02	Reported by Ciavatta [1988CIA].
	NO_3^-	—	
Cu^+	Cl^-	—	
	ClO_4^-	0.11 ± 0.01	Reported by Ciavatta [1980CIA].
	NO_3^-	—	
Ag^+	Cl^-	—	
	ClO_4^-	0.00 ± 0.01	Reported by Ciavatta [1980CIA].
	NO_3^-	$-0.12 \pm 0.05^\dagger$	

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Table B-4 (continued)

j	*k*	$\varepsilon(j,k)$	Comments
$NiOH^+$	Cl^-	-0.01 ± 0.07	Evaluated in [2005GAM/BUG] (Section V.3.1.1) for the reaction $Ni^{2+} + H_2O \rightleftharpoons NiOH^+ + H^+$ from $\Delta\varepsilon$ in chloride media / perchlorate media.
	ClO_4^-	0.14 ± 0.07	
	NO_3^-	—	
NiF^+	Cl^-	—	
	ClO_4^-	0.34 ± 0.08	Derived from $\Delta\varepsilon = \varepsilon(NiF^+,ClO_4^-) - \varepsilon(Ni^{2+},ClO_4^-) - \varepsilon(Na^+,F^-) = -(0.049 \pm 0.060)$ kg·mol^{-1} (see Section V.4.2.3 of [2005GAM/BUG]).
	NO_3^-	—	
$NiCl^+$	Cl^-	—	
	ClO_4^-	0.47 ± 0.06	See details in Section V.4.2.4 of [2005GAM/BUG].
	NO_3^-	—	
$NiNO_3^+$	Cl^-	—	
	ClO_4^-	0.44 ± 0.14	See details in Section V.6.1.2 of [2005GAM/BUG], specially sub-section V.6.1.2.1 for an alternative treatment of this system.
	NO_3^-	—	
$Ni(H_2cit)^+$	Cl^-	—	
	ClO_4^-	0.12 ± 0.50	See Section VII.7 in [2005HUM/AND].
	NO_3^-	—	
$NiBr^+$	Cl^-	—	
	ClO_4^-	0.59 ± 0.10	See details in [2005GAM/BUG], *cf.* Section V.4.2.5, specially sub-section V.4.2.5.1 for an alternative treatment of this system.
	NO_3^-	—	
$NiHS^+$	Cl^-	—	
	ClO_4^-	-0.85 ± 0.39	See details in [2005GAM/BUG], Section V.5.1.1.2.
	NO_3^-	—	
$NiSCN^+$	Cl^-	—	
	ClO_4^-	0.31 ± 0.04	Derived from $\Delta\varepsilon = \varepsilon(NiSCN^+,ClO_4^-) - \varepsilon(Na^+,SCN^-) - \varepsilon(Ni^{2+},ClO_4^-) = -(0.109 \pm 0.025)$ kg·mol^{-1} (see [2005GAM/BUG], Section V.7.1.3.1).
	NO_3^-	—	
$Fe(OH)_2^+$	Cl^-	—	
	ClO_4^-	0.37 ± 0.18	Determined in Section VII.1.3.2 of this review..
	NO_3^-	—	

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Table B-4 (continued)

j	*k*	*ε*(*j*,*k*)	Comments
FeF^+	Cl^-		
	ClO_4^-	0.34 ± 0.07	Determined in Section VIII.2.1.3 of this review.
	NO_3^-		
$FeCl_2^+$	Cl^-	—	
	ClO_4^-	0.52 ± 0.05	Determined in Section VIII.2.3.2.2.1 of this review..
	NO_3^-	—	
$FeSO_4^+$	Cl^-	—	
	ClO_4^-	0.4 ± 0.1	Determined in Section IX.1.2.1.4.1 of this review.
	NO_3^-	—	
$Zr_4(OH)_{15}^+$	Cl^-	—	
	ClO_4^-	0.09 ± 0.92	Determined in [2005BRO/CUR] from the overall fit of the hydrolysis data as described in Appendix D.
	NO_3^-	– 0.02 ± 1.46	
ZrF_3^+	Cl^-	—	
	ClO_4^-	0.20 ± 0.06	Determined from SIT plot in [2005BRO/CUR].
	NO_3^-	—	
YCO_3^+	Cl^-	—	
	ClO_4^-	0.17 ± 0.04	Taken from Spahiu [1983SPA].
	NO_3^-	—	
$Am(OH)_2^+$	Cl^-	– 0.27 ± 0.20	Evaluated in [2003GUI/FAN] (*cf.* Section 12.3.1.1) from $\Delta\varepsilon$ (in NaCl solution) for the reactions $An^{3+} + nH_2O(l) \rightleftharpoons An(OH)_n^{(3-n)} + n\,H^+$ (An = Am, Cm).
	ClO_4^-	0.17 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
AmF_2^+	Cl^-	—	
	ClO_4^-	0.17 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
$AmSO_4^+$	Cl^-	—	
	ClO_4^-	0.22 ± 0.08	Evaluated in [1995SIL/BID].
	NO_3^-	—	
$AmCO_3^+$	Cl^-	0.01 ± 0.05	Evaluated in [2003GUI/FAN] (Section 12.6.1.1.1) from $\Delta\varepsilon$ (in NaCl solution) for the reactions $An^{3+} + n\,CO_3^{2-} \rightleftharpoons An(CO_3)_n^{(3-2n)}$ (based on $\varepsilon(Am^{3+}, Cl^-) = (0.23 \pm 0.02)$ kg·mol^{-1} and $\varepsilon(Na^+, CO_3^{2-}) = -(0.08 \pm 0.03)$ kg·mol^{-1}.
	ClO_4^-	0.17 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	

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Table B-4 (continued)

j	k	$\varepsilon(j,k)$	Comments
$Am(ox)^{+}$	Cl^{-}	—	
	ClO_4^{-}	0.08 ± 0.10	See Section VI.13 of [2005HUM/AND].
	NO_3^{-}	—	
PuO_2^{+}	Cl^{-}	—	
	ClO_4^{-}	0.24 ± 0.05	Derived from $\Delta\varepsilon = \varepsilon(PuO_2^{2+}, ClO_4^{-}) - \varepsilon(PuO_2^{+}, ClO_4^{-}) = (0.22 \pm 0.03)$ kg·mol^{-1} [1995CAP/VIT]. In [1992GRE/FUG], $\varepsilon(PuO_2^{+}, ClO_4^{-}) = (0.17 \pm 0.05)$ kg·mol^{-1} was tabulated based on [1989ROB], [1989RIG/ROB] and [1990RIG]. Capdevila and Vitorge’s data [1992CAP], [1994CAP/VIT] and [1995CAP/VIT] were unavailable at that time.
	NO_3^{-}	—	
PuO_2F^{+}	Cl^{-}	—	
	ClO_4^{-}	0.29 ± 0.11	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding Np(IV) reaction.
	NO_3^{-}	—	
PuO_2Cl^{+}	Cl^{-}	—	
	ClO_4^{-}	0.50 ± 0.09	From $\Delta\varepsilon$ evaluated by Giffaut [1994GIF].
	NO_3^{-}	—	
NpO_2^{+}	Cl^{-}	0.09 ± 0.05	See Section 12.1 of [2001LEM/FUG].
	ClO_4^{-}	0.25 ± 0.05	Derived from $\Delta\varepsilon = \varepsilon(NpO_2^{2+}, ClO_4^{-}) - \varepsilon(NpO_2^{+}, ClO_4^{-}) = (0.21 \pm 0.03)$ kg·mol^{-1} [1987RIG/VIT], [1989RIG/ROB] and [1990RIG].
	NO_3^{-}	—	
NpO_2OH^{+}	Cl^{-}	—	
	ClO_4^{-}	– 0.06 ± 0.40	Estimated in [2001LEM/FUG].
	NO_3^{-}	—	
$(NpO_2)_3(OH)_5^{+}$	Cl^{-}	—	
	ClO_4^{-}	0.45 ± 0.20	See Section 8.1.2 of [2001LEM/FUG].
	NO_3^{-}	—	
NpO_2F^{+}	Cl^{-}	—	
	ClO_4^{-}	0.29 ± 0.12	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding U(IV) reaction.
	NO_3^{-}	—	

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Table B-4 (continued)

j	*k*	$\varepsilon(j,k)$	Comments
NpO_2Cl^+	Cl^-	—	
	ClO_4^-	0.50 ± 0.14	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding Pu(VI) reaction.
	NO_3^-	—	
$NpO_2IO_3^+$	Cl^-	—	
	ClO_4^-	0.33 ± 0.04	Estimated in [2001LEM/FUG] by assuming $\varepsilon(NpO_2IO_3^+, ClO_4^-) \approx \varepsilon(UO_2IO_3^+, ClO_4^-)$.
	NO_3^-	—	
$Np(SCN)_3^+$	Cl^-	—	
	ClO_4^-	0.17 ± 0.04	Estimated in [2001LEM/FUG] by assuming $\varepsilon(Np(SCN)_3^+, ClO_4^-) \approx \varepsilon(AmF_2^+, ClO_4^-)$.
	NO_3^-	—	
UO_2^+	Cl^-	—	
	ClO_4^-	0.26 ± 0.03	Evaluated in [1992GRE/FUG], using $\varepsilon(UO_2^{2+}, ClO_4^-)$ = (0.46 ± 0.03) kg·mol^{-1}.
	NO_3^-	—	
UO_2OH^+	Cl^-	—	
	ClO_4^-	−0.06 ± 0.40	Evaluated in [1992GRE/FUG], using $\varepsilon(UO_2^{2+}, X)$ = (0.46 ± 0.03) kg·mol^{-1}, where X = Cl^-, ClO_4^- and NO_3^- .
	NO_3^-	0.51 ± 1.4	
$(UO_2)_3(OH)_5^+$	Cl^-	0.81 ± 0.17	Evaluated in [1992GRE/FUG], using $\varepsilon(UO_2^{2+}, X)$ = (0.46 ± 0.03) kg·mol^{-1}, where X = Cl^-, ClO_4^- and NO_3^- .
	ClO_4^-	0.45 ± 0.15	
	NO_3^-	0.41 ± 0.22	
UF_3^+	Cl^-	0.1 ± 0.1	Estimated in [1992GRE/FUG].
	ClO_4^-	0.1 ± 0.1	
	NO_3^-	—	
UO_2F^+	Cl^-	0.04 ± 0.07	Taken from Riglet *et al.* [1989RIG/ROB], where the following assumptions were made: $\varepsilon(Np^{3+}, ClO_4^-) \approx \varepsilon(Pu^{3+}, ClO_4^-)$ = 0.49 kg·mol^{-1} as for other (M^{3+}, ClO_4^-) interactions, and $\varepsilon(NpO_2^{2+}, ClO_4^-) \approx \varepsilon(PuO_2^{2+}, ClO_4^-) \approx \varepsilon(UO_2^{2+}, ClO_4^-)$ = 0.46 kg·mol^{-1}.
	ClO_4^-	0.28 ± 0.04	See Section 9.4.2.2.1 of [2003GUI/FAN].
	NO_3^-	—	
UO_2Cl^+	Cl^-	—	
	ClO_4^-	0.33 ± 0.04	Evaluated in [1992GRE/FUG], using $\varepsilon(UO_2^{2+}, X)$ = (0.46 ± 0.03) kg·mol^{-1}, where X = Cl^-, ClO_4^- and NO_3^- .
	NO_3^-	—	

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Table B-4 (continued)

j	*k*	$\varepsilon(j,k)$	Comments
$UO_2ClO_3^+$	Cl^-	—	
	ClO_4^-	0.33 ± 0.04	Estimated in [1992GRE/FUG].
	NO_3^-	—	
UO_2Br^+	Cl^-	—	
	ClO_4^-	0.24 ± 0.04	Estimated in [1992GRE/FUG].
	NO_3^-	—	
$UO_2BrO_3^+$	Cl^-	—	
	ClO_4^-	0.33 ± 0.04	Estimated in [1992GRE/FUG].
	NO_3^-	—	
$UO_2IO_3^+$	Cl^-	—	
	ClO_4^-	0.33 ± 0.04	Estimated in [1992GRE/FUG].
	NO_3^-	—	
$UO_2N_3^+$	Cl^-	—	
	ClO_4^-	0.3 ± 0.1	Estimated in [1992GRE/FUG].
	NO_3^-	—	
$UO_2NO_3^+$	Cl^-	—	
	ClO_4^-	0.33 ± 0.04	Estimated in [1992GRE/FUG].
	NO_3^-	—	
UO_2SCN^+	Cl^-	—	
	ClO_4^-	0.22 ± 0.04	Estimated in [1992GRE/FUG].
	NO_3^-	—	
$Th(OH)_3^+$	Cl^-	0.06 ± 0.05	See Table VII-16 in Section VII.3.6.1 of [2008RAN/FUG].
	ClO_4^-	0.15 ± 0.10	
	NO_3^-	0.05 ± 0.15	
ThF_3^+	Cl^-	—	
	ClO_4^-	0.1 ± 0.1	See Table VIII-8 in Section VIII.1.2.1 of [2008RAN/FUG].
	NO_3^-	0.0 ± 0.2	
$Th(NO_3)_3^+$	Cl^-	—	
	ClO_4^-	0.25 ± 0.15	Evaluated in Section X.1.3.3 of [2008RAN/FUG], using $\varepsilon(Th^{4+},X) = (0.70 \pm 0.10)$ kg·mol^{-1} where X = ClO_4^- and NO_3^-.
	NO_3^-	0.25 ± 0.15	
H_6edta^{2+}	Cl^-	−0.20 ± 0.16	Evaluated in [2005HUM/AND] (Section VIII.3.7).
	ClO_4^-	−0.20 ± 0.16	
	NO_3^-	−0.20 ± 0.16	

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Table B-4 (continued)

j	*k*	$\varepsilon(j,k)$	Comments
Sn^{2+}	Cl^-	0.19 ± 0.04	See Section VI.2.1 of [2012GAM/GAJ].
	ClO_4^-	0.19 ± 0.04	See Section VI.2.1 of [2012GAM/GAJ].
	NO_3^-	—	
$Sn_3(OH)_4^{2+}$	Cl^-	—	
	ClO_4^-	-0.02 ± 0.16	See Section VII.1.1 of [2012GAM/GAJ].
	NO_3^-	—	
Pb^{2+}	Cl^-	—	
	ClO_4^-	0.15 ± 0.02	Reported by Ciavatta [1980CIA].
	NO_3^-	$-0.20 \pm 0.12^{\dagger}$	
$AlOH^{2+}$	Cl^-	0.09	Taken from Hedlund [1988HED].
	ClO_4^-	0.31	
	NO_3^-	—	
$Al_2CO_3(OH)_2^{2+}$	Cl^-	0.26	Taken from Hedlund [1988HED].
	ClO_4^-	—	
	NO_3^-	—	
Zn^{2+}	Cl^-	—	
	ClO_4^-	0.33 ± 0.03	Reported by Ciavatta [1980CIA].
	NO_3^-	0.16 ± 0.02	
$ZnCO_3^{2+}$	Cl^-	0.35 ± 0.05	Taken from Ferri *et al.* [1985FER/GRE].
	ClO_4^-	—	
	NO_3^-	—	
Cd^{2+}	Cl^-	—	
	ClO_4^-	—	
	NO_3^-	0.09 ± 0.02	Reported by Ciavatta [1980CIA].
Hg^{2+}	Cl^-	—	
	ClO_4^-	0.34 ± 0.03	Reported by Ciavatta [1980CIA].
	NO_3^-	$-0.1 \pm 0.1^{\dagger}$	
Hg_2^{2+}	Cl^-	—	
	ClO_4^-	0.09 ± 0.02	Reported by Ciavatta [1980CIA].
	NO_3^-	$-0.2 \pm 0.1^{\dagger}$	
Cu^{2+}	Cl^-	0.08 ± 0.01	Reported by Ciavatta [1980CIA].
	ClO_4^-	0.32 ± 0.02	
	NO_3^-	0.11 ± 0.01	

