Thermodynamic Properties of the Aqueous Ions (2+ and 3+) of Iron and the Key Compounds of Iron

V. B. Parker  
Chemical Kinetics and Thermodynamics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-0001

and

I. L. Khodakovskii  
Vernadsky Institute of Geochemistry and Analytical Chemistry, Moscow, Russia

Received January 25 1995; revised manuscript received July 5 1995

Recommended thermochrometry property values, $\Delta H^o$, $\Delta G^o$, and $S^o$ for the aqueous ions of iron, Fe$^{2+}$ and Fe$^{3+}$, are given at 298.15 K in SI units. They are consistent with the CODATA Key Values for Thermodynamics. The values are: $\Delta H^o = -90.0 \pm 0.5$ kJ·mol$^{-1}$, $\Delta G^o = -90.53 \pm 1.0$ kJ·mol$^{-1}$, $S^o = -101.6 \pm 3.7$ J·mol$^{-1}$·K$^{-1}$ for Fe$^{2+}$(aq) and $\Delta H^o = -49.0 \pm 1.5$ kJ·mol$^{-1}$, $\Delta G^o = -16.28 \pm 1.1$ kJ·mol$^{-1}$, $S^o = -278.4 \pm 7.7$ J·mol$^{-1}$·K$^{-1}$ for Fe$^{3+}$(aq). The evaluation involves the analysis of the enthalpy changes, Gibbs energy changes, and the entropy measurements for all key substances in the key network. A consistent set of thermochrometry property values is given for FeOOH(cr, Goethite), FeCl$_2$(cr), FeCl$_3$(cr), FeBr$_2$(cr), FeBr$_3$(cr), FeI$_2$(cr), and FeSO$_4$$^\cdot$7H$_2$O(cr), as well as "reconstituted" recommended process values with uncertainties involving these substances. All recommended values are also given for a standard state of $p^o$=1 atm. A computer based reaction catalog of measurements accompanies the text analysis. © 1995 American Institute of Physics and American Chemical Society.

Key words: data evaluation; aqueous Fe$^{2+}$; aqueous Fe$^{3+}$; CODATA; enthalpy; entropy; Gibbs energy; iron compounds; key values; reaction catalog; thermochrometric measurements.

Contents

1. Introduction ........................................ 1701
   1.1. General ....................................... 1701
   1.2. Conventions and Auxiliary Data .............. 1701
   1.2.1. Definitions and Symbols .................. 1701
   1.2.2. Reference States ........................... 1702
   1.2.3. Molar Masses ............................... 1702
   1.2.4. Units, Fundamental Constants, and Thermochrometric Property Values for Auxiliary Data ........................................ 1702
   1.2.5. Description of Bibliographic References ........................................ 1702
   1.2.6. Content and Description of the Reaction Catalog ........................................ 1702
   1.2.7. Uncertainties ................................... 1702
   1.3. Acknowledgments ............................... 1703
   1.4. Method of Approach ............................ 1703
   1.4.1. General ...................................... 1703
   1.4.2. The Systematic Analysis ................... 1703

2. The Evaluation of the Enthalpy of Formation of the Aqueous Ion Fe$^{2+}$, $\Delta H^o$(Fe$^{2+}$, aq) ............ 1704
   2.1. The Chloride System ........................... 1704
   2.1.1. $\Delta H^o$(FeCl$_2$, cr) .................. 1704
   2.1.1.1. Calorimetric Measurements of Fe(cr) and FeCl$_2$(cr) in HCl Solutions ............ 1704
   2.1.1.2. Calorimetric Measurements of Fe(cr), FeBr$_2$(cr), and FeBr$_3$(cr) in Aqueous (KBr, Br$_2$) Solutions .................... 1704
   2.1.1.3. The High Temperature Reduction of FeCl$_2$(cr) by H$_2$(g) .................. 1705
   2.1.1.4. Summary ................................... 1705
   2.1.2. The Standard Enthalpy of Solution of FeCl$_2$(cr) in H$_2$O(l) and the $\Delta H^o$(Fe$^{2+}$, aq) .................... 1705
   2.2. The Bromide System .......................... 1705
   2.2.1. $\Delta H^o$(FeBr$_2$, cr) ................. 1705
   2.2.1.1. Calorimetric Measurements of Fe(cr) and FeBr$_2$(cr) in Aqueous (KBr, Br$_2$) Solutions .................... 1705
   2.2.2. The Standard Enthalpy of Solution of FeBr$_2$(cr) in H$_2$O(l) and
4.2.4.2. Gibbs Energy of Solution of FeCl₂-4H₂O(cr). 1715
4.3. The Tentative Selected Value for Δ_{G}^{o}(Fe^{2+}, \text{ao}). 1716
5. The Evaluation of the Gibbs Energy of Formation of the Aqueous Ion Fe^{3+}, Δ_{G}^{o}(Fe^{3+}, \text{ao}) 1716
5.1. The properties of Goethite, FeOOH(cr, α). 1716
5.1.1. Δ_{H}^{o}(FeOOH, cr α)—Goethite 1716
5.1.2. Δ_{G}^{o}(FeOOH, cr α)—Goethite 1717
5.1.3. Gibbs Energy of Solution of FeOOH(cr, α) and Δ_{G}^{o}(Fe^{3+}, \text{ao}) 1717
5.1.4. The Direct Relationship between Δ_{G}^{o}(Fe^{2+}, \text{ao}) and Δ_{G}^{o}(Fe^{3+}, \text{ao}) 1717
5.1.4.1. The cell measurements 1717
5.1.4.2. The Equilibrium Constants 1717
5.1.5. The selected value for the Relationship between Δ_{G}^{o}(Fe^{2+}, \text{ao}) and Δ_{G}^{o}(Fe^{3+}, \text{ao}) 1718
5.2. The Selection of the Δ_{G}^{o}(Fe^{3+}, \text{ao}) 1718
6. Summary 1719
6.1. The Final Recommended Values 1719
6.2. Other Cycles in the Fe Network 1720
6.3. Effect of Values on Other Networks 1720
7. Bibliography on Selected Fe Compounds 1720
Appendix I: Reaction Catalogs for Selected Fe Compounds 1723
Al.a. Descriptive Information 1723
Al.b. Reaction Catalog 1724
Al.c. Reaction Catalog for Selected Iron Provided by IVTAN 1742

**LIST OF IADIES**

1. The enthalpy of formation of FeCl₂(cr) from the reaction, FeCl₂(cr) + H₂(g) = Fe(cr) + 2HCl(g). 1705
2. The values for AΔ_{H}^{o}(Fe^{2+}, \text{ao}). 1708
3. The enthalpy of oxidation of Fe^{2+}(ao) by H₂O₂ (α) and Δ_{H}^{o}(Fe^{3+}, \text{ao})−Δ_{H}^{o}(Fe^{2+}, \text{ao}) 1711
4. The enthalpy of formation of Fe^{3+}(ao) and Δ_{f} H^{o}(Fe^{3+}, \text{ao})−Δ_{f} H^{o}(Fe^{2+}, \text{ao}) 1711
5. The enthalpy of formation of FeOOH (cr, Goethite) from Fe₂O₃ (cr) and H₂O(l) 1716
6. The Gibbs energies of formation of Fe^{2+}(ao) and Fe^{3+}(ao) and Δ(Δ_{G}^{o}) = Δ_{G}^{o}(Fe^{3+}, \text{ao}) − Δ_{G}^{o}(Fe^{2+}, \text{ao}) (p₀ = 1 atm) 1718
7. Recommended thermodynamic property values (p₀ = 1 atm) 1719
8. Recommended thermodynamic property values (p₀ = 1 bar) 1719
9. The standard thermodynamic properties of reaction (p₀ = 1 bar) 1719
1. Introduction

1.1. General

This paper is concerned with the evaluation and selection of the thermochemical properties of the aqueous ions \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \), and with those related key compounds that are in the "key network." The properties studied are \( \Delta H^o \), \( \Delta L^o \), and \( S^o \) at 298.15 K; all recommended values are given in SI units. All values are consistent with the CODATA Key Values [89COX/WAG].

Values are also given for a standard state pressure of 1 atm since the CODATA recommended thermochemical values [89COX/WAG] for \( S^o \) and \( \Delta L^o \) used here are given in joules with the 1 atm standard state.

The evaluation of the above mentioned species is part of a study of the thermochemical properties of iron and some of its compounds, undertaken as part of a larger international project of thermodynamic tables under the auspices of the CODATA Task Group on Chemical Thermodynamic Tables. The concept and scope of this project are described in 87GAR/PAR, which contains the study of calcium and some of its compounds.