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Table B-4 (continued)

j	k	$\varepsilon(j,k)$	Comments
$\mathrm{Ni^{2+}}$	$\mathrm{Cl^-}$	0.17 ± 0.02	Reported by Ciavatta [1980CIA].
	$\mathrm{ClO_4^-}$	0.370 ± 0.032	Derived from the ionic strength dependence of the osmotic and mean activity coefficient of $\mathrm{Ni(ClO_4)_2}$ solution ([2005GAM/BUG], Section V.4.3).
	$\mathrm{NO_3^-}$	0.182 ± 0.010	Derived from the ionic strength dependence of the osmotic and mean activity coefficient of $\mathrm{Ni(NO_3)_2}$ solution ([2005GAM/BUG], Section V.6.1.2.1).
$\mathrm{Co^{2+}}$	$\mathrm{Cl^-}$	0.16 ± 0.02	Reported by Ciavatta [1980CIA].
	$\mathrm{ClO_4^-}$	0.34 ± 0.03	
	$\mathrm{NO_3^-}$	0.14 ± 0.01	
$\mathrm{Fe^{2+}}$	$\mathrm{Cl^-}$	0.17 ± 0.01	Determined in Section VI.4.3 of this review.
	$\mathrm{ClO_4^-}$	0.37 ± 0.04	Determined in Section VI.4.4 of this review.
	$\mathrm{NO_3^-}$	—	
$\mathrm{FeOH^{2+}}$	$\mathrm{Cl^-}$	—	
	$\mathrm{ClO_4^-}$	0.46 ± 0.05	Section VII.1.3.1 of this review
	$\mathrm{NO_3^-}$	—	
$\mathrm{FeCl^{2+}}$	$\mathrm{Cl^-}$	0.64 ± 0.06	Determined in Section VIII.2.3.1.3 of this review.
	$\mathrm{ClO_4^-}$	0.63 ± 0.05	Determined in Section VIII.2.3.2.2.1 of this review.
	$\mathrm{NO_3^-}$	—	
$\mathrm{FeSCN^{2+}}$	$\mathrm{Cl^-}$	—	
	$\mathrm{ClO_4^-}$	0.45	Taken from Spahiu [1983SPA].
	$\mathrm{NO_3^-}$	—	
$\mathrm{Mn^{2+}}$	$\mathrm{Cl^-}$	0.13 ± 0.01	Reported by Ciavatta [1980CIA].
	$\mathrm{ClO_4^-}$	—	
	$\mathrm{NO_3^-}$	—	
$\mathrm{Zr(OH)_2^{2+}}$	$\mathrm{Cl^-}$	—	
	$\mathrm{ClO_4^-}$	0.62 ± 0.39	Determined in [2005BRO/CUR] from the overall fit of the hydrolysis data as described in Appendix D.
	$\mathrm{NO_3^-}$	—	
$\mathrm{ZrF_2^{2+}}$	$\mathrm{Cl^-}$	—	
	$\mathrm{ClO_4^-}$	0.47 ± 0.08	Determined from SIT plot in [2005BRO/CUR].
	$\mathrm{NO_3^-}$	—	
$\mathrm{ZrCl_2^{2+}}$	$\mathrm{Cl^-}$	—	
	$\mathrm{ClO_4^-}$	0.84 ± 0.11	Determined from SIT plot in [2005BRO/CUR].
	$\mathrm{NO_3^-}$	—	

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Table B-4 (continued)

j	*k*	$\varepsilon(j,k)$	Comments
$Zr(NO_3)_2^{2+}$	Cl^-	—	
	ClO_4^-	0.84 ± 0.11	Determined from SIT plot in [2005BRO/CUR].
	NO_3^-	—	
$YHCO_3^{2+}$	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Taken from Spahiu [1983SPA].
	NO_3^-	—	
$AmOH^{2+}$	Cl^-	– 0.04 ± 0.07	Evaluated in [2003GUI/FAN] (*cf.* Section 12.3.1.1) from $\Delta\varepsilon$ (in NaCl solution) for the reactions $An^{3+} + n\,H_2O(l) \rightleftharpoons An(OH)_n^{(3-n)} + n\,H^+$.
	ClO_4^-	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
AmF^{2+}	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
$AmCl^{2+}$	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
AmN_3^{2+}	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
$AmNO_2^{2+}$	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
$AmNO_3^{2+}$	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
$AmH_2PO_4^{2+}$	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
$AmSCN^{2+}$	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	

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Table B-4 (continued)

j	*k*	$\varepsilon(j,k)$	Comments
PuO_2^{2+}	Cl^-	—	
	ClO_4^-	0.46 ± 0.05	By analogy with $\varepsilon(UO_2^{2+},ClO_4^-)$ as derived from isopiestic measurements in [1992GRE/FUG].The uncertainty is increased because the value is estimated by analogy.
	NO_3^-	—	
PuF_2^{2+}	Cl^-		
	ClO_4^-	0.36 ± 0.17	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding U(IV) reaction.
	NO_3^-	—	
$PuCl^{2+}$	Cl^-	—	
	ClO_4^-	0.39 ± 0.16	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding Am(III) reaction.
	NO_3^-	—	
PuI^{2+}	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Estimated in [2001LEM/FUG] by assuming $\varepsilon(PuI^{2+},ClO_4^-) \approx \varepsilon(AmSCN^{2+},ClO_4^-)$ and $\varepsilon(NH_4^+,I^-) \approx \varepsilon(Na^+,SCN^-)$.
	NO_3^-	—	
$PuSCN^{2+}$	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Estimated in [2001LEM/FUG] by assuming $\varepsilon(PuSCN^{2+},ClO_4^-) \approx \varepsilon(AmSCN^{2+},ClO_4^-)$.
	NO_3^-	—	
NpO_2^{2+}	Cl^-	—	
	ClO_4^-	0.46 ± 0.05	By analogy with $\varepsilon(UO_2^{2+},ClO_4^-)$ as derived from isopiestic measurements noted in [1992GRE/FUG]. The uncertainty is increased because the value is estimated by analogy.
	NO_3^-	—	
$(NpO_2)_2(OH)_2^{2+}$	Cl^-	—	
	ClO_4^-	0.57 ± 0.10	See Section 8.1.2 in [2001LEM/FUG].
	NO_3^-	—	
NpF_2^{2+}	Cl^-	—	
	ClO_4^-	0.38 ± 0.17	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding U(IV) reaction.
	NO_3^-	—	

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Table B-4 (continued)

j	*k*	$\varepsilon(j,k)$	Comments
$NpSO_4^{2+}$	Cl^-	—	
	ClO_4^-	0.48 ± 0.11	Estimated on Section 10.1.2.1 of [2001LEM/FUG].
	NO_3^-	—	
$Np(SCN)_2^{2+}$	Cl^-	—	
	ClO_4^-	0.38 ± 0.20	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding U(IV) reaction.
	NO_3^-	—	
UO_2^{2+}	Cl^-	0.21 ± 0.02	Reported by Ciavatta [1980CIA].
	ClO_4^-	0.46 ± 0.03	Reported by Ciavatta [1980CIA].
	NO_3^-	0.24 ± 0.03	Reported by Ciavatta [1980CIA]. These coefficients were not used in [1992GRE/FUG] because they were evaluated by Ciavatta [1980CIA] without taking chloride and nitrate complexation into account. Instead, Grenthe *et al.* used $\varepsilon(UO_2^{2+},X) = (0.46 \pm 0.03)\ kg{\cdot}mol^{-1}$, for X = Cl^-, ClO_4^- and NO_3^-.
$(UO_2)_2(OH)_2^{2+}$	Cl^-	0.69 ± 0.07	Evaluated in [1992GRE/FUG], using $\varepsilon(UO_2^{2+},X) = (0.46 \pm 0.03)\ kg{\cdot}mol^{-1}$, where X = Cl^-, ClO_4^- and NO_3^-.
	ClO_4^-	0.57 ± 0.07	
	NO_3^-	0.49 ± 0.09	
$(UO_2)_3(OH)_4^{2+}$	Cl^-	0.50 ± 0.18	Evaluated in [1992GRE/FUG], using $\varepsilon(UO_2^{2+},X) = (0.46 \pm 0.03)\ kg{\cdot}mol^{-1}$, where X = Cl^-, ClO_4^- and NO_3^-.
	ClO_4^-	0.89 ± 0.23	
	NO_3^-	0.72 ± 1.0	
UF_2^{2+}	Cl^-	—	
	ClO_4^-	0.3 ± 0.1	Estimated in [1992GRE/FUG].
	NO_3^-	—	
USO_4^{2+}	Cl^-	—	
	ClO_4^-	0.3 ± 0.1	Estimated in [1992GRE/FUG].
	NO_3^-	—	
$U(NO_3)_2^{2+}$	Cl^-	—	
	ClO_4^-	0.49 ± 0.14	Evaluated in [1992GRE/FUG] using $\varepsilon(U^{4+},ClO_4^-) = (0.76 \pm 0.06)\ kg{\cdot}mol^{-1}$.
	NO_3^-	—	
$Th(OH)_2^{2+}$	Cl^-	0.13 ± 0.05	Calculated in Section VII.3.6.1 of [2008RAN/FUG].
	ClO_4^-	0.33 ± 0.10	
	NO_3^-	0.10 ± 0.15	

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Table B-4 (continued)

j	*k*	$\varepsilon(j,k)$	Comments
ThF_2^{2+}	Cl^-	—	
	ClO_4^-	0.3 ± 0.1	See Table VIII-8 in Section VIII.1.2.1 of [2008RAN/FUG].
	NO_3^-	0.15 ± 0.20	
$ThSO_4^{2+}$	Cl^-	0.14 ± 0.15	See Section IX.1.3.2 of [2008RAN/FUG].
	ClO_4^-	0.3 ± 0.1	
	NO_3^-	—	
$Th(N_3)_2^{2+}$	Cl^-	—	
	ClO_4^-	0.40 ± 0.15	Estimated in Section X.1.2 of [2008RAN/FUG].
	NO_3^-	—	
$Th(NO_3)_2^{2+}$	Cl^-	—	
	ClO_4^-	0.43 ± 0.18	Estimated in Section X.1.3.3 of [2008RAN/FUG], using $\varepsilon(Th^{4+}, X) = (0.70 \pm 0.10)$ kg·mol^{-1} for X = ClO_4^- and NO_3^-.
	NO_3^-	0.43 ± 0.18	
$Th(H_2PO_4)_2^{2+}$	Cl^-	—	
	ClO_4^-	0.4 ± 0.1	Estimated in Section X.2.3.2 of [2008RAN/FUG].
	NO_3^-	—	
$Th(SCN)_2^{2+}$	Cl^-	—	
	ClO_4^-	0.38 ± 0.20	See Section XI.1.3.6.1 of [2008RAN/FUG].
	NO_3^-	—	
Be^{2+}	Cl^-	—	
	ClO_4^-	0.30 ± 0.04	Taken from [1986BRU], where it appears to have been based on the average of the values for $\varepsilon(Mg^{2+}, ClO_4^-)$ and $\varepsilon(Ca^{2+}, ClO_4^-)$ [1980CIA].
	NO_3^-	—	
Mg^{2+}	Cl^-	0.19 ± 0.02	Reported by Ciavatta [1980CIA].
	ClO_4^-	0.33 ± 0.03	
	NO_3^-	0.17 ± 0.01	
Ca^{2+}	Cl^-	0.14 ± 0.01	Reported by Ciavatta [1980CIA].
	ClO_4^-	0.27 ± 0.03	
	NO_3^-	0.02 ± 0.01	
Ba^{2+}	Cl^-	0.07 ± 0.01	Reported by Ciavatta [1980CIA].
	ClO_4^-	0.15 ± 0.02	
	NO_3^-	− 0.28 ± 0.03	
Al^{3+}	Cl^-	0.33 ± 0.02	Reported by Ciavatta [1980CIA].
	ClO_4^-	—	
	NO_3^-	—	

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Table B-4 (continued)

j	*k*	$\varepsilon(j,k)$	Comments
Ni_2OH^{3+}	Cl^-	—	
	ClO_4^-	0.59 ± 0.15	By assuming $\varepsilon(Ni_2OH^{3+}, ClO_4^-) \approx \varepsilon(Be_2OH^{3+}, ClO_4^-)$, see Section V.3.1.1 in [2005GAM/BUG].
	NO_3^-	—	
Fe^{3+}	Cl^-	0.76 ± 0.03	Determined in Section VI.4.2.2 of this review.
	ClO_4^-	0.73 ± 0.04	Determined in Sections VI.1.2.1.1.1 and VI.4.1 of this review.
	NO_3^-	—	
Cr^{3+}	Cl^-	0.30 ± 0.03	Reported by Ciavatta [1980CIA].
	ClO_4^-	—	
	NO_3^-	0.27 ± 0.02	Reported by Ciavatta [1980CIA].
$ZrOH^{3+}$	Cl^-	—	
	ClO_4^-	0.57 ± 0.13	Determined in [2005BRO/CUR] from the overall fit of the hydrolysis data as described in Appendix D.
	NO_3^-	—	
$Zr_3(OH)_9^{3+}$	Cl^-	—	
	ClO_4^-	0.93 ± 0.35	Determined in [2005BRO/CUR] from the overall fit of the hydrolysis data as described in Appendix D.
	NO_3^-	—	
ZrF^{3+}	Cl^-	—	
	ClO_4^-	0.63 ± 0.10	Determined from SIT plot in [2005BRO/CUR].
	NO_3^-	—	
$ZrCl^{3+}$	Cl^-	—	
	ClO_4^-	0.87 ± 0.10	Determined from SIT plot in [2005BRO/CUR].
	NO_3^-	—	
$Zr(NO_3)^{3+}$	Cl^-	—	
	ClO_4^-	0.88 ± 0.11	Determined from SIT plot in [2005BRO/CUR].
	NO_3^-	—	
La^{3+}	Cl^-	0.22 ± 0.02	Reported by Ciavatta [1980CIA].
	ClO_4^-	0.47 ± 0.03	
	NO_3^-	—	
$La^{3+} \rightarrow Lu^{3+}$	Cl^-	—	
	ClO_4^-	0.47 → 0.52	Taken from Spahiu [1983SPA].
	NO_3^-	—	

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Table B-4 (continued)

j	*k*	$\varepsilon(j,k)$	Comments
Am^{3+}	Cl^-	0.23 ± 0.02	The $\varepsilon(An^{3+},Cl^-)$ for An = Am and Cm is assumed to be equal to $\varepsilon(Nd^{3+},Cl^-)$ which is calculated from trace activity coefficients of Nd^{3+} ion in 0 − 4 m NaCl. These trace activity coefficients are based on the Pitzer ion interaction parameters evaluated in [1997KON/FAN] from osmotic coefficients in aqueous $NdCl_3$ – NaCl and $NdCl_3$ – $CaCl_2$.
	ClO_4^-	0.49 ± 0.03	Estimated in [1995SIL/BID].
	NO_3^-	—	
Pu^{3+}	Cl^-	—	
	ClO_4^-	0.49 ± 0.05	Estimated by analogy with $\varepsilon(Ho^{3+},ClO_4^-)$ [1983SPA] as in [1992GRE/FUG], [1995SIL/BID]. The uncertainty is increased because the value is estimated by analogy.
	NO_3^-	—	
$PuOH^{3+}$	Cl^-	—	
	ClO_4^-	0.50 ± 0.05	Estimated in [2001LEM/FUG].
	NO_3^-	—	
PuF^{3+}	Cl^-	—	
	ClO_4^-	0.56 ± 0.11	Estimated in [2001LEM/FUG].
	NO_3^-	—	
$PuCl^{3+}$	Cl^-	—	
	ClO_4^-	0.85 ± 0.09	Derived from the $\Delta\varepsilon$ evaluated in [2001LEM/FUG].
	NO_3^-	—	
$PuBr^{3+}$	Cl^-	—	
	ClO_4^-	0.58 ± 0.16	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding U(IV) reaction, and by assuming $\varepsilon(H^+,Br^-) \approx \varepsilon(Na^+,Br^-)$.
	NO_3^-	—	
Np^{3+}	Cl^-	—	
	ClO_4^-	0.49 ± 0.05	Estimated by analogy with $\varepsilon(Ho^{3+},ClO_4^-)$ [1983SPA] as in previous books in this series [1992GRE/FUG], [1995SIL/BID]. The uncertainty is increased because the value is estimated by analogy.
	NO_3^-	—	
$NpOH^{3+}$	Cl^-	—	
	ClO_4^-	0.50 ± 0.05	Estimated in [2001LEM/FUG].
	NO_3^-	—	

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Table B-4 (continued)

j	*k*	$\varepsilon(j,k)$	Comments
NpF^{3+}	Cl^-	—	
	ClO_4^-	0.58 ± 0.07	Evaluated in [2001LEM/FUG].
	NO_3^-	—	
$NpCl^{3+}$	Cl^-	—	
	ClO_4^-	0.81 ± 0.09	Derived from the $\Delta\varepsilon$ selected in [2001LEM/FUG].
	NO_3^-	—	
NpI^{3+}	Cl^-	—	
	ClO_4^-	0.77 ± 0.26	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding Np(IV) chloride reaction, and by assuming $\varepsilon(H^+, I^-) \approx \varepsilon(Na^+, I^-)$.
	NO_3^-	—	
$NpSCN^{3+}$	Cl^-	0.76 ± 0.12	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding U(IV) reaction.
	ClO_4^-	—	
	NO_3^-	—	
U^{3+}	Cl^-	—	
	ClO_4^-	0.49 ± 0.05	Evaluated in [2001LEM/FUG] by analogy with $\varepsilon(Am^{3+}, ClO_4^-)$.
	NO_3^-	—	
UOH^{3+}	Cl^-	—	
	ClO_4^-	0.48 ± 0.08	Evaluated in [1992GRE/FUG].
	NO_3^-	—	
UF^{3+}	Cl^-	—	
	ClO_4^-	0.48 ± 0.08	Estimated in [1992GRE/FUG].
	NO_3^-	—	
UCl^{3+}	Cl^-	—	
	ClO_4^-	0.50 ± 0.10	Estimated in [2003GUI/FAN].
	NO_3^-	—	
UBr^{3+}	Cl^-	—	
	ClO_4^-	0.52 ± 0.10	Estimated in [1992GRE/FUG] using $\varepsilon(U^{4+}, X) =$ (0.76 ± 0.06) kg·mol^{-1}, for X = Br^- and ClO_4^-.
	NO_3^-	—	
UI^{3+}	Cl^-	—	
	ClO_4^-	0.55 ± 0.10	Estimated in [1992GRE/FUG] using $\varepsilon(U^{4+}, X) =$ (0.76 ± 0.06) kg·mol^{-1}, for X = I^- and ClO_4^-.
	NO_3^-	—	

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Table B-4 (continued)

j	*k*	$\varepsilon(j,k)$	Comments
UNO_3^{3+}	Cl^-	—	
	ClO_4^-	0.62 ± 0.08	Evaluated in [1992GRE/FUG] using $\varepsilon(U^{4+},X)$ = (0.76 ± 0.06) $kg{\cdot}mol^{-1}$ for X = NO_3^- and ClO_4^-.
	NO_3^-	—	
$ThOH^{3+}$	Cl^-	0.19 ± 0.05	See Table VII-18 in Section VII.3.6.1 of [2008RAN/FUG].
	ClO_4^-	0.48 ± 0.08	
	NO_3^-	0.20 ± 0.15	
ThF^{3+}	Cl^-	—	
	ClO_4^-	0.48 ± 0.08	Estimated in Section VIII.1.2.1 of [2008RAN/FUG] (Table VIII-8).
	NO_3^-	0.25 ± 0.20	
$ThCl^{3+}$	Cl^-	0.62 ± 0.11	Calculated in Section VIII.2.2.1.2 of [2008RAN/FUG] using $\varepsilon(Th^{4+},X)$ = (0.70 ± 0.10) $kg{\cdot}mol^{-1}$, for X = Cl^- and ClO_4^-
	ClO_4^-	0.62 ± 0.11	
	NO_3^-	—	
$ThClO_3^{3+}$	Cl^-	—	
	ClO_4^-	0.62 ± 0.11	Calculated in Section VIII.2.2.2 of [2008RAN/FUG] using $\varepsilon(Th^{4+},X)$ = (0.70 ± 0.10) $kg{\cdot}mol^{-1}$, for X = ClO_3^- and ClO_4^-
	NO_3^-	—	
$ThBr^{3+}$	Cl^-	—	
	ClO_4^-	0.62 ± 0.11	Calculated in Section VIII.3.2.1 of [2008RAN/FUG] using $\varepsilon(Th^{4+},X)$ = (0.70 ± 0.10) $kg{\cdot}mol^{-1}$, for X = Br^- and ClO_4^-
	NO_3^-	—	
$ThBrO_3^{3+}$	Cl^-	—	
	ClO_4^-	0.62 ± 0.08	Calculated in Section VIII.3.2.2 of [2008RAN/FUG] using $\varepsilon(Th^{4+},X)$ = (0.70 ± 0.10) $kg{\cdot}mol^{-1}$, for X = BrO_3^- and ClO_4^-
	NO_3^-	—	
ThN_3^{3+}	Cl^-	—	
	ClO_4^-	0.55 ± 0.15	See Section X.1.2 of [2008RAN/FUG].
	NO_3^-	—	
$ThNO_3^{3+}$	Cl^-	—	
	ClO_4^-	0.56 ± 0.14	Calculated in Section X.1.3.3 of [2008RAN/FUG] using $\varepsilon(Th^{4+},X)$ = (0.70 ± 0.10) $kg{\cdot}mol^{-1}$, for X = ClO_4^- and NO_3^-.
	NO_3^-	0.56 ± 0.14	

(Continued on next page)

Table B-4 (continued)

j	*k*	$\varepsilon(j,k)$	Comments
$Th(H_2PO_4)^{3+}$	Cl^-	—	
	ClO_4^-	0.5 ± 0.1	Estimated in Section X.2.3.2 of [2008RAN/FUG].
	NO_3^-	—	
$Th(H_2PO_4)(H_3PO_4)^{3+}$	Cl^-	—	
	ClO_4^-	0.5 ± 0.1	Estimated in Section X.2.3.2 of [2008RAN/FUG].
	NO_3^-	—	
$ThSCN^{3+}$	Cl^-	—	
	ClO_4^-	0.50 ± 0.10	See Section XI.1.3.6.1 of [2008RAN/FUG].
	NO_3^-	—	
Be_2OH^{3+}	Cl^-	—	
	ClO_4^-	0.50 ± 0.05	Taken from [1986BRU], where the assumption was made that $\varepsilon(Be^{2+},ClO_4^-)$ = 0.30 kg·mol^{-1}, apparently based on the average of the values for $\varepsilon(Mg^{2+}, ClO_4^-)$ and $\varepsilon(Ca^{2+}, ClO_4^-)$ [1980CIA].
	NO_3^-	—	
$Be_3(OH)_3^{3+}$	Cl^-	—	
	ClO_4^-	0.51 ± 0.05	Taken from [1986BRU], where the assumption was made that $\varepsilon(Be^{2+},ClO_4^-)$ = 0.30 kg·mol^{-1}, apparently based on the average of the values for $\varepsilon(Mg^{2+}, ClO_4^-)$ and $\varepsilon(Ca^{2+}, ClO_4^-)$ [1980CIA].
	NO_3^-	—	
Sn^{4+}	Cl^-	—	
	ClO_4^-	0.7 ± 0.2	See Section VI.3.1 of [2012GAM/GAJ].
	NO_3^-	—	
$Al_3HCO_3(OH)_4^{4+}$	Cl^-	0.41	Taken from Hedlund [1988HED].
	ClO_4^-	—	
	NO_3^-	—	
$Ni_4(OH)_4^{4+}$	Cl^-	—	
	ClO_4^-	1.08 ± 0.08	Derived from $\Delta\varepsilon = 4\varepsilon(H^+,ClO_4^-) - \varepsilon(Ni_4OH_4^{4+},ClO_4^-) - 4\varepsilon(Ni^{2+},ClO_4^-)$ = (0.16 ± 0.05) kg·mol^{-1} (see [2005GAM/BUG], Section V.3.1.1.1).
	NO_3^-	—	
$Fe_2(OH)_2^{4+}$	Cl^-	—	
	ClO_4^-	1.04 ± 0.10	Determined in Section VII.1.3.3 of this review.
	NO_3^-	—	

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Table B-4 (continued)

j	*k*	$\varepsilon(j,k)$	Comments
Zr^{4+}	Cl^-	0.33 ± 0.09	Determined in [2005BRO/CUR]
	ClO_4^-	0.89 ± 0.10	
	NO_3^-	0.33 ± 0.35	
$Y_2CO_3^{4+}$	Cl^-	—	
	ClO_4^-	0.80 ± 0.04	Taken from Spahiu [1983SPA].
	NO_3^-	—	
Pu^{4+}	Cl^-	0.37 ± 0.05	Calculated in Section VI.3.1 of [2008RAN/FUG].
	ClO_4^-	0.82 ± 0.07	Derived from $\Delta\varepsilon = \varepsilon(Pu^{4+},ClO_4^-) - \varepsilon(Pu^{3+},ClO_4^-) =$ (0.33 ± 0.035) kg·mol^{-1} [1995CAP/VIT]. Uncertainty estimated in [2001LEM/FUG]. In the [1992GRE/FUG], $\varepsilon(Pu^{3+},ClO_4^-)$ = (1.03 ± 0.05) kg·mol^{-1} was tabulated based on references [1989ROB], [1989RIG/ROB], [1990RIG]. Capdevila and Vitorge's data [1992CAP], [1994CAP/VIT] and [1995CAP/VIT] were unavailable at that time.
	NO_3^-	—	
Np^{4+}	Cl^-	—	
	ClO_4^-	0.84 ± 0.06	Derived from $\Delta\varepsilon = \varepsilon(Np^{4+},ClO_4^-) - \varepsilon(Np^{3+},ClO_4^-) =$ (0.35 ± 0.03) kg·mol^{-1} [1989ROB], [1989RIG/ROB], [1990RIG].
	NO_3^-	—	
U^{4+}	Cl^-	—	
	ClO_4^-	0.76 ± 0.06	Estimated in [1992GRE/FUG]. Using the measured value of $\Delta\varepsilon = \varepsilon(U^{4+},ClO_4^-) - \varepsilon(U^{3+},ClO_4^-)$ = (0.35 ± 0.06) kg·mol^{-1} p.89 [1990RIG], where the uncertainty is recalculated in [2001LEM/FUG] from the data given in this thesis, and $\varepsilon(U^{3+},ClO_4^-)$ = (0.49 ± 0.05) kg·mol^{-1}, a value for $\varepsilon(U^{4+},ClO_4^-)$ can be calculated in the same way as is done for $\varepsilon(Np^{4+},ClO_4^-)$ and $\varepsilon(Pu^{4+},ClO_4^-)$. This value, $\varepsilon(U^{4+},ClO_4^-)$ = (0.84 ± 0.06) kg·mol^{-1} is consistent with that tabulated $\varepsilon(U^{4+},ClO_4^-)$ = (0.76 ± 0.06) kg·mol^{-1}, since the uncertainties overlap. The authors of [2001LEM/FUG] do not believe that a change in the previously selected value for $\varepsilon(U^{4+},ClO_4^-)$ is justified at present.
	NO_3^-	—	
Th^{4+}	Cl^-	0.25 ± 0.03	Reported by Ciavatta [1980CIA].
	ClO_4^-	0.70 ± 0.10	Evaluated in Section VI.3.1 of [2008RAN/FUG].
	NO_3^-	0.31 ± 0.12	Evaluated in Section VI.3.1 of [2008RAN/FUG].