Although all sections of 87GAR/PAR are consistent, the contribution of each participating group was distinct. In the endeavor on the thermochemistry of some Fe compounds, closer cooperation occurred. The analysis of the thermochemical behavior, the accompanying reaction catalog, and the evaluation and selection of the property values for these species were achieved in close cooperation and consultation by the participating organizations: National Institute of Standards and Technology (NIST), Institute of High Temperatures (IVTAN), and Vernadsky Institute of Geochemistry and Analytical Chemistry (VIGAC).

There are three major aspects to this paper.

(1) The key network reactions and compounds related to the aqueous ions \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) are discussed in the heart of the text and used to define the key values. By a "key" compound we mean a species whose thermochemical properties are of strategic importance because many other compounds are dependent upon its thermochemical properties. The properties of this compound may, in turn, be dependent upon those of other compounds (from various reaction paths). This group of compounds and its interconnections comprise the "key network." These reactions are also contained in the Reaction Catalogs (Appendix I). For ease of location in the catalog, the number of the reaction in the catalog is given. Unless otherwise specified, all reactions are in Alb (Reaction Catalog) and, unless otherwise specified, reaction energies are to be assumed to be at 298.15 K and are given as kJ mol\(^{-1}\); the energy value is for the reaction as written.

For convenience to the users, \( E \) values and \( \Delta G \) values given in Secs. 4 and 5 are as originally obtained using \( p^o = 1 \text{ atm} \), unless otherwise stated; calculation to \( \Delta G^o(\text{Fe}^{2+}, \text{ao}) \) and \( \Delta G^o(\text{Fe}^{3+}, \text{ao}) \) is also made at \( p^o = 1 \text{ atm} \). Final conversion is made to \( p^o = 1 \text{ bar} \) in Sec. 6.

(2) Other pertinent reactions contributing to, but not considered definitive for, the key compounds' values are given.

(3) A reaction catalog which includes all reactions available or considered on many compounds of interest with detailed commentary on the specifics of the reactions is given. Each reaction is numbered.

1.2. Conventions and Auxiliary Data

1.2.1. Definitions and Symbols

The recommendations of the Division of Physical Chemistry of the International Union of Pure and Applied Chemistry (82IUPAC) are followed for thermodynamic conventions, standard states, terminology, nomenclature, symbols, and units. The symbols used here are also given in 89COX/WAG.

In addition, in order to maintain the same symbols base in the text as is given in the database reaction catalog (Alb), the following are used:

- \( a = \) hypothetical standard state, \( m = 1 \text{ mol} \cdot \text{kg}^{-1} \) for an electrolyte in aqueous solution (the sum of the values for the ions)
- \( ao = \) hypothetical standard state, undissociated
- \( aq = \) aqueous, unspecified concentration, usually dilute 250 H_2O, etc.,=solution of specified composition
- \( D = \) differential (partial molar property).

For aqueous solutions the following are used:

- \( \Phi_L = \) the relative apparent molar enthalpy = the integral enthalpy of dilution of the solute to infinite dilution
- \( \bar{L}_2 = \) the relative partial molar enthalpy of the solute in the given solution

\[
\Phi_{L(D-H)} = \Delta L^2 \left[ \frac{G_H}{4B_1} \right] + \frac{W_H}{(4B_1)^{1/2}}
\]

where

\[
y_1 = 1 - \frac{2}{4B_1^{1/2}} + \frac{2 \ln (1 + 4B_1^{1/2})}{(4B_1^{1/2})^2},
\]

\[
y_2 = 1 - \frac{4}{4B_1^{1/2}} + \frac{1}{(4B_1^{1/2})^2} \left[ \ln (1 + 4B_1^{1/2}) - 1 \right],
\]

\[
\Delta L^2 = \Sigma (z^2 \text{ ions, products} - z^2 \text{ ions, reactants}),
\]

\( z = \) charge on the ion,

at 298.15 K, B = 0.3285,

\( S_H = 1.4703 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \),

\( W_H = -54183 \text{ kJ} \cdot \text{mol}^{-1} \).

So that

---

*This is a reference code used in the text and in the accompanying reaction catalog. It is keyed to the bibliographic references given in Sec. 7. A description of the reference code is given in 1.2.5 and Alb.
This equation is used where applicable.

1.2.2. Reference States
The reference states used are as given in 89COX/WAG.

1.2.3. Molar Masses
The molar masses used are consistent with the relative atomic masses recommended by 86IUP and given in 88MIL/CVI.

1.2.4. Units, Fundamental Constants, and Thermochemical Property Values for Auxiliary Data
All recommended values in the tables are given in SI units as recommended by 82IUP. Values for the fundamental constants are taken from 86COH/TAY (see 88MIL/CVI for consolidated IUPAC Physical Chemistry units, etc.).
The primary source for all thermochemical property values is 89COX/WAG which gives the CODATA Key Values for thermodynamics; those used here will not be repeated. Citation to readily available literature values consistent with CODATA selections will be made. Those values not readily available will be given here.

1.2.5. Description of Bibliographic References
In order to use the same reference citation in the text as in the computer based reaction catalog, a reference code is used. The citation is given as follows:
The final two digits of the year (nineteenth century citations carry the four digits) precede the first three letters of the first two authors’ last names (separated by a slash) in upper case letters. A number at the end of the code indicates that there is more than one reference having the same first two authors’ codes and year of publication.
The Bibliography in Sec. 7 is arranged chronologically by this reference code and alphabetically by the first author within each year. A full reference, including all authors, journal volume, page, and year of publication accompanies each reference code. Protocols for the computer format for entering references into the bibliography have been prepared by 83NEU.

1.2.6. Content and Description of the Reaction Catalog
The reaction catalog (Appendix I) is setup as a databank in a format developed for input of the information into a form more suitable for storage and calculation [83NEU]. This format was used as input for the calcium reaction catalog output published in 87GAR/PAR. A description follows:

Z: the reference code as described in Sec. 1.2.5
R: the reaction studied or the substance studied. If it is for a substance studied, the substance formula will be preceded by an = sign. This is primarily used for the entropy of a substance.

DV: the thermodynamic property measured for the reaction listed, the temperature, the value and uncertainty, and the units. The uncertainties in the values for reactions listed in the reaction catalog and used in the text are initial uncertainties assumed by the evaluator as discussed in 87PAR/EVA and may not agree with the experimentalist’s appraisal.

F: a flag to indicate special features such as a subcatalog. Here it is used with TN to indicate that the reaction was used in the 69WAG/EVA (Technical Note Series) evaluation. However, the absence of this flag does not indicate that it was not considered for the 1969 evaluation.

W: this is a weighting code. If it is followed by -1, it is a constraint to accept the value with no modification; if it is followed by 99, it is for information only (i.e., the measurement is not given any weight in the evaluation).

C: (and CC:) comments pertaining to the reaction or other pertinent information
*: private comments and working notes
S: Name or initials of the evaluator and the date of the preparation or modification of the entries.
The thermochemistry property designation for reactions is H for ΔH: G for ΔG; S for ΔS: and S° (if the R: entry is for a substance, the formula is preceded by an =).
The temperature is given in degrees Kelvin or Celsius. If the temperature is not specified, the measurement is assumed to refer to 298.15 K. The pressure can be assumed to be either one bar or one atmosphere. For ΔG's (where needed) or S°'s of gases, the pressure is stated in the comments. The thermochemical value and uncertainty are given as decimal numbers. The currency symbol (in the U.S., the "$" is used to separate the value and its uncertainty and represents ±.
The shorthand abbreviations for the units used in the catalog are dependent on the property so that:
kJ=kJ·mol⁻¹ for H,G, and kJ·mol⁻¹·K⁻¹ for S, Cp kJ=kJ·mol⁻¹ for H,G, and kJ·mol⁻¹·K⁻¹ for S, Cp

J=J·mol⁻¹·K⁻¹ for S, Cp

C=cal·mol⁻¹·K⁻¹ for S, Cp

K, °C = degrees Kelvin, Celsius temperature.
All values are for the reaction as given.

1.2.7. Uncertainties
The uncertainties in the values for reactions listed in the reaction catalog (Appendix I) and used in the text are initial uncertainties assumed by the evaluator, as discussed in 87PAR/EVA and may or may not agree with the experimentalist’s appraisal. In the course of the evaluation and in rationalizing the property values of a substance from the various measurement paths and from replicate measurements of the same path, this initial judgment may prove to be unrealistic.
The thermodynamic properties of the aquo ions of iron

The uncertainties listed in the tables of recommended property values for the substances are the evaluator’s final estimate of the reliability of the predicted value. Use of these uncertainties, however, to calculate the uncertainty of a process value (as the square root of the sum of the squares of all the uncertainties in the properties of the substances in the process) may result in too high a value since (1) the assigned uncertainty on the property value incorporates the uncertainties on the process values from which it is derived and (2) the property values of the substances in the process could be highly correlated. In order to avoid this, the recommended reconstituted process values for the processes of interest are tabulated with the evaluator’s estimated reliability (assumed to have a level of confidence of 95%).