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Table B-4 (continued)

j	*k*	$\varepsilon(j,k)$	Comments
$Th_4(OH)_{12}^{4+}$	Cl^-	0.25 ± 0.20	See Section VII.3.4.1.3 of [2008RAN/FUG].
	ClO_4^-	0.56 ± 0.42	
	NO_3^-	0.42 ± 0.50	
$Th(H_3PO_4)^{4+}$	Cl^-	—	
	ClO_4^-	0.7 ± 0.1	Estimated in Section X.2.3.2 of [2008RAN/FUG].
	NO_3^-	—	
$Al_3(OH)_4^{5+}$	Cl^-	0.66	Taken from Hedlund [1988HED]
	ClO_4^-	1.30	Taken from Hedlund [1988HED]
	NO_3^-	—	
$Th_2(OH)_3^{5+}$	Cl^-	0.29 ± 0.09	Calculated in Section VII.3.4.1.1 of [2008RAN/FUG].
	ClO_4^-	0.91 ± 0.21	
	NO_3^-	0.69 ± 0.25	
$Th_2(OH)_2^{6+}$	Cl^-	0.40 ± 0.16	Evaluated in Section VII.3.4.1.1 of [2008RAN/FUG].
	ClO_4^-	1.22 ± 0.24	
	NO_3^-	0.69 ± 0.26	
$Zr_3(OH)_4^{8+}$	Cl^-	0.33 ± 0.28	Determined in [2005BRO/CUR] from the overall fit of the hydrolysis data as described in Appendix D.
	ClO_4^-	1.89 ± 0.31	
	NO_3^-	2.28 ± 0.35	
$Zr_4(OH)_8^{8+}$	Cl^-	—	
	ClO_4^-	3.61 ± 1.02	Determined in [2005BRO/CUR] from the overall fit of the hydrolysis data as described in Appendix D.
	NO_3^-	—	
$Th_4(OH)_8^{8+}$	Cl^-	0.70 ± 0.20	Evaluated in Section VII.3.4.1.3 of [2008RAN/FUG].
	ClO_4^-	1.69 ± 0.42	
	NO_3^-	1.59 ± 0.51	
$Th_6(OH)_{15}^{9+}$	Cl^-	0.72 ± 0.30	See details in Section VII.3.4.1.4 of [2008RAN/FUG].
	ClO_4^-	1.85 ± 0.74	
	NO_3^-	2.20 ± 0.77	
$Th_6(OH)_{14}^{10+}$	Cl^-	0.83 ± 0.30	Estimated in Section VII.3.4.1.4 of [2008RAN/FUG].
	ClO_4^-	2.2 ± 0.3	
	NO_3^-	2.9 ± 0.5	

Table B-5: Ion interaction coefficients, $\varepsilon(j,k)$ (kg·mol^{-1}), for anions j with k = Li$^+$, Na$^+$ and K$^+$ at 298.15 K. The uncertainties represent the 95% confidence level. The ion interaction coefficients marked with † can be described more accurately with an ionic strength dependent function, listed in Table B-6.

j	k	$\varepsilon(j,k)$	Comments
$\mathrm{OH^-}$	$\mathrm{Li^+}$	-0.02 ± 0.03†	
	$\mathrm{Na^+}$	0.04 ± 0.01	Reported by Ciavatta [1980CIA].
	$\mathrm{K^+}$	0.09 ± 0.01	
$\mathrm{F^-}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	0.02 ± 0.02	Evaluated in [1992GRE/FUG].
	$\mathrm{K^+}$	0.03 ± 0.02	[1988CIA]
$\mathrm{HF_2^-}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	-0.11 ± 0.06	Evaluated in [1992GRE/FUG].
	$\mathrm{K^+}$	—	
$\mathrm{Cl^-}$	$\mathrm{Li^+}$	0.10 ± 0.01	Reported by Ciavatta [1980CIA].
	$\mathrm{Na^+}$	0.03 ± 0.01	
	$\mathrm{K^+}$	0.00 ± 0.01	
$\mathrm{ClO_3^-}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	-0.01 ± 0.02	Reported by Ciavatta [1980CIA].
	$\mathrm{K^+}$	—	
$\mathrm{ClO_4^-}$	$\mathrm{Li^+}$	0.15 ± 0.01	Reported by Ciavatta [1980CIA].
	$\mathrm{Na^+}$	0.01 ± 0.01	
	$\mathrm{K^+}$	—	
$\mathrm{Br^-}$	$\mathrm{Li^+}$	0.13 ± 0.02	Reported by Ciavatta [1980CIA].
	$\mathrm{Na^+}$	0.05 ± 0.01	
	$\mathrm{K^+}$	0.01 ± 0.02	
$\mathrm{BrO_3^-}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	-0.06 ± 0.02	Reported by Ciavatta [1980CIA].
	$\mathrm{K^+}$	—	
$\mathrm{I^-}$	$\mathrm{Li^+}$	0.16 ± 0.01	Reported by Ciavatta [1980CIA].
	$\mathrm{Na^+}$	0.08 ± 0.02	
	$\mathrm{K^+}$	0.02 ± 0.01	
$\mathrm{IO_3^-}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	-0.06 ± 0.02	Estimated in [1992GRE/FUG].
	$\mathrm{K^+}$	—	

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Table B-5 (continued)

j	*k*	$\varepsilon(j,k)$	Comments
HSO_4^-	Li^+	— [1]	
	Na^+	-0.01 ± 0.02 [1]	Reported by Ciavatta [1980CIA].
	K^+	— [1]	
N_3^-	Li^+	—	
	Na^+	0.015 ± 0.020	See Section X.1.2 of [2008RAN/FUG].
	K^+	—	
NO_2^-	Li^+	0.06 ± 0.04†	
	Na^+	0.00 ± 0.02	Reported by Ciavatta [1980CIA].
	K^+	-0.04 ± 0.02	Reported by Ciavatta [1988CIA].
NO_3^-	Li^+	0.08 ± 0.01	Reported by Ciavatta [1980CIA].
	Na^+	-0.04 ± 0.03†	
	K^+	-0.11 ± 0.04†	
$H_2PO_4^-$	Li^+	—	
	Na^+	-0.08 ± 0.04†	
	K^+	-0.14 ± 0.04†	
HCO_3^-	Li^+	—	
	Na^+	0.00 ± 0.02	These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for CO_3^{2-} and HCO_3^- are based on [1980CIA].
	K^+	-0.06 ± 0.05	Calculated in [2001LEM/FUG] from Pitzer coefficients [1998RAI/FEL].
Hox^-	Li^+	-0.28 ± 0.09	Evaluated in Section VI.3.5 of [2005HUM/AND].
	Na^+	-0.07 ± 0.01	
	K^+	-0.01 ± 0.08	
H_2cit^-	Li^+	-0.11 ± 0.03	Evaluated in Section VII.3.6 of [2005HUM/AND].
	Na^+	-0.05 ± 0.01	
	K^+	-0.04 ± 0.01	
CN^-	Li^+	—	
	Na^+	0.07 ± 0.03	As reported in [1992BAN/BLI].
	K^+	—	

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[1] No value is tabulated here for $\varepsilon(H^+, HSO_4^-)$; possible values are discussed in the footnote to the Appendix A entry for [1955LIS/RIV2].

Table B-5 (continued)

j	k	$\varepsilon(j,k)$	Comments
SCN^-	Li^+	—	
	Na^+	0.05 ± 0.01	Reported by Ciavatta [1980CIA].
	K^+	-0.01 ± 0.01	
$HCOO^-$	Li^+	—	
	Na^+	0.03 ± 0.01	Reported by Ciavatta [1980CIA].
	K^+	—	
CH_3COO^-	Li^+	0.05 ± 0.01	Reported by Ciavatta [1980CIA].
	Na^+	0.08 ± 0.01	
	K^+	0.09 ± 0.01	
H_3edta^-	Li^+	—	
	Na^+	-0.33 ± 0.14	Evaluated in Section VIII.3.7 of [2005HUM/AND].
	K^+	-0.14 ± 0.17	
$SiO(OH)_3^-$	Li^+	—	
	Na^+	-0.08 ± 0.03	Evaluated in [1992GRE/FUG].
	K^+	—	
$Si_2O_2(OH)_5^-$	Li^+	—	
	Na^+	-0.08 ± 0.04	Estimated in [1992GRE/FUG].
	K^+	—	
$Sn(OH)_3^-$	Li^+	—	
	Na^+	0.22 ± 0.03	See Section VII.1.1 of [2012GAM/GAJ].
	K^+	—	
$SnCl_3^-$	Li^+	—	
	Na^+	0.04 ± 0.07	See Section VIII.3.2.1 of [2012GAM/GAJ].
	K^+	—	
$SnBr_3^-$	Li^+	—	
	Na^+	0.16 ± 0.08	See Section VIII.3.3.1 of [2012GAM/GAJ].
	K^+	—	
$B(OH)_4^-$	Li^+	—	
	Na^+	-0.07 ± 0.05†	
	K^+	—	
$Ni(SCN)_3^-$	Li^+	—	
	Na^+	0.66 ± 0.13	Evaluated in [2005GAM/BUG] (see Section V.7.1.3.1).
	K^+	—	
$Ni(cit)^-$	Li^+	—	
	Na^+	0.22 ± 0.50	Evaluated in Section VII.7 of [2005HUM/AND].
	K^+	—	

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Table B-5 (continued)

j	*k*	$\varepsilon(j,k)$	Comments
$\mathrm{Fe(SO_4)_2^-}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	0.24 ± 0.14	Estimated in Section IX.1.2.1.4.3 of this review.
	$\mathrm{K^+}$	—	
$\mathrm{ZrF_5^-}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	-0.14 ± 0.03	Determined from SIT plots in [2005BRO/CUR].
	$\mathrm{K^+}$	—	
$\mathrm{Am(SO_4)_2^-}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	-0.05 ± 0.05	Estimated in [1995SIL/BID].
	$\mathrm{K^+}$	—	
$\mathrm{Am(CO_3)_2^-}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	-0.14 ± 0.06	Evaluated Section 12.6.1.1.1 [2003GUI/FAN], from $\Delta\varepsilon_n$ in NaCl solution for the reactions $\mathrm{An^{3+}} + n\,\mathrm{CO_3^{2-}} \rightleftharpoons \mathrm{An(CO_3)}_n^{(3-2n)}$ (An = Am, Cm) based on $\varepsilon(\mathrm{Am^{3+}},\mathrm{Cl^-})$ = $(0.23 \pm 0.02)\,\mathrm{kg{\cdot}mol^{-1}}$ and $\varepsilon(\mathrm{Na^+},\mathrm{CO_3^{2-}})$ = – (0.08 ± 0.03) $\mathrm{kg{\cdot}mol^{-1}}$.
	$\mathrm{K^+}$	—	
$\mathrm{Am(ox)_2^-}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	-0.21 ± 0.08	Evaluated in Section VI.13 of [2005HUM/AND].
	$\mathrm{K^+}$	—	
$\mathrm{Am(edta)^-}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	0.01 ± 0.16	Evaluated in Section VIII.13.2.1 of [2005HUM/AND].
	$\mathrm{K^+}$	0.01 ± 0.16	Estimated in [2005HUM/AND] Section VIII.13.2.1 by assuming $\varepsilon(\mathrm{K^+},\mathrm{Am(edta)^-}) \approx \varepsilon(\mathrm{Na^+},\mathrm{Am(edta)^-})$.
$\mathrm{PuO_2CO_3^-}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	-0.18 ± 0.18	Estimated in [2001LEM/FUG] by analogy with $\varepsilon(\mathrm{Na^+},\mathrm{NpO_2CO_3^-})$.
	$\mathrm{K^+}$	—	
$\mathrm{Pu(edta)^-}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	—	
	$\mathrm{K^+}$	0.01 ± 0.16	Estimated in [2005HUM/AND], Section VIII.12.2.1 by assuming $\varepsilon(\mathrm{K^+},\mathrm{Pu(edta)^-}) \approx \varepsilon(\mathrm{Na^+},\mathrm{Am(edta)^-})$.
$\mathrm{NpO_2(OH)_2^-}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	-0.01 ± 0.07	Estimated in [2001LEM/FUG] (Section 8.1.3).
	$\mathrm{K^+}$	—	

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Table B-5 (continued)

j	*k*	$\varepsilon(j,k)$	Comments
$NpO_2CO_3^-$	Li^+	—	
	Na^+	-0.18 ± 0.15	Calculated in [2001LEM/FUG] (Section 12.1.2.1.3).
	K^+	—	
$NpO_2(ox)^-$	Li^+	—	
	Na^+	-0.4 ± 0.1	Evaluated in Section VI.11.2.3 of [2005HUM/AND].
	K^+	—	
$NpO_2(H_2edta)^-$	Li^+	—	
	Na^+	-0.18 ± 0.16	Evaluated in Section VIII.11.2.3 of [2005HUM/AND].
	K^+	—	
$(NpO_2)_2CO_3(OH)_3^-$	Li^+	—	
	Na^+	0.00 ± 0.05	Estimated by analogy in [2001LEM/FUG] (Section 12.1.2.1.2).
	K^+	—	
$UO_2(OH)_3^-$	Li^+	—	
	Na^+	-0.09 ± 0.05	Estimated in [1992GRE/FUG].
	K^+	—	
$UO_2F_3^-$	Li^+	—	
	Na^+	-0.14 ± 0.05	Evaluated in [2003GUI/FAN], Section 9.4.2.2.1.1.
	K^+	—	
$UO_2(N_3)_3^-$	Li^+	—	
	Na^+	0.0 ± 0.1	Estimated in [1992GRE/FUG].
	K^+	—	
$(UO_2)_2CO_3(OH)_3^-$	Li^+	—	
	Na^+	0.00 ± 0.05	Estimated in [1992GRE/FUG].
	K^+	—	
UO_2cit^-	Li^+	—	
	Na^+	-0.11 ± 0.09	Evaluated in [2005HUM/AND].
	K^+	—	
$Th(OH)_3(CO_3)^-$	Li^+	—	
	Na^+	-0.05 ± 0.20	See Section XI.1.3.2 of [2008RAN/FUG].
	K^+	—	
$Mg(cit)^-$	Li^+	—	
	Na^+	0.03 ± 0.03	Evaluated in [2005HUM/AND].
	K^+	—	

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Table B-5 (continued)

j	*k*	ε(*j*,*k*)	Comments
$UO_2(Hedta)^-$	Li^+	—	
	Na^+	-0.18 ± 0.16	Evaluated in Section VIII.10.2.4 of [2005HUM/AND].
	K^+	—	
$Mg(Hedta)^-$	Li^+	—	
	Na^+	0.11 ± 0.20	Estimated in Section VIII.5.1 of [2005HUM/AND]
	K^+	—	
SO_3^{2-}	Li^+	—	
	Na^+	-0.08 ± 0.05†	
	K^+	—	
SO_4^{2-}	Li^+	-0.03 ± 0.04†	
	Na^+	-0.12 ± 0.06†	
	K^+	-0.06 ± 0.02	Reported by Ciavatta [1988CIA].
$S_2O_3^{2-}$	Li^+	—	
	Na^+	-0.08 ± 0.05†	
	K^+	—	
HPO_4^{2-}	Li^+	—	
	Na^+	-0.15 ± 0.06†	
	K^+	-0.10 ± 0.06†	
CO_3^{2-}	Li^+	—	
	Na^+	-0.08 ± 0.03	These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for CO_3^{2-} and HCO_3^- are based on [1980CIA].
	K^+	0.02 ± 0.01	Reported by Ciavatta [1980CIA].
ox^{2-}	Li^+	-0.51 ± 0.09	Evaluated in Section VI.3.5 of [2005HUM/AND].
	Na^+	-0.08 ± 0.01	
	K^+	0.07 ± 0.08	
$Hcit^{2-}$	Li^+	-0.17 ± 0.04	Evaluated in Section VII.3.6 of [2005HUM/AND].
	Na^+	-0.04 ± 0.02	
	K^+	-0.01 ± 0.02	
H_2edta^{2-}	Li^+	—	
	Na^+	-0.37 ± 0.14	Evaluated in Section VII.3.7 of [2005HUM/AND].
	K^+	-0.17 ± 0.18	
$SiO_2(OH)_2^{2-}$	Li^+	—	
	Na^+	-0.10 ± 0.07	Evaluated in [1992GRE/FUG].
	K^+	—	