1.3. Acknowledgments

We wish to acknowledge the early contributions of V. Medvedev (IVTAN) and O. Devina (VIGAC) towards the evaluation, to M. Efimov (IVTAN) for releasing his experimental results to us before publication, and to L. Gurvich (IVTAN) for thermal function data. We wish to thank the Standard Reference Data Program (NIST) for their financial support and M. W. Chase and his staff for their editorial assistance.

1.4. Method of Approach

1.4.1. General

The sequential method, as described by 76GAR/PAR and 77GAR/PAR, is used. In this method all data on the compounds of interest in the network of the element are assembled and the properties, \( \Delta H^o \), \( \Delta G^o \), and \( S^o \) are calculated and evaluated compound by compound, starting with the compounds whose properties can be determined independently, that is, they depend only on known auxiliary data (in this case, CODATA KEY VALUES [89COX/WAG] and CODATA Compatible Values), and not on any other compounds of the same element. Then the properties of other compounds dependent on these first selections are set. If several measurement paths involve the same compound, a confirmation of the choice may be obtained. If confirmation of the choice (within the stated uncertainty) is not obtained, a “reworking” of the previous selections may be made and revised values selected in order to obtain a reasonable over-all fit. This manual sequential method is iterative. More than one pass is involved in establishing the final values for the key compounds in the key network. In order to show the evolution to final recommended values in the evaluation we indicate in each section our initial selection, that is, our tentative or working value, and its modification as we proceed in our evaluation to test, rationalize or modify, and finalize our recommendations. So that the user will understand this, we will also indicate in each section what the final resolved recommendations will be.

1.4.2. The Systematic Analysis

The major compounds in the key network for the determination of the properties of Fe\(^{2+}\)(ao) and Fe\(^{3+}\)(ao) are: Fe\(_2\)O\(_4\)(cr), FeOOH(cr), Goethite), FeCl\(_2\)(cr), FeCl\(_3\)-4H\(_2\)O(cr), FeCl\(_3\)(cr), FeBr\(_2\)(cr), FeBr\(_3\)(cr), FeI\(_2\)(cr), FeSO\(_4\)-7H\(_2\)O(cr), and (NH\(_4\))\(_2\)Fe(SO\(_4\))\(_2\)-6H\(_2\)O(cr).

The following chapter descriptions show the approach. The relevant information also is repeated at the beginning of each chapter.

Section 2—Here we evaluate the measurements leading to \( \Delta H^o(\text{Fe}^{2+}, \text{ao}) \) beginning with:

1. the determinations of \( \Delta H^o(\text{FeCl}_2, \text{cr}) \), independent of other Fe compounds, and the \( \Delta_{\text{mol}}H^o \) of FeCl\(_2\)(cr) in H\(_2\)O(l); an initial selection is made for \( \Delta H^o(\text{FeCl}_2, \text{cr}) \);

2. the determinations of \( \Delta H^o(\text{FeBr}_2, \text{cr}) \), independent of other Fe compounds, and the \( \Delta_{\text{mol}}H^o \) of FeBr\(_2\)(cr) in H\(_2\)O(l); this also requires an initial selection for \( \Delta H^o(\text{FeBr}_2, \text{cr}) \);

3. the measurements of \( \Delta H^o(\text{FeI}_2, \text{cr}) \); those independent of other Fe compounds, and then that dependent upon \( \Delta H^o(\text{FeBr}_2, \text{cr}) \); an initial selection is also made for \( \Delta H^o(\text{FeI}_2, \text{cr}) \), as well as \( \Delta_{\text{mol}}H^o \);

4. the independently determined \( \Delta H^o(\text{FeSO}_4\cdot7\text{H}_2\text{O}, \text{cr}) \) and the \( \Delta_{\text{mol}}H^o \) in H\(_2\)O(l);

5. the independently arrived at \( \Delta H^o((\text{NH}_4)_2\text{Fe(SO}_4)_2\cdot\text{cr}) \) and its \( \Delta_{\text{mol}}H^o \) in H\(_2\)O(l).

In Sec. 2.5 we tabulate the various values obtained for \( \Delta H^o(\text{Fe}^{2+}, \text{ao}) \) from our initial selections for the \( \Delta H^o \)’s of the ferrous halides and sulfates and make our tentative selection for \( \Delta H^o(\text{Fe}^{2+}, \text{ao}) \) and also make adjustments to our initial selections for the salts.

Section 3—The \( \Delta H^o(\text{Fe}^{3+}, \text{ao}) \) is evaluated. We begin with:

1. the determinations for \( \Delta H^o(\text{FeCl}_3, \text{cr}) \), those independent of other Fe compounds as well as those linked to FeCl\(_2\)(cr), combined with a selection for \( \Delta_{\text{mol}}H^o(\text{FeCl}_3, \text{cr}) \) which in itself requires a working value;

2. the direct determination of \( \Delta H^o(\text{Fe}^{3+}, \text{ao}) \) through oxidation of Fe(cr);

3. the enthalpy relationship between Fe\(^{3+}\)(ao) and Fe\(^{2+}\)(ao).

In Sec. 3.4 we summarize the various possibilities and select a value for \( \Delta H^o(\text{Fe}^{3+}, \text{ao}) \), modify our initial selection for \( \Delta H^o(\text{FeCl}_3, \text{cr}) \), and also select a value for \( \Delta H^o(\text{FeBr}_3, \text{cr}) \). These selections will eventually become our final recommended values.

Section 4—The \( \Delta G^o(\text{Fe}^{2+}, \text{ao}) \) is evaluated from:

1. e.m.f. (Sec. 4.1) and some equilibrium constant measurements (Sec. 4.2) that result in values for \( \Delta G^o \) independent of other Fe species;

2. equilibrium measurements involving solubilities of Fe\(_2\)O\(_4\)(cr, magnetite) (Sec. 4.2.2) and FeSO\(_4\)-7H\(_2\)O(cr) (Sec. 4.2.3) and FeCl\(_3\)-4H\(_2\)O(cr) (Sec. 4.2.4) which also involves its vapor pressure.

In Sec. 4.7 a tentative selection is made (\( \rho^o = 1 \) atm).

Section 5—The \( \Delta G^o(\text{Fe}^{3+}, \text{ao}) \) is evaluated by:
V. B. PARKER AND I. L. KHODAKOVSKII

(1) establishing the thermochemical property values of FeOOH(cr, Goethite) and its $\Delta_{sol}G^\circ$ (Sec. 5.1.3) to obtain a value for $\Delta_H^\circ$ and

(2) by obtaining values for $\Delta H^\circ(\text{Fe}^{3+}, \text{ao}) - \Delta H^\circ(\text{Fe}^{2+}, \text{ao})$ (Sec. 5.1.4) that are independent of the properties of other iron compounds, from cell measurements and other equilibrium measurements and using our tentative value for $\Delta H^\circ(\text{Fe}^{2+}, \text{ao})$ to obtain other values for $\Delta H^\circ(\text{Fe}^{3+}, \text{ao})$.

In Secs. 5.1.5 and 5.2 we finalize the selections for the $\Delta (\Delta H^\circ)$’s and for $\Delta H^\circ(\text{Fe}^{3+}, \text{ao})$ ($p^\circ = 1$ atm), rationalising our selections by reviewing the effect on values for $\Delta H^\circ$ and $\Delta_{sol}H^\circ$ of substances in the key network.

Section 6—All final recommended property values and uncertainties are tabulated (at $p^\circ = 1$ atm and $p^\circ = 1$ bar). Predicted (calculated) process values and uncertainties for many of the reactions used in this evaluation are also tabulated. In addition, a list of reactions (contained in the reaction catalog) pertinent to this evaluation but not definitive are given (Sec. 6.2).

2. The Evaluation of the Enthalpy of Formation of Aqueous Fe$^{2+}$, $\Delta H^\circ(\text{Fe}^{2+}, \text{ao})$

Here we evaluate the measurements leading to $\Delta H^\circ(\text{Fe}^{2+}, \text{ao})$ beginning with:

(1) the determinations of $\Delta H^\circ(\text{FeCl}_2, \text{cr})$, independent of other Fe compounds, and the $\Delta_{sol}H^\circ$ of FeCl$_2$(cr) in H$_2$O(l); an initial selection is made for $\Delta H^\circ(\text{FeCl}_2, \text{cr})$;

(2) the determinations of $\Delta H^\circ(\text{FeBr}_2, \text{cr})$, independent of other Fe compounds, and the $\Delta_{sol}H^\circ$ of FeBr$_2$(cr) in H$_2$O(l); this also requires an initial selection for $\Delta H^\circ(\text{FeBr}_2, \text{cr})$;

(3) the measurements of $\Delta H^\circ(\text{Fe}_2, \text{cr})$; those values independent of other Fe compounds, and then that dependent upon $\Delta H^\circ(\text{FeBr}_2, \text{cr})$; an initial selection is also made for $\Delta H^\circ(\text{Fe}_2, \text{cr})$, as well as $\Delta_{sol}H^\circ$;

(4) the independently determined $\Delta H^\circ(\text{FeSO}_4\cdot7\text{H}_2\text{O}, \text{cr})$ and the $\Delta H^\circ$ in H$_2$O(l);

(5) the independently arrived at $\Delta H^\circ(\text{NH}_4\text{Cl}_2\text{FeSO}_4\cdot2\text{cr}, \text{cr})$ and its $\Delta_{sol}H^\circ$ in H$_2$O(l).