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Table B-5 (continued)

j	*k*	ε(*j*,*k*)	Comments
$Si_2O_3(OH)_4^{2-}$	Li^+	—	
	Na^+	-0.15 ± 0.06	Estimated in [1992GRE/FUG].
	K^+	—	
$Ni(ox)_2^{2-}$	Li^+	—	
	Na^+	-0.26 ± 0.03	Evaluated in Section VI.7.2 of [2005HUM/AND].
	K^+	—	
$Ni(CN)_4^{2-}$	Li^+	—	
	Na^+	0.185 ± 0.081	Evaluated in [2005GAM/BUG] (see Section V.7.1.2.1.1).
	K^+	—	
$Fe(CO_3)_2^{2-}$	Li^+		
	Na^+	-0.05 ± 0.05	By analogy. See Appendix A entry for [1992BRU/WER].
	K^+		
CrO_4^{2-}	Li^+	—	
	Na^+	-0.06 ± 0.04†	
	K^+	-0.08 ± 0.04†	
$Zr(OH)_6^{2-}$	Li^+	—	
	Na^+	-0.10 ± 0.10	Determined in [2005BRO/CUR] by analogy to known interaction coefficients of doubly charged anionic species with alkali ions (source: [2001LEM/FUG]).
	K^+	—	
ZrF_6^{2-}	Li^+	—	
	Na^+	-0.15 ± 0.06	Determined from SIT plots in [2005BRO/CUR].
	K^+	—	
$NpO_2(HPO_4)_2^{2-}$	Li^+	—	
	Na^+	-0.1 ± 0.10	Estimated in [2001LEM/FUG].
	K^+	—	
$NpO_2(CO_3)_2^{2-}$	Li^+	—	
	Na^+	-0.02 ± 0.14	Estimated by analogy in [2001LEM/FUG] (Section 12.1.2.1.2).
	K^+	—	
NpO_2cit^{2-}	Li^+	—	
	Na^+	-0.06 ± 0.03	Evaluated in Section VII.11 of [2005HUM/AND].
	K^+	—	
$NpO_2(Hedta)^{2-}$	Li^+	—	
	Na^+	0.07 ± 0.16	Estimated in Section VIII.11.2.3 of [2005HUM/AND].
	K^+	—	

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Table B-5 (continued)

j	*k*	ε(*j*,*k*)	Comments
$UO_2F_4^{2-}$	Li^+	—	
	Na^+	-0.30 ± 0.06	Evaluated in [2003GUI/FAN], Section 9.4.2.2.1.1.
	K^+	—	
$UO_2(SO_4)_2^{2-}$	Li^+	—	
	Na^+	-0.12 ± 0.06	Estimated in [1992GRE/FUG].
	K^+	—	
$UO_2(N_3)_4^{2-}$	Li^+	—	
	Na^+	-0.1 ± 0.1	Estimated in [1992GRE/FUG].
	K^+	—	
$UO_2(ox)_2^{2-}$	Li^+	—	
	Na^+	-0.18 ± 0.07	Estimated in Section VI.1.2.4.1 of [2005HUM/AND].
	K^+	—	
UO_2edta^{2-}	Li^+	—	
	Na^+	-0.22 ± 0.18	Estimated in Section VIII.10.2.4 of [2005HUM/AND].
	K^+	—	
$UO_2(CO_3)_2^{2-}$	Li^+	—	
	Na^+	-0.02 ± 0.09	These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for CO_3^{2-} and HCO_3^- are based on [1980CIA].
	K^+	—	
$(UO_2)_2(OH)_2(SO_4)_2^{2-}$	Li^+	—	
	Na^+	-0.14 ± 0.22	Evaluated in Section 9.5.1.1.2 of [2003GUI/FAN].
	K^+	—	
ThF_6^{2-}	Li^+	—	
	Na^+	-0.30 ± 0.06	See Table VIII-8 in Section VIII.1.2.1 of [2008RAN/FUG].
	K^+	—	
$Th(SO_4)_3^{2-}$	Li^+	-0.068 ± 0.003	In combination with $\varepsilon_2 = (0.093 \pm 0.007)$.
	Na^+	-0.091 ± 0.038	See Section IX.1.3.2 of [2008RAN/FUG].
	K^+	-0.091 ± 0.038	
$Th(OH)_2(CO_3)_2^{2-}$	Li^+	—	
	Na^+	-0.1 ± 0.2	See Section XI.1.3.2 of [2008RAN/FUG].
	K^+	—	
$Th(OH)_4(CO_3)^{2-}$	Li^+	—	
	Na^+	-0.1 ± 0.2	See Section XI.1.3.2 of [2008RAN/FUG].
	K^+	—	

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Table B-5 (continued)

j	*k*	$\varepsilon(j,k)$	Comments
$Mg(ox)_2^{2-}$	Li^+	—	
	Na^+	-0.15 ± 0.03	Estimated in Section VI.5.1 of [2005HUM/AND].
	K^+	-0.15 ± 0.10	Estimated in [2005HUM/AND], Section VI.5.1 by assuming $\varepsilon(K^+, Mg(ox)_2^{2-}) \approx \varepsilon(Na^+, Mg(ox)_2^{2-})$.
$Mg(edta)^{2-}$	Li^+	—	
	Na^+	-0.01 ± 0.15	Evaluated in Section VIII.5.2 of [2005HUM/AND].
	K^+	—	
$Ca(ox)_2^{2-}$	Li^+	—	
	Na^+	-0.15 ± 0.10	Estimated in [2005HUM/AND], Section VI.5.2 by assuming $\varepsilon(Na^+, Ca(ox)_2^{2-}) \approx \varepsilon(Na^+, Mg(ox)_2^{2-})$.
	K^+	-0.15 ± 0.10	Estimated in [2005HUM/AND], Section VI.5.2 by assuming $\varepsilon(K^+, Ca(ox)_2^{2-}) \approx \varepsilon(Na^+, Mg(ox)_2^{2-})$.
cit^{3-}	Li^+	-0.44 ± 0.15†	
	Na^+	-0.076 ± 0.030†	
	K^+	0.02 ± 0.02	Evaluated in Section VI.3.6 of [2005HUM/AND].
$Hedta^{3-}$	Li^+	—	
	Na^+	-0.10 ± 0.14	Evaluated in Section VIII.3.7 of [2005HUM/AND].
	K^+	0.31 ± 0.18	
PO_4^{3-}	Li^+	—	
	Na^+	-0.25 ± 0.03†	
	K^+	-0.09 ± 0.02	Reported by Ciavatta [1980CIA].
$Si_3O_6(OH)_3^{3-}$	Li^+	—	
	Na^+	-0.25 ± 0.03	Estimated in [1992GRE/FUG].
	K^+	—	
$Si_3O_5(OH)_5^{3-}$	Li^+	—	
	Na^+	-0.25 ± 0.03	Estimated in [1992GRE/FUG].
	K^+	—	
$Si_4O_7(OH)_5^{3-}$	Li^+	—	
	Na^+	-0.25 ± 0.03	Estimated in [1992GRE/FUG].
	K^+	—	
$Ni(CN)_5^{3-}$	Li^+	—	
	Na^+	0.25 ± 0.14	Evaluated in [2005GAM/BUG] (see Section V.7.1.2.1.1).
	K^+	—	
$Fe(CO_3)_3^{3-}$	Li^+	—	
	Na^+	-0.23 ± 0.07	By analogy. See Appendix A entry for [2005GRI].
	K^+	—	

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Table B-5 (continued)

j	*k*	$\varepsilon(j,k)$	Comments
$Am(CO_3)_3^{3-}$	Li^+	—	
	Na^+	-0.23 ± 0.07	Evaluated Section 12.6.1.1.1 [2003GUI/FAN], from $\Delta\varepsilon_n$ in NaCl solution for the reactions $An^{3+} + n\,CO_3^{2-} \rightleftharpoons An(CO_3)_n^{(3-2n)}$ (An = Am, Cm) based on $\varepsilon(Am^{3+},Cl^-)$ = $(0.23 \pm 0.02)\ kg{\cdot}mol^{-1}$ and $\varepsilon(Na^+, CO_3^{2-})$ = – (0.08 ± 0.03) $kg{\cdot}mol^{-1}$.
	K^+	—	
$Am(ox)_3^{3-}$	Li^+	—	
	Na^+	-0.23 ± 0.10	Estimated in [2005HUM/AND], Section VI.13.2.1 by assuming $\varepsilon(Na^+, Am(ox)_3^{3-}) \approx \varepsilon(Na^+, Am(CO_3)_3^{3-})$.
	K^+	—	
$Np(CO_3)_3^{3-}$	Li^+	—	
	Na^+	—	
	K^+	-0.15 ± 0.07	Estimated by analogy in [2001LEM/FUG] (Section 12.1.2.1.5).
$NpO_2(CO_3)_2^{3-}$	Li^+	—	
	Na^+	-0.33 ± 0.17	Calculated in [2001LEM/FUG] (Section 12.1.2.1.3).
	K^+	—	
$NpO_2(CO_3)_2OH^{3-}$	Li^+	—	
	Na^+	-0.40 ± 0.19	Estimated in [2001LEM/FUG] by analogy with $NpO_2(CO_3)_3^{4-}$.
	K^+	—	
$NpO_2(ox)_2^{3-}$	Li^+	—	
	Na^+	-0.3 ± 0.2	Evaluated in Section VI.11.2.3 of [2005HUM/AND].
	K^+	—	
NpO_2edta^{3-}	Li^+	—	
	Na^+	0.20 ± 0.16	Estimated in Section VIII.11.2.3 of [2005HUM/AND].
	K^+	—	
$edta^{4-}$	Li^+	—	
	Na^+	0.32 ± 0.14	Evaluated in Section VIII.3.7 of [2005HUM/AND].
	K^+	1.07 ± 0.19	
$P_2O_7^{4-}$	Li^+	—	
	Na^+	-0.26 ± 0.05	Reported by Ciavatta [1988CIA].
	K^+	-0.15 ± 0.05	Reported by Ciavatta [1988CIA].

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Table B-5 (continued)

j	k	$\varepsilon(j,k)$	Comments
$Fe(CN)_6^{4-}$	Li^+	—	
	Na^+	—	
	K^+	-0.17 ± 0.03	
$Zr(CO_3)_4^{4-}$	Li^+	—	
	Na^+	-0.09 ± 0.20	This value, referring to $\varepsilon(NH_4^+, Zr(CO_3)_4^{4-})$ has been estimated in [2005BRO/CUR] by analogy with the homovalent ion pair ($Na^+, U(CO_3)_4^{4-}$), see [1997GRE/PLY].
	K^+	—	
$NpO_2(CO_3)_3^{4-}$	Li^+	—	
	Na^+	-0.40 ± 0.19	Calculated in [2001LEM/FUG] (Section 12.1.2.1.2).
	K^+	-0.62 ± 0.42	$\varepsilon(NH_4^+, NpO_2(CO_3)_3^{4-}) = -(0.78 \pm 0.25)$ kg·mol^{-1} is calculated in [2001LEM/FUG] (Section 12.1.2.2.1).
$U(CO_3)_4^{4-}$	Li^+	—	
	Na^+	-0.09 ± 0.10	These values differ from those estimated in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for CO_3^{2-} and HCO_3^- are based on [1980CIA].
	K^+	—	
$UO_2(CO_3)_3^{4-}$	Li^+	—	
	Na^+	-0.01 ± 0.11	These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for CO_3^{2-} and HCO_3^- are based on [1980CIA].
	K^+	—	
$UO_2(ox)_3^{4-}$	Li^+	—	
	Na^+	-0.01 ± 0.11	Estimated in [2005HUM/AND], Section VI.10.2.4.1 by assuming $\varepsilon(Na^+, UO_2(ox)_3^{4-}) \approx \varepsilon(Na^+, UO_2(CO_3)_3^{4-})$.
	K^+	—	
$(UO_2)_3(OH)_4(SO_4)_3^{4-}$	Li^+	—	
	Na^+	0.6 ± 0.6	Estimated in Section 9.5.1.1.2 of [2003GUI/FAN].
	K^+	—	

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Table B-5 (continued)

j	k	$\varepsilon(j,k)$	Comments
$NpO_2(CO_3)_3^{5-}$	Li^+	—	
	Na^+	-0.53 ± 0.19	Calculated in [2001LEM/FUG] (Section 12.1.2.1.3).
	K^+	-0.22 ± 0.03	Evaluated in [2003GUI/FAN] (discussion of [1998ALM/NOV] in Appendix A) from $\Delta\varepsilon$ for the reactions $KNpO_2CO_3(s) + 2CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_3^{5-} + K^+$ (in K_2CO_3–KCl solution) and $K_3NpO_2(CO_3)_2(s) + CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_3^{5-} + 3K^+$ (in K_2CO_3 solution) (based on $\varepsilon(K^+, CO_3^{2-}) = (0.02 \pm 0.01)$ kg·mol^{-1}).
$UO_2(CO_3)_3^{5-}$	Li^+	—	
	Na^+	-0.62 ± 0.15	These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for CO_3^{2-} and HCO_3^- are based on [1980CIA].
	K^+	—	
$Th(OH)(CO_3)_4^{5-}$	Li^+	—	
	Na^+	-0.22 ± 0.13	Evaluated in Section XI.1.3.2.1 of [2008RAN/FUG].
	K^+	—	
$Np(CO_3)_5^{6-}$	Li^+	—	
	Na^+	—	
	K^+	-0.73 ± 0.68	Calculated in [2001LEM/FUG] (Section 12.1.2.1.4).
$(NpO_2)_3(CO_3)_6^{6-}$	Li^+	—	
	Na^+	-0.46 ± 0.73	Calculated in [2001LEM/FUG] (Section 12.1.2.1.2).
	K^+	—	
$U(CO_3)_5^{6-}$	Li^+	—	
	Na^+	-0.30 ± 0.15	These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for CO_3^{2-} and HCO_3^- are based on [1980CIA].
	K^+	-0.70 ± 0.31	Calculated in [2001LEM/FUG] from Pitzer coefficients [1998RAI/FEL].
$(UO_2)_3(CO_3)_6^{6-}$	Li^+	—	
	Na^+	0.37 ± 0.11	These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for CO_3^{2-} and HCO_3^- are based on [1980CIA].
	K^+	—	
$(UO_2)_2NpO_2(CO_3)_6^{6-}$	Li^+	—	
	Na^+	0.09 ± 0.71	Estimated by analogy in [2001LEM/FUG] (Section 12.1.2.2.1).
	K^+	—	

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Table B-5 (continued)

j	*k*	$\varepsilon(j,k)$	Comments
$(UO_2)_5(OH)_8(SO_4)_4^{6-}$	Li^+	—	
	Na^+	1.10 ± 0.5	Estimated in Section 9.5.1.1.2 of [2003GUI/FAN].
	K^+	—	
$Th(CO_3)_5^{6-}$	Li^+	—	
	Na^+	– 0.30 ± 0.15	Estimated in Section XI.1.3.2.1 of [2008RAN/FUG].
	K^+	—	
$(UO_2)_4(OH)_7(SO_4)_4^{7-}$	Li^+	—	
	Na^+	2.80 ± 0.7	Estimated in Section 9.5.1.1.2 of [2003GUI/FAN].
	K^+	—	

Table B-6: Ion interaction coefficients, $\varepsilon_1(j,k)$ and $\varepsilon_2(j,k)$, both in $\text{kg}\cdot\text{mol}^{-1}$, for cations *j* with k = Cl^-, ClO_4^- and NO_3^- (first part), and for anions *j* with k = Li^+, Na^+ and K^+ (second part), according to the relationship $\varepsilon = \varepsilon_1 + \varepsilon_2 \log_{10} I_m$ at 298.15 K. The data are taken from Ciavatta [1980CIA], [1988CIA] unless indicated otherwise. The uncertainties represent the 95% confidence level.

$j\ k \rightarrow$	Cl^-		ClO_4^-		NO_3^-	
$\downarrow$	ε_1	ε_2	ε_1	ε_2	ε_1	ε_2
NH_4^+			-0.088 ± 0.002	0.095 ± 0.012	-0.075 ± 0.001	0.057 ± 0.004
Tl^+			-0.18 ± 0.02	0.09 ± 0.02		
Ag^+					-0.1432 ± 0.0002	0.0971 ± 0.000
Pb^{2+}					-0.329 ± 0.007	0.288 ± 0.018
Hg^{2+}					-0.145 ± 0.001	0.194 ± 0.002
Hg_2^{2+}					-0.2300 ± 0.0004	0.194 ± 0.002

$j\ k \rightarrow$	Li^+		Na^+		K^+	
$\downarrow$	ε_1	ε_2	ε_1	ε_2	ε_1	ε_2
OH^-	-0.039 ± 0.002	0.072 ± 0.006				
NO_2^-	0.02 ± 0.01	0.11 ± 0.01				
NO_3^-			-0.049 ± 0.001	0.044 ± 0.002	-0.131 ± 0.002	0.082 ± 0.006
H_2PO_4^-			-0.109 ± 0.001	0.095 ± 0.003	-0.1473 ± 0.0008	0.121 ± 0.004
B(OH)_4^-			-0.092 ± 0.002	0.103 ± 0.005		
SO_3^{2-}			-0.125 ± 0.008	0.106 ± 0.009		
SO_4^{2-}	-0.068 ± 0.003	0.093 ± 0.007	-0.184 ± 0.002	0.139 ± 0.006		
$\text{S}_2\text{O}_3^{2-}$			-0.125 ± 0.008	0.106 ± 0.009		
HPO_4^{2-}			-0.19 ± 0.01	0.11 ± 0.03	-0.152 ± 0.007	0.123 ± 0.016
CrO_4^{2-}			-0.090 ± 0.005	0.07 ± 0.01	-0.123 ± 0.003	0.106 ± 0.007
cit^{3-}	-0.55 ± 0.11 [a]	0.3 ± 0.2[a]	-0.15 ± 0.03[a]	0.13 ± 0.03[a]		
PO_4^{3-}			-0.29 ± 0.02	0.10 ± 0.01		

a: See Section VII.3.6 of [2005HUM/AND].

Table B-7: SIT interaction coefficients $\varepsilon(j,k)$ ($kg\cdot mol^{-1}$) for neutral species, j, with k, electroneutral combination of ions at 298.15 K.

j $k \rightarrow$ $\downarrow$	$Na^+ + ClO_4^-$	$Na^+ + Cl^-$	$K^+ + NO_3^-$
$H_2ox(aq)$	0.00 ± 0.01 [b]	0.00 ± 0.01 [b]	0.00 ± 0.01 [b]
$H_3cit(aq)$	0.00 ± 0.01 [b]	0.00 ± 0.01 [b]	0.00 ± 0.01 [b]
$H_4edta(aq)$	– 0.29 ± 0.14	– 0.29 ± 0.14	– 0.29 ± 0.14
$SnBr_2(aq)$	0.14 ± 0.07		
$SnSO_4(aq)$	0.19 ± 0.35		
$Sn(NO_3)_2(aq)$	0.130 ± 0.111		
Ni(ox)(aq)	– 0.07 ± 0.03	– 0.07 ± 0.03	
Ni(Hcit)(aq)	– 0.07 ± 0.5		
$Ni(SCN)_2(aq)$	0.38 ± 0.06 [a]		
Am(cit)(aq)		0.00 ± 0.05	
Np(edta)(aq)	– 0.19 ± 0.19 [g]		
$UO_2ox(aq)$	– 0.05 ± 0.06	– 0.05 ± 0.06	
Uedta(aq)	– 0.19 ± 0.19		
Mg(ox)(aq)		0.00 ± 0.03	0.0 ± 0.1[c]
Mg(Hcit)(aq)	0.02 ± 0.05	0.02 ± 0.05	
Ca(ox)(aq)	0.0 ± 0.1 [d]	0.0 ± 0.1 [e]	0.0 ± 0.1 [f]

(a): See Section V.7.1.3.1 in [2005GAM/BUG].

(b): Basic assumption made in [2005HUM/AND]. See Sections VI.3.5 and VII.3.6 of that review for discussions.

(c): Estimated in Section VI.5.2 of [2005HUM/AND] by assuming $\varepsilon(Mg(ox)(aq), KNO_3) \approx \varepsilon(Mg(ox)(aq), NaCl)$.

(d): Estimated in Section VI.5.2 of [2005HUM/AND] by assuming $\varepsilon(Ca(ox)(aq), NaClO_4) \approx \varepsilon(Mg(ox)(aq), NaCl)$.

(e): Estimated in Section VI.5.1 of [2005HUM/AND] by assuming $\varepsilon(Ca(ox)(aq), NaCl) \approx \varepsilon(Mg(ox)(aq), NaCl)$.

(f): Estimated in Section VI.5.2 of [2005HUM/AND] by assuming $\varepsilon(Ca(ox)(aq), KNO_3) \approx \varepsilon(Mg(ox)(aq), NaCl)$.

(g): Estimated in Section VIII.11.2.2 of [2005HUM/AND] by assuming $\varepsilon(Np(edta)(aq), NaClO_4) \approx \varepsilon(Uedta(aq), NaClO_4)$.

Appendix C

Assigned uncertainties[1]

This appendix describes the origin of the uncertainty estimates that are given in the TDB tables of selected data. The original text in [1992GRE/FUG] has been retained in [1995SIL/BID], [1999RAR/RAN] and [2001LEM/FUG], except for some minor changes. Because of the importance of the uncertainty estimates, the present review offers a more comprehensive description of the procedures used.

C.1 The general problem

The focus of this section is on the uncertainty estimates of equilibria in solution, where the key problem is analytical, *i.e.*, the determination of the stoichiometric composition and equilibrium constants of complexes that are in rapid equilibrium with one another. We can formulate analyses of the experimental data in the following way: From N measurements, y_i, of the variable y we would like to determine a set of n equilibrium constants k_r, $r = 1, 2,\ldots, n$, assuming that we know the functional relationship:

$$y = f(k_1, k_2, \ldots k_r \ldots k_n; a_1, a_2, \ldots.) \qquad \text{(C.1)}$$

where a_1, a_2 , *etc.* are quantities that can be varied but whose values (a_{1i}; a_{2i}; *etc.*) are assumed to be known accurately in each experiment from the data sets (y_i, a_{1i}, a_{2i},…), $i = 1, 2, \ldots N$. The functional relationship (C.1) is obtained from the chemical model proposed and in general several different models have to be tested before the "best" one is selected. Details of the procedures are given in Rossotti and Rossotti [1961ROS/ROS].

When selecting the functional relationship (C.1) and determining the set of equilibrium constants that best describes the experiments one often uses a least-squares method. Within this method, the “best” description is the one that will minimise the residual sum of squares, U:

$$U = \sum_i w_i \left[y_i - f(k_1 \ldots k_n;\ a_{1i},\ a_{2i} \ldots) \right]^2 \qquad \text{(C.2)}$$

where w_i is the weight of each experimental measurement y_i.

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[1] This appendix essentially contains the text of the TDB-3 Guideline, [1999WAN/OST], earlier versions of which have been printed in all the previous NEA TDB reviews. Because of its importance in the selection of data and to guide the users of the values in Chapters III and IV the text is reproduced here with minor revisions.

The minimum of the function (C.2) is obtained by solving a set of normal equations:

$$\frac{\partial U}{\partial k_r} = 0,\ r = 1,\dots..n \qquad \text{(C.3)}$$

A “true” minimum is only obtained if:

- the functional relationship (C.1) is correct, *i.e.*, if the chemical model is correct;
- all errors are random errors in the variable y, in particular there are no systematic errors;
- the random errors in y follow a Gaussian (normal) distribution;
- the weight $w_i(y_i,\ a_{1i},\ a_{2i},\dots.)$ 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 types of systematic error.

The experimentalist usually selects the variable that he/she finds most appropriate to fulfill the second condition. If the estimated errors in a_{1i}, a_{2i} … are smaller than the error in y_i, the second condition is reasonably well fulfilled. The choice of the error-carrying variable is a matter of choice based on experience, but one must be aware that it has implications, especially in the estimated uncertainty.

The presence of systematic errors is, potentially, the most important source of uncertainty. There is no possibility to handle systematic errors using statistics; statistical methods may indicate their presence, no more. Systematic errors in the chemical model have been mentioned. In addition there may be systematic errors in the methods used. By comparing experimental data obtained with different experimental methods one can obtain an indication of the presence and magnitude of such errors. The systematic errors of this type are accounted for both in the review of the literature and when taking the average of data obtained with different experimental methods. This type of systematic error does not seem to affect the selected data very much, as judged by the usually very good agreement between the equilibrium data obtained using spectroscopic, potentiometric and solubility methods.

The electrode calibration, especially the conversion between measured pH and $-\log_{10}[\mathrm{H}^+]$ is an important source of systematic error. The reviewers have when possible corrected this error, as seen in many instances in Appendix A.

The assumption of a normal distribution of the random errors is a choice made in the absence of better alternatives.

Finally, a comment on the weights used in least-squares refinements; this is important because it influences the uncertainty estimate of the equilibrium constants. The weights of individual experimental points can be obtained by repeating the experiment several times and then calculating the average and standard deviation of these data. This procedure is rarely used, instead most experimentalists seem to use unit weight when making a least-squares analysis of their data. However, also in this case there is a weighting of the data by the number of experimental determinations in the parameter range where the different complexes are formed. In order to have comparable uncertainty estimates for the different complexes, one should try to have the same number of experimental data points in the concentration ranges where each of these complexes is predominant; a procedure very rarely used.

As indicated above, the assignment of uncertainties to equilibrium constants is not a straightforward procedure and it is complicated further when there is lack of primary experimental data. The uncertainty estimates given for the individual equilibrium constants reported by the authors and for some cases re-estimated by this review are given in the tables of this and previous reviews. The procedure used to obtain these estimates is given in the original publications and in the Appendix A discussions. However, this uncertainty is still a subjective estimate and to a large extent based on "expert judgment".

C.2 Uncertainty estimates in the selected thermodynamic data

The uncertainty estimate in the selected thermodynamic data is based on the uncertainty of the individual equilibrium constants or other thermodynamic data, calculated as described in the following sections. A weighted average of the individual $\log_{10}K$ values is calculated using the estimated uncertainty of the individual experimental values to assign its weight. The uncertainty in this average is then calculated using the formulae given in the following text. This uncertainty depends on the number of experimental data points – for N data points with the same estimated uncertainty, σ, the uncertainty in the average is $\sigma/\sqrt{N}$. The average and the associated uncertainty reported in the tables of selected data are reported with many more digits than justified only in order to allow the users to back-track the calculations. The reported uncertainty is much smaller than the estimated experimental uncertainty and the users of the tables should look at the discussion of the selected constants in order to get a better estimate of the uncertainty in an experimental determination using a specific method.

One of the objectives of the NEA Thermochemical Database (TDB) project is to provide an idea of the uncertainties associated with the data selected in this review. As a rule, the uncertainties define the range within which the corresponding data can be reproduced with a probability of 95% at any place and by any appropriate method. In many cases, the statistical treatment is limited or impossible due to the availability of only one or few data points. A particular problem has to be solved when significant discrepancies occur between different source data. This appendix outlines the statistical procedures, which were used for fundamentally different problems, and explains the philosophy used in this review when statistics were inapplicable. These rules are followed consistently throughout the series of reviews within the TDB Project. Four fundamentally different cases are considered:

1. One source datum available
2. Two or more independent source data available
3. Several data available at different ionic strengths
4. Data at non-standard conditions: Procedures for data correction and recalculation.

C.3 One source datum

The assignment of an uncertainty to a selected value that is based on only one experimental source is a highly subjective procedure. In some cases, the number of data points, on which the selected value is based, allows the use of the “root mean square” [1982TAY] deviation of the data points, X_i, to describe the standard deviation, s_X, associated with the average, $\overline{X}$:

$$s_{\mathrm{X}} = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(X_i - \overline{X})^2}\ . \tag{C.4}$$

The standard deviation, s_X, is thus calculated from the dispersion of the equally weighted data points, X_i, around the average $\overline{X}$, and the probability is 95% that an X_i is within $\overline{X} \pm 1.96\, s_X$, see Taylor [1982TAY] (pp. 244-245). The standard deviation, s_X, is a measure of the precision of the experiment and does not include any systematic errors.

Many authors report standard deviations, s_X, calculated with Eq. (C.4) (but often not multiplied by 1.96), but these do not represent the quality of the reported values in absolute terms. Therefore, it is thus important not to confuse the standard deviation, s_X, with the uncertainty, σ. The latter reflects the reliability and reproducibility of an experimental value and also includes all kinds of systematic errors,

s_j, that may be involved. The uncertainty, σ, can be calculated with Eq. (C.5), assuming that the systematic errors are independent.

$$\sigma_X = \sqrt{s_X^2 + \sum_j (s_j^2)} \qquad \text{(C.5)}$$

The estimation of the systematic errors s_j (which, of course, have to relate to $\overline{X}$ and be expressed in the same units) can only be made by a person who is familiar with the experimental method. The uncertainty, σ, has to correspond to the 95% confidence level preferred in this review. It should be noted that for all the corrections and recalculations made (*e.g.*, temperature or ionic strength corrections) the rules of the propagation of errors have to be followed, as outlined in Section 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 σ in the resulting value can still be estimated using Eq. (C.5) assuming that s_X^2 is much smaller than $\sum_j (s_j^2)$, which is usually the case anyway.