In Sec. 2.5 we tabulate the various values obtained for $\Delta H^\circ(\text{Fe}^{2+}, \text{ao})$ from our initial selections for the $\Delta H^\circ$’s of the ferrous halides and sulfates and make our tentative selection for $\Delta H^\circ(\text{Fe}^{2+}, \text{ao})$ and also make adjustments to our initial selections for the salting.

2.1. The Chloride System

2.1.1. $\Delta H^\circ(\text{FeCl}_2, \text{cr})$

2.1.1.1. Calorimetric measurements of the enthalpies of the reaction of Fe(cr) and FeCl$_2$(cr) in HCl solutions

There are two determinations for the enthalpy of the reaction:

$$\text{Fe(cr)} + 2\text{HCl}$$.n$\text{H}_2\text{O}) = \text{FeCl}_2(\text{cr}) + \text{H}_2(\text{g})$$

\[ \Delta H = -17.04 \pm 0.21 \text{ kJ mol}^{-1} \ (n=12.731)[59KOE/COU (No. 90)] \]

and

\[ \Delta H = -12.85 \pm 0.20 \text{ kJ mol}^{-1} \ (n=200)[1882THO (No. 89)] \]

Correction to the standard state of HCl(aq), using $\phi_i$ from 65PAR, results in $\Delta H^\circ = -7.50 \pm 0.21$ and $-11.08 \pm 2.0$ kJ mol$^{-1}$, respectively, for

$$\text{Fe(cr)} + 2\text{HCl(aq)} = \text{FeCl}_2(\text{cr}) + \text{H}_2(\text{g})$$

and

\[ \Delta H^\circ(\text{FeCl}_2, \text{cr}) = -341.66 \pm 0.25 \text{ and } -345.24 \pm 2.0 \text{ kJ mol}^{-1} \]

2.1.1.2. Calorimetric measurements of the enthalpies of the reaction of Fe(cr), FeBr$_2$(cr) and FeCl$_2$(cr) in aqueous (KBr, Br$_2$) solutions.

Recently, 89EF/3V3 and 89V3/EF3 (Nos. 115 and 166) measured the enthalpies of reaction of Fe(cr), FeBr$_2$(cr), and FeCl$_2$(cr) in (KBr, Br$_2$) solutions, as well as the enthalpy of solution of KCl(cr) and KBr(cr) in the same medium to result in the following summations:

1. Fe(cr) + Br$_2$(l) = FeBr$_2$(cr);

\[ \Delta H^\circ = -244.737 \pm 0.22 \text{ kJ mol}^{-1} \]

2. FeBr$_2$(cr) + 2KCl(cr) = FeCl$_2$(cr) + 2KBr(cr);

\[ \Delta H^\circ = -10.032 \pm 0.21 \text{ kJ mol}^{-1} \]

Using the following:

3a. KCl(cr) = K$^+$ (ao) + Cl$^-$ (ao);

\[ \Delta H^\circ = 17.245 \pm 0.045 \text{ kJ mol}^{-1}[87GAR/PAR] \]

and

3b. KBr(cr) = K$^+$ (ao) + Br$^-$ (ao);

\[ \Delta H^\circ = 19.75 \pm 0.05 \text{ kJ mol}^{-1}[89PAR] \]

we obtain

4. FeBr$_2$(cr) + 2Cl$^-$ (ao) = FeCl$_2$(cr) + 2Br$^-$ (ao);

\[ \Delta H^\circ = -5.032 \pm 0.22 \text{ kJ mol}^{-1} \]

Thus, $\Delta H^\circ(\text{FeCl}_2, \text{cr}) - \Delta H^\circ(\text{FeBr}_2, \text{cr}) = -96.372 \pm 0.24 \text{ kJ mol}^{-1}$, and using $\Delta H^\circ(\text{H}^+)$, $\Delta H^\circ(\text{FeCl}_2, \text{cr}) = -341.10 \pm 0.22 \text{ kJ mol}^{-1}$, in support of 59KOE/COU (Sec. 2.1.1.1). Similar measurements were made by 34HIE/WOE (No. 167) at 273.15 K for Fe(cr), Br$_2$(l) and FeBr$_2$(cr) to obtain (corrected to 298.15 K)

\[ \Delta H^\circ(\text{FeBr}_2, \text{cr}) = -251.84 \pm 5.0 \text{ kJ mol}^{-1} \]

Since 34HIE/AP (No. 168) measured the enthalpies of solution of FeCl$_2$(cr) and FeBr$_2$(cr) in 2 mol dm$^{-3}$ HCl (see 8.2 for all details) we have, in place of the above reaction (2):

$^5$Selected from sources cited and used by 89COX/WAG in developing the key values for the thermodynamic property values of the ions.
TABLE 1. The enthalpy of formation of FeCl₂ (cr) from the reaction, FeCl₂(cr)+H₂(g)=Fe(cr)+2HCl(g)  

<table>
<thead>
<tr>
<th></th>
<th>ΔH°, kJ·mol⁻¹</th>
<th>−ΔH°, kJ·mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>161.6±12</td>
<td>156.93±3.0</td>
</tr>
<tr>
<td>III</td>
<td>385AN</td>
<td></td>
</tr>
<tr>
<td></td>
<td>158±4.0</td>
<td>154.84±1.7</td>
</tr>
<tr>
<td></td>
<td>(No. 86)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>43WAG/EVE</td>
<td>157.10±1.0</td>
</tr>
<tr>
<td></td>
<td>(No. 88)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50KAN/PET</td>
<td>155.8±5.2</td>
</tr>
<tr>
<td></td>
<td>(No. 83)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>52NOV/ORA</td>
<td>137.±10</td>
</tr>
<tr>
<td></td>
<td>(No. 84)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60NOV/MAK</td>
<td>134.6±4.3</td>
</tr>
<tr>
<td></td>
<td>(No. 85)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>This study</td>
<td>127.1±1.0</td>
</tr>
</tbody>
</table>

These values were obtained using φL calculated from the 82COB/MUR measurements of ΔH° of FeCl₂(cr) as a function of moleality in the range 0.0002 to 0.0111 mol·kg⁻¹ (total ionic strength 0.0115 to 0.0373 mol·kg⁻¹) and the direct enthalpies of dilution of a FeCl₂ solution by 79BER/MOR (No. 116) (m=4.43 mol·kg⁻¹) to final solutions in the range 0.0016 to 0.0052 mol·kg⁻¹ (total ionic strength 0.0049 to 0.0157 mol·kg⁻¹).

We accept for a "tentative" or working value, ΔH°(FeCl₂, cr) = −83.00±0.10 kJ·mol⁻¹. With the initial value ΔH°(FeCl₂, cr) = −341.66±0.25 kJ·mol⁻¹ and ΔH°(FeCl₂, cr) = −340.4±2.0 kJ·mol⁻¹, we obtain ΔH°(FeCl₂, cr) = −49±0.6 kJ·mol⁻¹ and ΔH°(FeCl₂, cr) = −345±5.3 kJ·mol⁻¹, in support of 1882THO. It should be pointed out that the ΔH°(FeCl₂, cr) of 89EVE/EF1 from 89EVE/EF1 and 89EVE/WOE and the measurements of 34H/EVE/APP are in closer agreement than the enthalpies of formation indicate.

2.1.1.3. The high-temperature reduction of FeCl₂(cr) by H₂(g)

For the reaction: FeCl₂(cr)+H₂(g)=Fe(cr)+2HCl(g), we tabulate (Table 1) the second (II) and third (III) law results from six studies considered in this analysis (see Sec. 8.2 entries for details) and the weighted average of the third law values.

2.1.4. Summary

The considered values for ΔH°(FeCl₂, cr)/kJ·mol⁻¹ are −341.66±0.25 [59KOE/COU], −341.11±0.22 [89EVE/EV] and −341.72±1.0 [see Sec. 2.1.1.3] (we reject from consideration the early 1882THO value of −345.74±2.0 kJ·mol⁻¹) from which we initially select −341.66±0.25 kJ·mol⁻¹ and which we will use in Sec. 2.1.2.

2.1.2. The Standard Enthalpy of Solution of FeCl₂(cr) in H₂O(l)

For the process: FeCl₂(cr)=Fe²⁺(aq)+2Cl⁻(aq), the measurements lead to the following:

3. FeCl₂(cr) + H₂O(l) = Fe²⁺(aq) + 2Cl⁻(aq) + 2H⁺(aq)

ΔH° = −245.00±0.25 kJ·mol⁻¹.

2.2. The Bromide System

2.2.1. ΔH°(FeBr₂, cr)

2.2.1.1. Calorimetric measurements of the enthalpies of reaction of Fe(cr) and FeBr₂(cr) in aqueous (KBBr) solutions

In Sec. 2.1.1.2 we obtain two values for ΔH°(FeBr₂, cr), −244.74±0.22 kJ·mol⁻¹ [89EVE/EV] and −251.44±5.2 kJ·mol⁻¹ [34H/EVE/APP], although the ΔH°(FeCl₂, cr)=ΔH°(FeBr₂, cr)'s are in closer agreement, −96.9±0.24 [89EVE/EF1] and −94.3±1.6 kJ·mol⁻¹, respectively. We initially select ΔH°(FeBr₂, cr) = −245.00±0.25 kJ·mol⁻¹.

2.2.2. The Standard Enthalpy of Solution of FeBr₂(cr) in H₂O(l)

From Al, we have ΔH°(FeBr₂, cr)/kJ·mol⁻¹ = −86.85±0.10 [90EVE/FUR (No. 178)], −85.53±0.20 [52GRE/LI (No. 186)], −85.75±0.6 [65PAO (No. 174)]², and −88.3±4.0 [34H/EVE/APP (No. 170)]². We take for our initial selection ΔH°(FeBr₂, cr)=−86.85±0.12 kJ·mol⁻¹, resulting in ΔH°(Fe²⁺(aq), −89.0±0.28 kJ·mol⁻¹. However, com-

One can also obtain ΔH°(FeCl₂, cr)−ΔH°(FeBr₂, cr) = −98.0±0.5 kJ·mol⁻¹ from the difference in the standard enthalpies of solution of both salts in H₂O (−83.11 and −86.85 kJ·mol⁻¹, respectively) [90EVE/FUR (Nos. 94 and 178)] and the difference in ΔH°(Fe²⁺, (aq) = −89.0±0.28 kJ·mol⁻¹. However, com-

²Using estimated φL values based on φL(0,0) and the behavior of other bivalent-univalent halides [82WAG/EVA].
2.3. The Iodide System

2.3.1. ΔH°(FeI₂, cr)

2.3.1.1. Calorimetric measurements of the enthalpies of reactions of Fe(cr), FeI₂(cr), and I₂(cr) in aqueous (KBr, Br₂) solutions.

The measurements of 90E8_F/VOE (No. 194) on the ΔǝH of all three components in aqueous KBr, Br₂ solutions lead to:

Fe(cr) + I₂(cr) = FeI₂(cr); ΔH° = -118.079 ± 0.27 kJ·mol⁻¹.

From the results of 34HIE/WOE (No. 198), we obtain ΔH° = -125.9 ± 5.0 kJ·mol⁻¹.

2.3.1.2. Decomposition of FeI₂(cr)

The measurements of 66ZAI/CRES (No. 196) on the decomposition pressure of FeI₂(cr) lead to a third law ΔH° = 166.1 ± 5.0 kJ·mol⁻¹ for

FeI₂(cr) = Fe(cr) + I₂(g)

and ΔH° = 103.7 ± 5.1 kJ·mol⁻¹.

The measurements of 65SCH/ORA (No. 197) on the decomposition of FeI₂(l) yield widely different values, a second law ΔH° = 193.9 ± 20 kJ·mol⁻¹ and a third law ΔH° = 149.4 kJ·mol⁻¹, which result in ΔH° = -131 and -87 kJ·mol⁻¹, respectively.

We reject the values obtained from the decomposition of FeI₂(cr) and FeI₂(l).

2.3.1.3. ΔH°(FeI₂, cr) - ΔH°(FeBr₂, cr) and ΔH°(FeI₂, cr)

The measurements of 89E8_F/EVD (Nos. 165 and 194) and 90E8_F/EVD (No. 195) on the ΔǝH of all components in aqueous KBr, Br₂ lead to:

1. FeBr₂(cr) + I₂(cr) = FeI₂(cr) + Br₂(l);
ΔH° = 126.658 ± 0.24 kJ·mol⁻¹,

and

2. FeBr₂(cr) + 2KI(cr) = FeI₂(cr) + 2KBr(cr);
ΔH° = 1.677 ± 0.19 kJ·mol⁻¹.

Reaction (1) yields ΔH°(FeI₂, cr) - ΔH°(FeBr₂, cr) = 126.658 ± 0.24 kJ·mol⁻¹. Since ΔǝH°(FeI₂, cr) = 197.5 ± 0.05 kJ·mol⁻¹ and ΔǝH°(FeBr₂, cr) = 28.20 ± 0.10 kJ·mol⁻¹, we obtain from reaction (2)

3. FeBr₂(cr) + 2I⁻(aq) = FeI₂(cr) + 2Br⁻(aq);
ΔH° = 2.94 ± 0.30 kJ·mol⁻¹ and Δ(ΔH°)
= 163.52 ± 0.30 kJ·mol⁻¹.

Earlier, we obtained from 34HIE/WOE's similar measurements in (KBr,Br₂) solutions ΔH°(FeBr₂, cr) = -251.44 kJ·mol⁻¹ so that Δ(ΔH°) = 125.54 kJ·mol⁻¹.

We can also obtain from the results of 34HIE/APP on the ΔǝH°(FeBr₂, cr) and ΔǝH°(FeI₂, cr) in 2 mol·dm⁻³ HCl (see Al.b, Nos. 168 and 199 for details)

ΔH° = 1.49 kJ·mol⁻¹ for reaction (3) leading to Δ(ΔH°) = 130.5 kJ·mol⁻¹.

The measurements on the ΔǝH of FeBr₂(cr) in 2000H₂O(l) [65PAO (No. 174)] and on FeI₂(cr) in 4000H₂O(l) [65PAO/SAD (No. 201)] may be combined such that:

4. FeBr₂(cr) + FeI₂(4000H₂O) = FeI₂(cr) + FeBr₂(2000H₂O);
ΔH = -2.93 ± 0.56 kJ·mol⁻¹.

Estimating (Al.b, No. 176)

5. FeBr₂(2000H₂O) = FeBr₂(4000H₂O);
ΔH = -0.20 ± 0.20 kJ·mol⁻¹,

and assuming correction to standard conditions is essentially the same for FeBr₂(4000H₂O) and Fe₂, we obtain ΔH°(3) = -3.13 ± 0.6 kJ·mol⁻¹ and Δ(ΔH°) = 126.13 ± 0.6 kJ·mol⁻¹.

The Δ(ΔH°)'s are in good agreement, and using Δ(ΔH°) = 126.5 ± 0.3 kJ·mol⁻¹ and our tentative ΔH°(FeBr₂, cr) = -245.00 ± 0.25 kJ·mol⁻¹, we obtain -118.5 ± 0.4 kJ·mol⁻¹ for ΔH°(FeI₂, cr), in agreement with the direct determination = 118.08 ± 0.27 kJ·mol⁻¹ from 90E8_F/EVD and 89E8_F/EVD. We tentatively select -118.5 ± 0.4 kJ·mol⁻¹.

2.3.2. The Standard Enthalpy of Solution of FeI₂(cr) in H₂O(l)

and ΔH°(Fe²⁺, aq)

The enthalpy of solution of has been measured by 65PAO/SAB (No. 201) in 4000H₂O as -81.42 ± 0.25 kJ·mol⁻¹. With an estimate for φ = 2 ± 0.5 kJ·mol⁻¹, ΔH° becomes -82.62 ± 0.6 kJ·mol⁻¹ and with our "tentative" ΔH°(FeI₂, cr) = -118.5 ± 0.40 kJ·mol⁻¹, we obtain ΔH°(Fe₂I₄, aq) = -118.08 ± 0.27 kJ·mol⁻¹. If we use ΔH°(FeI₂, cr) = -118.08 ± 0.27 with the above ΔH°(FeI₂, cr) = -118.14 ± 0.7 kJ·mol⁻¹.
The values are tabulated (Table 2) in Sec. 2.5.

These values are tabulated (Table 2) in Sec. 2.5.

*From their ΔH°(FeBr₂, cr) - ΔH°(FeCl₂, cr) = 96.37 ± 0.24 kJ·mol⁻¹ one can obtain ΔH°(FeCl₂, cr) - ΔH°(FeBr₂, cr) = 222.97 ± 0.31 kJ·mol⁻¹. This relationship is equally important in the final smoothing process.