C.4 Two or more independent source data

Frequently, two or more experimental data sources are available, reporting experimental determinations of the desired thermodynamic data. In general, the quality of these determinations varies widely, and the data have to be weighted accordingly for the calculation of the mean. Instead of assigning weight factors, the individual source data, X_i, are provided with an uncertainty, σ_i, that also includes all systematic errors and represents the 95% confidence level, as described in Section C.3. The weighted mean $\overline{X}$ and its uncertainty, $\sigma_{\overline{X}}$, are then calculated according to Eqs. (C.6) and (C.7).

$$\overline{X} \equiv \frac{\sum_{i=1}^{N} \left(\frac{X_i}{\sigma_i^2}\right)}{\sum_{i=1}^{N} \left(\frac{1}{\sigma_i^2}\right)} \qquad \text{(C.6)}$$

$$\sigma_{\overline{X}} = \sqrt{\frac{1}{\sum_{i=1}^{N} \left(\frac{1}{\sigma_i^2}\right)}} \qquad \text{(C.7)}$$

Equations (C.6) and (C.7) may only be used if all the X_i belong to the same parent distribution. If there are serious discrepancies among the X_i, one proceeds as described below under Section C.4.1. It can be seen from Eq. (C.7) that $\sigma_{\overline{X}}$ is directly dependent on the absolute magnitude of the σ_i values, and not on the dispersion of the data points around the mean. This is reasonable because there are no discrepancies among the X_i, and because the σ_i values already represent the 95% confidence level. The selected uncertainty, $\sigma_{\overline{X}}$, will therefore also represent the 95% confidence level.

In cases where all the uncertainties are equal, $\sigma_i = \sigma$, Eqs. (C.6) and (C.7) reduce to Eqs. (C.8) and (C.9).

$$\overline{X} = \frac{1}{N}\sum_{i=1}^{N} X_i \tag{C.8}$$

$$\sigma_{\overline{X}} = \frac{\sigma}{\sqrt{N}} \tag{C.9}$$

Example C.1:

Five data sources report values for the thermodynamic quantity, *X*. The reviewer has assigned uncertainties that represent the 95% confidence level as described in Section C.3.

i	X_i	σ_i
1	25.3	0.5
2	26.1	0.4
3	26.0	0.5
4	24.85	0.25
5	25.0	0.6

According to Eqs. (C.6) and (C.7), the following result is obtained:

$$\overline{X} = (25.3 \pm 0.2).$$

The calculated uncertainty, $\sigma_{\overline{X}} = 0.2$, appears relatively small, but is statistically correct, as the values are assumed to follow a Gaussian distribution. As a consequence of Eq. (C.7), $\sigma_{\overline{X}}$ will always come out smaller than the smallest σ_i. Assuming $\sigma_4 = 0.10$ instead of 0.25 would yield $\overline{X} = (25.0 \pm 0.1)$ and $\sigma_4 = 0.60$ would result in $\overline{X} = (25.6 \pm 0.2)$. In fact, the values ($X_i \pm \sigma_i$) in this example are at the limit of consistency, *i.e.*, the range ($X_4 \pm \sigma_4$) does not overlap with the ranges ($X_2 \pm \sigma_2$) and ($X_3 \pm \sigma_3$). There might be a better way to solve this problem. Three possible choices seem more reasonable:

i. The uncertainties, σ_i, are reassigned because they appear too optimistic after further consideration. Some assessments may have to be reconsidered and the uncertainties reassigned. For example, multiplying all the σ_i by 2 would yield $\overline{X} = (25.3 \pm 0.3)$.

ii. If reconsideration of the previous assessments gives no evidence for reassigning the X_i and σ_i (95% confidence level) values listed above, the statistical conclusion will be that all the X_i do not belong to the same parent distribution and cannot therefore be treated in the same group (*cf.* item iii below for a non-statistical explanation). The values for i =1, 4 and 5 might be considered as belonging to Group A and the values for i = 2 and 3 to Group B. The weighted average of the values in Group A is X_A (i = 1, 4, 5) = (24.95 ± 0.21) and of those in Group B, X_B

(i = 2, 3) = (26.06 ± 0.31), the second digit after the decimal point being carried over to avoid loss of information. The selected value is now determined as described below under "Discrepancies" (Section 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 ± 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 $\bar{X}$ = (25.4 ± 1.0), which is rounded according to the rules in Section C.6.3 to $\bar{X}$ = (25.4 ± 1.1).

C.4.1 Discrepancies

Two data are called discrepant if they differ significantly, *i.e.*, their uncertainty ranges do not overlap. In this context, two cases of discrepancies are considered. Case I: Two significantly different source data are available. Case II: Several, mostly consistent source data are available, one of them being significantly different, *i.e.*, an "outlier".

Case I. Two discrepant data: This is a particularly difficult case because the number of data points is obviously insufficient to allow the preference of one of the two values. If there is absolutely no way of discarding one of the two values and selecting the other, the only solution is to average the two source data in order to obtain the selected value, because the underlying reason for the discrepancy must be unrecognised systematic errors. There is no point in calculating a weighted average, even if the two source data have been given different uncertainties, because there is obviously too little information to give even only limited preference to one of the values. The uncertainty, $\sigma_{\bar{X}}$, 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),

$$\sigma_{\bar{X}} = \left|X_i - \bar{X}\right| + \sigma_{\max} \qquad \text{(C.10)}$$

where i =1, 2, and $\sigma_{\max}$ is the larger of the two uncertainties σ_i, see Example C.1.ii and Example C.2.

Example C.2:

The following credible source data are given:

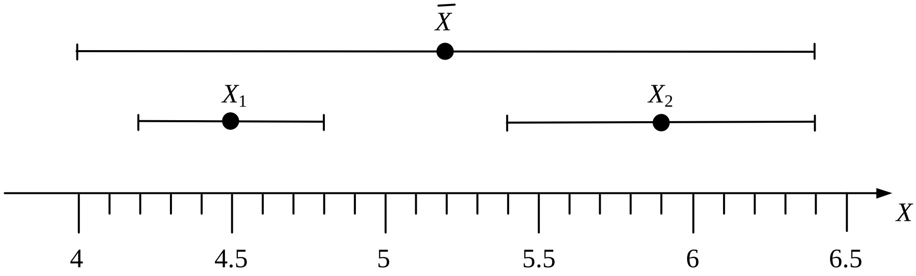
X_1 = (4.5 ± 0.3)

X_2 = (5.9 ± 0.5).

The uncertainties have been assigned by the reviewer. Both experimental methods are satisfactory and there is no justification to discard one of the data. The selected value is then:

$$\overline{X} = (5.2 \pm 1.2).$$

Figure C-1: Illustration for Example C.2.



Case II. Outliers: This problem can often be solved by either discarding the outlying data point, or by providing it with a large uncertainty to lower its weight. If, however, the outlying value is considered to be of high quality and there is no reason to discard all the other data, this case is treated in a way similar to Case I. Example C.3 illustrates the procedure.

Example C.3:

The following data points are available. The reviewer has assigned the uncertainties and sees no justification for any change.

i	X_i	σ_i
1	4.45	0.35
2	5.9	0.5
3	5.7	0.4
4	6.0	0.6
5	5.2	0.4

There are two data sets that, statistically, belong to different parent distributions, A and B. According to Eqs. (C.6) and (C.7), the following average values are found for the two groups: $X_A(i = 1) = (4.45 \pm 0.35)$ and $X_B(i = 2, 3, 4, 5) = (5.62 \pm 0.23)$. The selected value will be the straight average of X_A and X_B, analogous to Example C.1:

$$\overline{X} = (5.0 \pm 0.9).$$

C.5 Several data at different ionic strengths

The extrapolation procedure for aqueous equilibria used in this review is the specific ion interaction model outlined in Appendix B. The objective of this review is to provide selected data sets at standard conditions, *i.e.*, among others, at infinite dilution for aqueous species. Equilibrium constants determined at different ionic strengths can, according to the specific ion interaction equations, be extrapolated to $I = 0$ with a linear regression model, yielding as the intercept the desired equilibrium constant at $I = 0$, and as the slope the stoichiometric sum of the ion interaction coefficients, $\Delta\varepsilon$. The ion interaction coefficient of the target species can usually be extracted from $\Delta\varepsilon$ and would be listed in the corresponding table of Appendix B.

The available source data may sometimes be sparse or may not cover a sufficient range of ionic strengths to allow a proper linear regression. In this case, the correction to $I = 0$ should be carried out according to the procedure described in Section 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 $I = 0$, $\bar{X}^{\circ}$, and $\Delta\varepsilon$. The first step is the conversion of the ionic strength from the frequently used molar (mol·dm^{-3}, M) to the molal (mol·kg^{-1}, m) scale, as described in Section II.2. The second step is the assignment of an uncertainty, σ_i, to each data point X_i at the molality, $m_{k,i}$, according to the rules described in Section C.3. A large number of commercial and public domain computer programs and routines exist for weighted linear regressions. The subroutine published by Bevington [1969BEV] (pp.104 – 105) has been used for the calculations in the examples of this appendix. Eqs. (C.11) through (C.15) present the equations that are used for the calculation of the intercept $\bar{X}^{\circ}$ and the slope $-\Delta\varepsilon$:

$$\bar{X}^{\circ} = \frac{1}{\Delta}\left(\sum_{i=1}^{N}\frac{m_{k,i}^2}{\sigma_i^2}\sum_{i=1}^{N}\frac{X_i}{\sigma_i^2} - \sum_{i=1}^{N}\frac{m_{k,i}}{\sigma_i^2}\sum_{i=1}^{N}\frac{m_{k,i}X_i}{\sigma_i^2}\right) \tag{C.11}$$

$$-\Delta\varepsilon = \frac{1}{\Delta}\left(\sum_{i=1}^{N}\frac{1}{\sigma_i^2}\sum_{i=1}^{N}\frac{m_{k,i}X_i}{\sigma_i^2} - \sum_{i=1}^{N}\frac{m_{k,i}}{\sigma_i^2}\sum_{i=1}^{N}\frac{X_i}{\sigma_i^2}\right) \tag{C.12}$$

$$\sigma_{\bar{X}^{\circ}} = \sqrt{\frac{1}{\Delta}\sum_{i=1}^{N}\frac{m_{k,i}^2}{\sigma_i^2}} \tag{C.13}$$

$$\sigma_{\Delta\varepsilon} = \sqrt{\frac{1}{\Delta}\sum_{i=1}^{N}\frac{1}{\sigma_i^2}} \tag{C.14}$$

where

$$\Delta = \sum_{i=1}^{N}\frac{1}{\sigma_i^2}\sum_{i=1}^{N}\frac{m_{k,i}^2}{\sigma_i^2} - \left(\sum_{i=1}^{N}\frac{m_{k,i}}{\sigma_i^2}\right)^2 . \tag{C.15}$$

In this way, the uncertainties, σ_i, are not only used for the weighting of the data in Eqs. (C.11) and (C.12), but also for the calculation of the uncertainties, $\sigma_{\bar{X}^o}$ and $\sigma_{\Delta\varepsilon}$, in Eqs. (C.13) and (C.14). If the σ_i represents the 95% confidence level, $\sigma_{\bar{X}^o}$ and $\sigma_{\Delta\varepsilon}$ will also do so. In other words, the uncertainties of the intercept and the slope do not depend on the dispersion of the data points around the straight line, but rather directly on their absolute uncertainties, σ_i.

Example C.4:

Ten independent determinations of the equilibrium constant, $\log_{10}{}^*\beta$, for the reaction:

$$UO_2^{2+} + HF(aq) \rightleftharpoons UO_2F^+ + H^+ \qquad (C.16)$$

are available in $HClO_4/NaClO_4$ media at different ionic strengths. Uncertainties that represent the 95% confidence level have been assigned by the reviewer. A weighted linear regression, ($\log_{10}{}^*\beta + 2D$) *vs.* m_k, according to the formula, $\log_{10}{}^*\beta$ (C.16) + $2D = \log_{10}{}^*\beta^o$ (C.16) $- \Delta\varepsilon\, m_k$, will yield the correct values for the intercept, $\log_{10}{}^*\beta^o$ (C.16), and the slope, $\Delta\varepsilon$. In this case, m_k corresponds to the molality of ClO_4^-. D is the Debye-Hückel term, *cf.* Appendix B.

i	$m_{ClO_4^-,i}$	$\log_{10}{}^*\beta + 2D$	σ_i
1	0.05	1.88	0.10
2	0.25	1.86	0.10
3	0.51	1.73	0.10
4	1.05	1.84	0.10
5	2.21	1.88	0.10
6	0.52	1.89	0.11
7	1.09	1.93	0.11
8	2.32	1.78	0.11
9	2.21	2.03	0.10
10	4.95	2.00	0.32

The results of the linear regression are:

$$\text{intercept} = (1.837 \pm 0.054) = \log_{10}{}^*\beta^o\,(C.16)$$

$$\text{slope} = (0.029 \pm 0.036) = -\Delta\varepsilon\,.$$

Calculation of the ion interaction coefficient $\varepsilon(UO_2F^+, ClO_4^-) = \Delta\varepsilon + \varepsilon(UO_2^{2+}, ClO_4^-) - \varepsilon(H^+, ClO_4^-)$: from $\varepsilon(UO_2^{2+}, ClO_4^-) = (0.46 \pm 0.03)$ kg·mol^{-1}, $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)$ kg·mol^{-1} (see Appendix B) and the slope of the linear regression, $\Delta\varepsilon = -(0.03 \pm 0.04)$ kg·mol^{-1}, it follows that $\varepsilon(UO_2F^+, ClO_4^-) =$

(0.29 ± 0.05) $\text{kg}\cdot\text{mol}^{-1}$. Note that the uncertainty (± 0.05) $\text{kg}\cdot\text{mol}^{-1}$ is obtained based on the rules of error propagation as described in Section C.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 points 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 “outliers”. If, however, the eight points are scattered considerably and two points are just a bit further out, one can probably not consider them as “outliers”. It depends on the particular case and on the judgment of the reviewer whether it is reasonable to increase the uncertainties of the data to reach consistency, or whether the slope, $\Delta\varepsilon$, of the straight line should be estimated by analogy.

Example C.5:

Six reliable determinations of the equilibrium constant, $\log_{10}\beta$, of the reaction:

$$\mathrm{UO_2^{2+}} + \mathrm{SCN^-} \rightleftharpoons \mathrm{UO_2SCN^+} \qquad \text{(C.17)}$$

are available in different electrolyte media:

$I_c = 0.1$ M ($\mathrm{KNO_3}$) $\log_{10}\beta$ (C.17) = (1.19 ± 0.03)

$I_c = 0.33$ M ($\mathrm{KNO_3}$) $\log_{10}\beta$ (C.17) = (0.90 ± 0.10)

$I_c = 1.0$ M ($\mathrm{NaClO_4}$) $\log_{10}\beta$ (C.17) = (0.75 ± 0.03)

$I_c = 1.0$ M ($\mathrm{NaClO_4}$) $\log_{10}\beta$ (C.17) = (0.76 ± 0.03)

$I_c = 1.0$ M ($\mathrm{NaClO_4}$) $\log_{10}\beta$ (C.17) = (0.93 ± 0.03)

$I_c = 2.5$ M ($\mathrm{NaNO_3}$) $\log_{10}\beta$ (C.17) = (0.72 ± 0.03)

The uncertainties are assumed to represent the 95% confidence level. From the values at $I_c = 1$ M, it can be seen that there is a lack of consistency in the data, and that a linear regression similar to that shown in Example C.4 would be inappropriate. Instead, the use of $\Delta\varepsilon$ values from reactions of the same charge type is encouraged. Analogies with $\Delta\varepsilon$ are more reliable than analogies with single ε values due to canceling effects. For the same reason, the dependency of $\Delta\varepsilon$ on the type of electrolyte is often smaller than for single ε values.