*Selected from sources cited and used by 89COX/WAG in developing the key values of thermodynamic property values of the ions.
2.4. The Sulfate System

2.4.1. ΔH°(FeSO₄·7H₂O, cr)

The catalog entry in AI.b from 85VAS/DIM2 (No. 221) lists the following composite reaction from oxidation by H₂O₂ in HClO₄ solutions:

\[
\text{Fe(cr)} + \text{H₂O₂(3.5H₂O)} + \text{5H₂O(l)} + \text{H₂SO₄(0.3H₂O)} \rightarrow \text{FeSO₄·7H₂O(cr)};
\]

\[\Delta H = -569.96 \pm 0.28 \text{ kJ mol}^{-1}.\]

The resultant ΔH° is -3013.66 ± 0.5 kJ mol⁻¹. 63ADA/KEL (No. 211) measured the enthalpy of reaction of Fe(cr) and the ΔΔH of the dehydration in H₂SO₄·7.066H₂O such that

\[\text{Fe(cr)} + \text{H₂SO₄·7.068H₂O} \rightarrow \text{FeSO₄·7H₂O(cr)} + \text{H₂(g)}\]

\[\Delta H = -137.09 \pm 0.40 \text{ kJ mol}^{-1}.\]

The resultant ΔH° is -3014.47 ± 0.45 kJ mol⁻¹. The measurements are in excellent agreement with one another; an average value of -3014.06 ± 0.40 kJ mol⁻¹ shall be used for ΔH°(FeSO₄·7H₂O, cr) in the following section.

2.4.1.1. Enthalpy of solution of the dehydrate and ΔH°(Fe²⁺, ao)

2.4.1.1.1. Enthalpy of solution in H₂O

The process of interest is:

\[\text{FeSO₄·7H₂O(cr)} \rightarrow \text{FeSO₄(aq)} + \text{7H₂O(l)}\]

The early measurements of 68LAR/CER (No. 229) and 68LAR are given as ΔH° = 11.80 ± 0.42 kJ mol⁻¹ (see catalog entry for details). This value includes estimates for φ₁, based on φ₁(NiSO₄). The recent measurements of 83DIMI (No. 227) on ΔΔHₚ, as a function of m to enable one to calculate φ₁ in FeSO₄(aq) and to correct; although the φ₁(FeSO₄) values differ from those contained in 88LAR/CER, the average value for ΔΔHₚ remains essentially the same. The resultant value for ΔH°(Fe⁺, ao) = -92.11 ± 0.50 kJ mol⁻¹.

The more recent measurements of 83DIMI (No. 227) have been extrapolated by us to obtain at I=0

\[\Delta H° = 12.90 \pm 0.10 \text{ kJ mol}^{-1}\]

for the solution process. Dependence on ionic strength is described by the equation:

\[\Delta H°(\text{FeSO₄·7H₂O, cr}) = \Delta H°(\text{FeSO₄·7H₂O, cr}) + (12.90 \pm 0.10) \text{ kJ mol}^{-1} \times \text{I mol}^{-1}.\]

The calculated ΔH°(Fe⁺, ao) = -91.01 ± 0.20 kJ mol⁻¹ using our working value for ΔH°(FeSO₄·7H₂O, cr) = -3014.06 ± 0.40 kJ mol⁻¹. However, the measurements by 83DIMI are meant to be part of a cycle: hence, they may be used directly to obtain ΔH°(Fe⁺, ao) = -90.61 ± 0.20 kJ mol⁻¹ from ΔH°(FeSO₄·7H₂O, cr) = -3013.66 ± 0.5 and ΔΔHₚ = 12.90 ± 0.10 kJ mol⁻¹.

\[\Delta H°(\text{H₂O}_2, 3.5\text{H}_2\text{O}) = 828.752 \text{ kJ mol}^{-1}\]

\[\Delta H°(\text{H}_2\text{SO₄}, 0.3\text{H}_2\text{O}) = -876.568 \text{ kJ mol}^{-1}\]

\[\Delta H°(\text{H}_2\text{SO₄}, 7.068\text{H}_2\text{O}) = -823.752 \text{ kJ mol}^{-1}\]

\[\Delta H°(\text{FeSO₄·7H₂O, cr}) = -1182.30 \text{ kJ mol}^{-1}\]

2.4.1.1.2. Measurements in HClO₄

Measurements were also made of the solution of FeSO₄·7H₂O(cr) in 2, 3, and 4 mol dm⁻³ HClO₄ solutions [83DIMI (No. 223), 85VAS/DIMI (No. 222)]. In these acidic solutions the reaction is predominantly:

\[\text{FeSO₄·7H₂O(cr)} + \text{H}^+(\text{ao}) = \text{Fe}^{2+}(\text{ao}) + \text{HSO}_₄^-(\text{ao}) + 7\text{H}_2\text{O(l)}\]

Correction for residual SO₄²⁻(ao) at each concentration has been made using 89COX/WAG:

\[\Delta H°(\text{H}_2\text{SO₄}, \text{ao}) = \Delta H°(\text{H}_2\text{SO₄}, \text{ao}) = -22.44 \pm 1.0 \text{ kJ mol}^{-1}\]

The data contained in 83DIMI are sufficiently detailed, in giving the varying concentrations of FeSO₄(aq) at each concentration of HClO₄, to enable extrapolation to be carried out in two ways: (1) extrapolation to I=0 depending on total ionic strength of the solution, (2) a two-stage extrapolation i.e. first to infinite dilution against n/12 at fixed concentrations of HClO₄ and after that calculation of the enthalpy of solution at I=0 of the solution. The values obtained by the two different ways are in good accord with each other:

\[\Delta H°(\text{FeSO₄, 7H₂O, cr}) = -3014.06 \pm 0.40 \text{ kJ mol}^{-1}, \Delta H°(\text{Fe}^{2+}, \text{ao}) = -90.85 \pm 0.41 \text{ kJ mol}^{-1}\]

\[\Delta H°(\text{Fe}^{2+}, \text{ao}) = -90.85 \pm 0.41 \text{ kJ mol}^{-1}\]

In general, using only 83DIMI's value for consistency with his cycle, \[\Delta H°(\text{Fe}^{2+}, \text{ao}) = -90.45 \pm 0.30 \text{ kJ mol}^{-1}\]

(From the second equation, \[\Delta H°(\text{Fe}^{2+}, \text{ao}) = -91.5 \pm 0.6 \text{ kJ mol}^{-1}\], respectively.)

2.4.2. ΔH°[(NH₄)$_₂$Fe(SO₄)$_₂$·6H₂O, cr)—Moor’s Salt

The value for ΔH° is obtained from a series of measurements by 83DIMI (No. 228), 78VAS/VAS (No. 225) of all components in 1, 2, 3, 4 mol dm⁻³ HClO₄ solutions containing 1% or 1.5% H₂O₂. The composite reaction is:

\[\text{Fe(cr)} + \text{H₂O}_2(4.95\text{H}_2\text{O}) + (\text{NH}_4)_2\text{SO₄(cr)} + \text{H}_2\text{SO₄(0.2H}_2\text{O)} + 4\text{H}_2\text{O(l)} \rightarrow (\text{NH}_4)_2\text{Fe(SO₄)}_2(\text{6H}_2\text{O,cr})\]

The individual values are:

²89PAR calculations provide ΔH°(H₂SO₄, 0.2H₂O) = -820.668 kJ mol⁻¹ and ΔH°[(NH₄)$_₂$Fe(SO₄)$_₂$·6H₂O, cr] = -1816.70 kJ mol⁻¹ as values compatible with the CODATA Key Values.
V. B. PARKER AND I. L. KHODAKOVSKI

<table>
<thead>
<tr>
<th>HClO₄ mol·dm⁻³</th>
<th>1% H₂O₂</th>
<th>1.5 H₂O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-574.20±0.15</td>
<td>-576.06±0.73</td>
</tr>
<tr>
<td>2</td>
<td>-578.75±0.65</td>
<td>-579.49±0.56</td>
</tr>
<tr>
<td>3</td>
<td>-579.96±0.89</td>
<td>-579.72±0.78</td>
</tr>
<tr>
<td>4</td>
<td>-580.58±0.92</td>
<td>-580.72±0.96</td>
</tr>
</tbody>
</table>

The average value, ΔH = -579.68±0.44 kJ·mol⁻¹, excludes the values in 1 mol·dm⁻³ HClO₄. The calculated ΔH² = -3920.00±1.0 kJ·mol⁻¹.

2.4.2.1. The standard enthalpy of solution of (NH₄)₂Fe(SO₄)₂·6H₂O(cr) and ΔHᵐ⁺(Fe³⁺, ao)

2.4.2.1.1. Measurements in HClO₄

Measurements were also made by 83DMI (No. 226) on the enthalpy of solution of (NH₄)₂Fe(SO₄)₂·6H₂O(cr) in 2, 3, and 4 mol·dm⁻³ HClO₄. As for the measurements on FeSO₄·7H₂O(cr) the process is primarily:

(NH₄)₂FeSO₄·6H₂O(cr) + 2H⁺(ao) → 2NH₄⁺(ao) + Fe²⁺(ao) + 2HSO₄⁻(ao) + 6H₂O(l)

Correction for the residual SO₄²⁻(ao) at each concentration has been made using CODATA Key Values. 83DMI contains the experimental details that also allow extrapolation of ΔH to I=0 in two different ways: (1) extrapolation to I=0 depending on total ionic strength on the solution, and (2) a two-stage extrapolation, i.e., first to infinite dilution against m₁/₂ at fixed concentrations of HClO₄ and after that the calculation of the enthalpy of solution at I=0 of the solution. Calculations using the first method give:

(ΔH⁽I⁾ - ΔH⁽I=0⁾)/(kJ·mol⁻¹) = (69.47±0.18) + (0.31±0.05)/(I/mol·kg⁻¹).

The second method gives

(ΔH⁽I⁾ - ΔH⁽I=0⁾)/(kJ·mol⁻¹) = -68.4±1.1 + (0.2±0.3)/(I/mol·kg⁻¹).

Adopting 69.40±0.20 kJ·mol⁻¹ for the solution of Mohn’s salt results in ΔHᵐ⁺(Fe³⁺, ao) = -95.30±1.0 kJ·mol⁻¹.

2.5. The Tentative Selected Parameters

Table 2. Summarizes the values for ΔHᵐ⁺(Fe²⁺, ao).

<table>
<thead>
<tr>
<th></th>
<th>ΔHᵐ⁺(Fe²⁺, ao)</th>
</tr>
</thead>
<tbody>
<tr>
<td>kJ·mol⁻¹</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-90.50±0.25</td>
</tr>
</tbody>
</table>

Section 2.1.2

ΔHᵐ⁺(FeCl₃, cr) = -341.66±0.25 kJ·mol⁻¹

Section 2.2.2

ΔHᵐ⁺(FeBr₃, cr) = -245.00±0.25 kJ·mol⁻¹

Consistent cycle,

ΔHᵐ⁺(FeCl₃, cr) = -341.11±0.22 kJ·mol⁻¹

and ΔHᵐ⁺(FeBr₃, cr) = -244.14±0.22 kJ·mol⁻¹

ΔHᵐ⁺(FeCl₃, cr) = -89.05±0.32 kJ·mol⁻¹

Consistent cycle,

ΔHᵐ⁺(FeCl₃, cr) = -244.14±0.22 kJ·mol⁻¹

and ΔHᵐ⁺(FeBr₃, cr) = -88.77±0.30 kJ·mol⁻¹

Section 2.3.2

From ΔHᵐ⁺(FeCl₃, cr) = -341.66±0.25 kJ·mol⁻¹

ΔHᵐ⁺(FeCl₃, cr) = 126.5±0.30 kJ·mol⁻¹

the “tentative”

and ΔHᵐ⁺(FeBr₃, cr) = -245.00±0.25 kJ·mol⁻¹

ΔHᵐ⁺(FeCl₃, cr) = -82.62±0.6 kJ·mol⁻¹

ΔHᵐ⁺(FeBr₃, cr) = -118.08±0.27 kJ·mol⁻¹

and ΔHᵐ⁺(FeBr₃, cr) = -87.14±0.66 kJ·mol⁻¹

Sections 2.4.1.1.1 and 2.4.1.1.2

ΔHᵐ⁺(FeSO₄·7H₂O, cr) = -3014.06±0.40 kJ·mol⁻¹

and ΔHᵐ⁺(FeSO₄·7H₂O, cr) = -3013.66±0.50 kJ·mol⁻¹

Section 2.4.2.1

ΔHᵐ⁺((NH₄)₂Fe(SO₄)₂·6H₂O, cr)

= 3920.0±1.0 kJ·mol⁻¹ and ΔHᵐ⁺(FeSO₄·7H₂O, cr) = 3920.0±1.0 kJ·mol⁻¹

Tentative Selected Value

-90.00±0.5
THE THERMODYNAMIC PROPERTIES OF THE AQUEOUS IONS OF IRON

3. The Evaluation of the Enthalpy of Formation of the Aqueous Ion Fe\(^{3+}\), \(\Delta h^\circ\)(Fe\(^{3+}\), ao)

The \(\Delta h^\circ\) (Fe\(^{3+}\), ao) is evaluated. We begin with:

1. the determinations for \(\Delta h^\circ\)(FeCl\(_3\), cr), those independent of other Fe compounds as well as those linked to FeCl\(_3\)(cr), combined with a selection for \(\Delta h^\circ\)(FeCl\(_3\), cr) which in itself requires a working value.
2. the determination of \(\Delta h^\circ\)(Fe\(^{3+}\), ao) through oxidation of Fe(cr).
3. the enthalpy of formation relationship between Fe\(^{3+}\)(ao) and Fe\(^{2+}\)(ao).

In Sec. 3.4 we summarize the various possibilities and select a value for \(\Delta h^\circ\)(Fe\(^{3+}\), ao), modify our initial selection for \(\Delta h^\circ\)(FeCl\(_3\), cr), and also select a value for \(\Delta h^\circ\)(FeBr\(_3\), cr). These selections will eventually become our final recommended values.

3.1. The Chloride System

3.1.1. \(\Delta h^\circ\)(FeCl\(_3\), cr)

3.1.1.1. Solution calorimetry with aqueous H\(_2\)O\(_2\)

59KOE/COU (No. 124) have also measured the enthalpy of oxidation of the FeCl\(_2\) solution formed from the reaction of Fe(cr) with 4.36 mol·kg\(^{-1}\) HCl by H\(_2\)O\(_2\) (see reaction No. 90 and Sec. 2.1.1) and also the enthalpy of solution of FeCl\(_3\)(cr) in the same moality of HCl (see catalog entry). The composite reaction and its \(\Delta H\) are:

\[
\text{Fe(cr)} + 3\text{HCl(12.731H}_2\text{O)y} + 0.5\text{H}_2\text{O}_2(12.58H}_2\text{Oy)} = \text{FeCl}_3(cr) + H_2(g) + H_2O(0); \\
\Delta H = -102.59 \pm 0.30 \text{kJ·mol}^{-1}
\]

from which \(\Delta h^\circ\)(FeCl\(_3\), cr) = -399.24 ± 0.35 kJ·mol\(^{-1}\).

3.1.1.2. Solution calorimetry with aqueous (KBr, Br\(_2\))

89EVD/EFI (No. 127) have measured the enthalpy of reaction of FeCl\(_3\)(cr) with aqueous (KBr, Br\(_2\)) solutions. Rearranging the reaction listed in Al.b:

\[
\text{FeCl}_3(cr) + \frac{1}{2}\text{Br}_2(0) + \text{KCl(cr)} = \text{FeCl}_3(cr) + \text{KBr(cr)}; \\
\Delta H^\circ = -11.386 \pm 0.18 \text{kJ·mol}^{-1}
\]

with those cited in Sec. 2.1.1.2, (reactions (1), (3a and 3b), and (4)) we obtain

\[
\text{Fe(cr)} + 3/2\text{Br}_2(0) + 3\text{Cl}^-(ao) = \text{FeCl}_3(cr) + 3\text{Br}^-(ao); \\
\Delta H^\circ = -258.65 \pm 0.40 \text{kJ·mol}^{-1}
\]

and \(\Delta h^\circ\)(FeCl\(_3\), cr) = -395 66 ± 0.40 kJ·mol\(^{-1}\).

3.1.1.3 Bomb combustion

The direct Cl\(_2\)(g) bomb combustion enthalpy measurements of 82LAV/TIM (No. 125) led to \(\Delta H^\circ = -396.02 \pm 0.14 \text{kJ·mol}^{-1}\) for:

\[
\text{Fe(cr)} + 1.5\text{Cl}_2(g) = \text{FeCl}_3(cr).
\]

3.1.2. The Relationship Between \(\Delta h^\circ\)(FeCl\(_3\), cr) and \(\Delta h^\circ\)(FeCl\(_2\), cr)

The measurements of 59KOE/COU leading to \(\Delta h^\circ\)(FeCl\(_2\), cr) (No. 90) and \(\Delta h^\circ\)(FeCl\(_3\), cr) (No. 124) may also be rearranged so that:

\[
\text{FeCl}_2(cr) + \text{HCl(12.731H}_2\text{Oy}) + 0.5\text{H}_2\text{O}_2(12.58H}_2\text{Oy)} = \text{FeCl}_3(cr) + \text{H}_2O(0); \\
\Delta H = -85.55 \pm 0.21 \text{kJ·mol}^{-1}
\]

resulting in \(\Delta h^\circ\)(FeCl\(_3\), cr) = \(\Delta h^\circ\)(FeCl\(_2\), cr) = -57.58 ± 0.25 kJ·mol\(^{-1}\) and \(\Delta h^\circ\)(FeCl\(_3\), cr) = -399.30 ± 0.35 kJ·mol\(^{-1}\).