A reaction of the same charge type as Reaction (C.17), and for which $\Delta\varepsilon$ is well known, is:

$$\mathrm{UO_2^{2+}} + \mathrm{Cl^-} \rightleftharpoons \mathrm{UO_2Cl^+}. \qquad \text{(C.18)}$$

The value of $\Delta\varepsilon$ (C.18) = – (0.25 ± 0.02) $\mathrm{kg{\cdot}mol^{-1}}$ was obtained from a linear regression using 16 experimental values between $I_c = 0.1$ M and $I_c = 3$ M $\mathrm{Na(Cl,ClO_4)}$ [1992GRE/FUG]. It is thus assumed that:

$$\Delta\varepsilon\,\text{(C.17)} = \Delta\varepsilon\,\text{(C.18)} = -(0.25 \pm 0.02)\ \mathrm{kg{\cdot}mol^{-1}}.$$

The correction of $\log_{10}\beta$ (C.17) to $I = 0$ is done using the specific ion interaction equation, *cf.* TDB-2, which uses molal units:

$$\log_{10}\beta + 4D = \log_{10}\beta^{\circ} - \Delta\varepsilon\, I_m. \qquad \text{(C.19)}$$

D is the Debye-Hückel term and I_m the ionic strength converted to molal units by using the conversion factors listed in Table II-5. The following list gives the details of this calculation. The resulting uncertainties in $\log_{10}\beta$ are obtained based on the rules of error propagation as described in Section C.6.2.

Table C-1: Details of the calculation of the equilibrium constant for Reaction (C.17) corrected to $I = 0$, using (C.19).

I_m	electrolyte	$\log_{10}\beta$	$4D$	$\Delta\varepsilon\ I_m$.	$\log_{10}\beta^\circ$
0.101	KNO_3	(1.19 ± 0.03)	0.438	– 0.025	(1.68 ± 0.03)[a]
0.335	KNO_3	(0.90 ± 0.10)	0.617	– 0.084	(1.65 ± 0.10)[a]
1.050	$NaClO_4$	(0.75 ± 0.03)	0.822	– 0.263	(1.31 ± 0.04)
1.050	$NaClO_4$	(0.76 ± 0.03)	0.822	– 0.263	(1.32 ± 0.04)
1.050	$NaClO_4$	(0.93 ± 0.03)	0.822	– 0.263	(1.49 ± 0.04)
2.714	$NaNO_3$	(0.72 ± 0.03)	0.968	– 0.679	(1.82 ± 0.13)[a]

a: These values were corrected for the formation of the nitrate complex, $UO_2NO_3^+$, by using $\log_{10}\beta^\circ(UO_2NO_3^+)$ = (0.30 ± 0.15) [1992GRE/FUG].

As was expected, the resulting values, $\log_{10}\beta^\circ$, are inconsistent and have therefore to be treated as described in Case I of Section 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 involves application of the specific ion interaction equations described in detail in Appendix B. Two variables are needed for this correction, and both have to be provided with an uncertainty at the 95% confidence level: the experimental source value, $\log_{10}K$ or $\log_{10}\beta$, and the stoichiometric sum of the ion interaction coefficients, $\Delta\varepsilon$. The ion interaction coefficients (see Tables B-4, B-5, B-6 and B-7 of Appendix B) required to calculate $\Delta\varepsilon$ may not all be known. Missing values therefore need to be estimated. It is recalled that the electric charge has the most significant influence on the magnitude of the ion interaction coefficients, and that it is in general more reliable to estimate $\Delta\varepsilon$ from known reactions of the same charge type, rather than to estimate single ε values. The uncertainty of the corrected value at $I = 0$ is calculated by taking into account the propagation of errors, as described below. It should be noted that the ionic strength is frequently given in moles per dm^3 of solution (molar, M) and has to be converted to moles per kg H_2O (molal, *m*), as the model requires. Conversion factors for the most common inert salts are given in Table II.5.

Example C.6:

For the equilibrium constant of the reaction:

$$M^{3+} + 2H_2O(l) \rightleftharpoons M(OH)_2^+ + 2\,H^+\,, \qquad (C.20)$$

only one credible determination in 3 M $NaClO_4$ solution is known to be, $\log_{10}{}^*\beta$ (C.20) = – 6.31, to which an uncertainty of ± 0.12 has been assigned. The ion interaction coefficients are as follows:

$$\varepsilon(M^{3+},\ ClO_4^-) = (0.56 \pm 0.03)\ kg{\cdot}mol^{-1},$$

$$\varepsilon(M(OH)_2^+, ClO_4^-) = (0.26 \pm 0.11)\ kg{\cdot}mol^{-1},$$

$$\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)\ kg{\cdot}mol^{-1}.$$

The values of $\Delta\varepsilon$ and $\sigma_{\Delta\varepsilon}$ can be obtained readily (*cf.* Eq. (C.22)):

$$\Delta\varepsilon = \varepsilon(M(OH)_2^+, ClO_4^-) + 2\varepsilon(H^+, ClO_4^-) - \varepsilon(M^{3+}, ClO_4^-) = -\,0.22\ kg{\cdot}mol^{-1},$$

$$\sigma_{\Delta\varepsilon} = \sqrt{(0.11)^2 + (2\times 0.02)^2 + (0.03)^2} = 0.12\ kg{\cdot}mol^{-1}.$$

The two variables are thus:

$$\log_{10}{}^*\beta\ (C.20) = -\,(6.31 \pm 0.12),$$

$$\Delta\varepsilon = -\,(0.02 \pm 0.12)\ kg{\cdot}mol^{-1}.$$

According to the specific ion interaction model the following equation is used to correct for ionic strength for the reaction considered here:

$$\log_{10}{}^*\beta\ (C.20) + 6D = \log_{10}{}^*\beta^\circ\ (C.20) - \Delta\varepsilon\, m_{ClO_4^-}$$

D is the Debye-Hückel term:

$$D = \frac{0.509\sqrt{I_m}}{(1 + 1.5\sqrt{I_m})}.$$

The ionic strength, I_m, and the molality, $m_{ClO_4^-}$ ($I_m \approx m_{ClO_4^-}$), have to be expressed in molal units, 3 M $NaClO_4$ corresponding to 3.5 m $NaClO_4$ (see Section II.2), giving D = 0.25. This results in:

$$\log_{10}{}^*\beta^\circ\ (C.20) = -\,4.88.$$

The uncertainty in $\log_{10}{}^*\beta^\circ$ is calculated from the uncertainties in $\log_{10}{}^*\beta$ and $\Delta\varepsilon$ (*cf.* Eq. (C.22)):

$$\sigma_{\log_{10}{}^*\beta^o} = \sqrt{\sigma^2_{\log_{10}{}^*\beta} + (m_{ClO_4^-}\sigma_{\Delta\varepsilon})^2} = \sqrt{(0.12)^2 + (3.5\times 0.12)^2} = 0.44$$

The selected, rounded value is:

$$\log_{10} {}^{*}\beta^{\circ}\,(\text{C.20}) = -\,(4.9 \pm 0.4).$$

C.6.2 Propagation of errors

Whenever data are converted or recalculated, or other algebraic manipulations are performed that involve uncertainties, the propagation of these uncertainties has to be taken into account in a correct way. A clear outline of the propagation of errors is given by Bevington [1969BEV]. A simplified form of the general formula for error propagation is given by Eq. (C.21), supposing that X is a function of $Y_1, Y_2,\ldots,Y_N$.

$$\sigma_X^2 = \sum_{i=1}^{N}\left(\frac{\partial X}{\partial Y_i}\sigma_{Y_i}\right)^2 \qquad (\text{C.21})$$

Equation (C.21) can be used only if the variables, $Y_1, Y_2,\ldots,Y_N$, 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 formulae for a number of frequently encountered algebraic expressions, where c, c_1, c_2 are constants.

$X = c_1Y_1 \pm c_2Y_2$: $\quad \sigma_X^2 = (c_1\sigma_{Y_1})^2 + (c_2\sigma_{Y_2})^2$ (C.22)

$X = \pm\, cY_1Y_2$ and $X = \pm\dfrac{cY_1}{Y_2}$: $\quad \left(\dfrac{\sigma_X}{X}\right)^2 = \left(\dfrac{\sigma_{Y_1}}{Y_1}\right)^2 + \left(\dfrac{\sigma_{Y_2}}{Y_2}\right)^2$ (C.23)

$X = c_1Y^{\pm c_2}$: $\quad \dfrac{\sigma_X}{X} = c_2\dfrac{\sigma_Y}{Y}$ (C.24)

$X = c_1e^{\pm c_2 Y}$: $\quad \dfrac{\sigma_X}{X} = c_2\sigma_Y$ (C.25)

$X = c_1\ln\left(|c_2Y|\right)$: $\quad \sigma_X = c_1\dfrac{\sigma_Y}{Y}$ (C.26)

Example C.7:

A few simple calculations illustrate how these formulae are used. The values have not been rounded.

Eq. (C.22) : $\Delta_{\mathrm{r}}G_{\mathrm{m}} = 2[-(277.4 \pm 4.9)]\ \mathrm{kJ\cdot mol^{-1}} - [-(467.3 \pm 6.2)]\ \mathrm{kJ\cdot mol^{-1}}$

$= -\,(87.5 \pm 11.6)\ \mathrm{kJ\cdot mol^{-1}}$.

Eq. (C.23) : $K = \dfrac{(0.038 \pm 0.002)}{(0.0047 \pm 0.0005)} = (8.09 \pm 0.96)$

Eq. (C.24) : $K = 4(3.75 \pm 0.12)^3 = (210.9 \pm 20.3)$

Eq. (C.25) : $K^\circ = e^{\frac{-\Delta_\mathrm{r}G^\circ_\mathrm{m}}{RT}}$; $\Delta_\mathrm{r}G^\circ_\mathrm{m} = -\,(2.7 \pm 0.3)\ \mathrm{kJ{\cdot}mol^{-1}}$

$R = 8.3145\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$

$T = 298.15\ \mathrm{K}$

$K^\circ = (2.97 \pm 0.36).$

Note that powers of 10 have to be reduced to powers of *e*, *i.e.*, the variable has to be multiplied by ln(10), *e.g.*,

$$\log_{10} K = (2.45 \pm 0.10);\ K = 10^{\log_{10} K} = e^{(\ln(10)\cdot\log_{10} K)} = (282 \pm 65).$$

Eq. (C.26) : $\Delta_\mathrm{r}G^\circ_\mathrm{m} = -RT\ln K^\circ$; $K^\circ = (8.2 \pm 1.2) \times 10^6$

$R = 8.3145\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$

$T = 298.15\ \mathrm{K}$

$\Delta_\mathrm{r}G^\circ_\mathrm{m} = -\,(39.46 \pm 0.36)\ \mathrm{kJ{\cdot}mol^{-1}}$

$\ln K^\circ = (15.92 \pm 0.15)$

$\log_{10} K^\circ = \ln K^\circ / \ln(10) = (6.91 \pm 0.06).$

Again, it can be seen that the uncertainty in $\log_{10} K^\circ$ cannot be the same as in $\ln K^\circ$. The constant conversion factor of ln(10) = 2.303 is also to be applied to the uncertainty.

C.6.3 Rounding

The standard rules to be used for rounding are:

1. When the digit following the last digit to be retained is less than 5, the last digit retained is kept unchanged.
2. When the digit following the last digit to be retained is greater than 5, the last digit retained is increased by 1.
3. When the digit following the last digit to be retained is 5 and
   a) there are no digits (or only zeroes) beyond the 5, an odd digit in the last place to be retained is increased by 1 while an even digit is kept unchanged;
   b) other non-zero digits follow, the last digit to be retained is increased by 1, whether odd or even.

This procedure avoids introducing a systematic error from always dropping or not dropping a 5 after the last digit retained.

When adding or subtracting, the result is rounded to the number of decimal places (not significant digits) in the term with the least number of places. In multiplication and division, the results are rounded to the number of significant digits in the term with the least number of significant digits.

In general, all operations are carried out in full, and only the final results are rounded, in order to avoid the loss of information from repeated rounding. For this reason, several additional digits are carried in all calculations until the final selected data set is developed, and only then are data rounded.

C.6.4 Significant digits

The uncertainty of a value basically defines the number of significant digits a value should be given.

Example: (3.478 ± 0.008)

(3.48 ± 0.01)

(2.8 ± 0.4)

(10 ± 1)

(105 ± 20).

In the case of auxiliary data or values that are used for later calculations, it is often inconvenient to round to the last significant digit. In the value (4.85 ± 0.26), for example, the “5” is close to being significant and should be carried along a recalculation path in order to avoid loss of information. In particular cases, where the rounding to significant digits could lead to slight internal inconsistencies, digits with no significant meaning in absolute terms are nevertheless retained. The uncertainty of a selected value always contains the same number of digits after the decimal point as the value itself.

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Gianni, P.	[1972CAB/GIA]
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Gordon, R. S.	[1969RIZ/GOR], [1973GID/GOR], [1974GID/GOR]

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Goto, S.	[1977SAD/KAW]
Grunzweig, M.	[1913GRU]
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Grade, M.	[1984GRA/ROS], [1985GRA/ROS]
Graeme-Barber, A.	[1998CAR/SAL]
Grambow, B.	[2005BRO/CUR]
Grass, W.	[1933ESS/AVE]
Grauer, R.	[1997ALL/BAN]
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Greneche, J. M.	[2006BAR/GAR]
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Grodzicki, M.	[2007DAC/GEI]
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Gualtieri, A. F.	[1999GUA/VEN], [2004SCO/VEN]

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Häusermann, D.	[2000HAA/STO]
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Hüttig, G. F.	[1929HUT/GAR], [1931HUT/MOL]
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Hagemann, S.	[2004MOO/HAG], [2004RUM/HAG]
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Hallet, C.	[1985AUY/EAT]
Halow, I.	[1969WAG/EVA], [1982WAG/EVA]
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Heo, B.	[1999YU/HEO]
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Hilpert, K.	[1985HIL/VIS]
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Holmström, B.	[2007COH/CVI]
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Kennedy, D. W.	[2005KUK/ZAC]

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Merlini, M.	[2007PEK/PER]

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Salvatore, F.	[1983FER/GRE], [1985FER/GRE], [1990SAL/VAS]
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Sandino, M. C. A.	[1995GRE/PUI]
Sangster, J.	[2012GAM/GAJ]
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