For the reaction given in 3.1.1.2 [89EVD/EFI] and the \(\Delta h^\circ\)'s for KCl(cr) and KBr(cr), cited in 2.1.1.2, we have:

\[
\text{FeCl}_2(cr) + \frac{1}{2}\text{Br}_2(0) + \text{Cl}^-(ao) = \text{FeCl}_3(cr) + \text{Br}^-(ao); \\
\Delta H^\circ = -8.881 \pm 0.19 \text{kJ·mol}^{-1}
\]

from which we obtain \(\Delta h^\circ\)(FeCl\(_3\), cr) = \(\Delta h^\circ\)(FeCl\(_2\), cr) = -54.55 ± 0.20 kJ·mol\(^{-1}\).

The high-temperature decomposition measurements (third law) for FeCl\(_2\)(cr) = FeCl\(_3\)(cr) + \(\frac{1}{2}\)Cl\(_2\)(g) are tabulated.

\[
\Delta H^\circ, \text{kJ·mol}^{-1}
\]

| Reaction | \(
\Delta H^\circ
\) |
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>25MAI (No. 129)</td>
<td>53.51 ± 1.8</td>
</tr>
<tr>
<td>50KAN/PET (No. 130)</td>
<td>52.49 ± 1.2</td>
</tr>
<tr>
<td>55SCH/OEN (No. 131)</td>
<td>54.27 ± 0.75</td>
</tr>
<tr>
<td>58WIL/GRE (No. 132)</td>
<td>54.38 ± 0.75</td>
</tr>
</tbody>
</table>

It is obvious that the mean enthalpy of decomposition, \(~53.9 ± 0.70\) kJ·mol\(^{-1}\) from the vapor pressure measure-

\(^a\) From 65PAR.

\(^b\) From 82WAG/EVA.
ments (all in good agreement with one another) disagrees with the calorimetrically determined $\Delta H^o = 57.58 \pm 0.25$ kJ·mol$^{-1}$ from 39KOE/COU but agrees with that derived from 89EVD/EFI, $54.55 \pm 0.20$ kJ·mol$^{-1}$. From the $\Delta H^o = 53.9$ kJ·mol$^{-1}$ we obtain $\Delta H^o(\text{FeCl}_3, \text{cr}) = -395.16 \pm 0.75$ kJ·mol$^{-1}$; from the 89EVD/EFI $\Delta H^o = 54.55 \pm 0.20$ kJ·mol$^{-1}$, $\Delta H^o(\text{FeCl}_3, \text{cr}) = -395.71 \pm 0.54$ kJ·mol$^{-1}$ ($-395.66 \pm 0.40$ kJ·mol$^{-1}$ from 89EVD/EFI's consistent cycle) which supports the direct enthalpy of chlorine by measured at 82LAV/TIM, 84LAV/TIM, as $-396.02 \pm 0.14$ kJ·mol$^{-1}$ which is our initial working value that we shall use in the following section.

3.3. The Standard Enthalpy of Solution of FeCl$_3$(cr) and the Derived $\Delta H^o$(Fe$^{3+}$, ao)

There are some measurements of the enthalpy of solution of FeCl$_3$(cr) in various concentrations of HCl (35KAN/FLU, 76COR/OUW, 80STU/FER, and 59KOE/COU) (Nos. 134 – 140, 146 – 149) that allow us, using the Khodakovskii corrections (see Sec. 1.2.1), to extrapolate to $T = 0$.

In addition, 52LI/GRE and 85SOL/MON have measured the enthalpy of solution in H$_2$O (No. 133). The values have been corrected for the formation of complexes, FeOH$^{2+}$ (ao) and FeCl$^{2+}$ (ao).

The two approaches lead to:

FeCl$_3$(cr)$\rightarrow$FeCl$_3$(ao), $\Delta H^o = -146.5 \pm 3.0$ kJ·mol$^{-1}$

from the measurements in HCl and

FeCl$_3$(cr)$\rightarrow$FeCl$_3$(ao), $\Delta H^o = -158.99 \pm 0.84$ kJ·mol$^{-1}$

from the measurements in H$_2$O. The resultant $\Delta H^o(\text{FeCl}_3, \text{ao})$ values are $54.22 \pm 0.3$ and $55.01 \pm 0.85$ kJ·mol$^{-1}$, respectively and $\Delta H^o(\text{Fe}^{3+}, \text{ao}) = -41.3 \pm 3.1$ kJ·mol$^{-1}$ and $-53.79 \pm 0.85$ kJ·mol$^{-1}$, respectively. (A different selection for $\Delta H^o(\text{FeCl}_3, \text{cr})$, e.g. $-399.24$ kJ from 59KOE/COU would result in $\Delta H^o(\text{Fe}^{3+}, \text{ao}) = -44.55$ and $-56.01$ kJ·mol$^{-1}$).

The measurements of 90EFI/FUR (Nos. 142 – 144) on the enthalpy of solution of FeCl$_3$(cr) in HClO$_4$(ao) as a function of concentration of HClO$_4$, extrapolated to $T = 0$ result in $\Delta H^o = -156.58 \pm 1.2$ kJ·mol$^{-1}$ (No. 141) and this results in $\Delta H^o(\text{FeCl}_3, \text{ao}) = -51.36 \pm 1.2$ kJ·mol$^{-1}$, using our initial tentative selection of $-396.02 \pm 0.14$ kJ·mol$^{-1}$ for $\Delta H^o(\text{FeCl}_3, \text{cr})$.

However, if we maintain consistency with the 89EVD/EFI $\Delta H^o(\text{FeCl}_3, \text{cr}) - \Delta H^o(\text{FeCl}_2, \text{cr}) = -54.55 \pm 0.2$ kJ·mol$^{-1}$ and 90EFI/FUR $\Delta_{\text{sol}} H^o$ results we obtain $\Delta H^o(\text{Fe}^{3+}, \text{ao}) = -51.05 \pm 1.3$ kJ·mol$^{-1}$ ($-51.00 \pm 1.3$ kJ·mol$^{-1}$ in a summation of pertinent reactions from 89EVD/EFI and 90EFI/FUR). The measurements by 84NOV/BEL (No. 145) of $\Delta_{\text{sol}} H^o(\text{FeCl}_3, \text{cr})$ in aqueous 0.65 mol·dm$^{-3}$ HClO$_4$ are rejected (see comments attached to No. 145 for explanation).

3.2. The Direct Determination of $\Delta H^o$(Fe$^{3+}$, ao)

The measurements of 76VAS/RAS (No. 8) on the oxidation of Fe(cr) by aqueous solutions of H$_2$O$_2$ in varying concentrations of HClO$_4$ are applicable

Fe(cr)$+1.5\text{H}_2\text{O}_2$ (ao)$+3\text{H}^+$ (ao)$\rightarrow$Fe$^{3+}$ (ao)$+3\text{H}_2\text{O}$(l).

The standard enthalpy effect of this reaction was obtained by two methods: (1) by calculating the dependence of the thermal effects on the total ionic strength of the solutions, and (2) by a stage approach: extrapolation to infinite dilution against m(Fe$^{3+}$, ao)$^{1/2}$, and then extrapolation to J = 0 of the solution.

According to the first method

$\Delta H^o(\text{Fe}^{3+}, \text{ao}) = -(617.21 \pm 0.31) - (1.84 \pm 0.10) (l$/mol·kg$^{-1}$)

and to the second method

$\Delta H^o(\text{Fe}^{3+}, \text{ao}) = -(617.33 \pm 0.35) - (1.83 \pm 0.11) (l$/mol·kg$^{-1}$).

Both methods of extrapolation gave the same results and adopting the first mentioned equation $\Delta H^o = -617.21 \pm 0.31$ kJ·mol$^{-1}$ and $\Delta H^o(\text{Fe}^{3+}, \text{ao}) = -46.48 \pm 0.32$ kJ·mol$^{-1}$.

3.3. The Enthalpy Relationship Between Fe$^{2+}$ (ao) and Fe$^{3+}$ (ao)

Appendix Alb contains three calorimetric measurements of the oxidation of Fe$^{2+}$ (ao) by H$_2$O$_2$. The skeleton reaction is

Fe$^{2+}$(ao) + $\frac{1}{2}$H$_2$O$_2$(ao) + H$^+$ (ao) $\rightarrow$ Fe$^{3+}$(ao) + H$_2$O(l) + H$_2$(g).

The measurements are all in dilute solutions. The measurements, the $\Delta H^o$s and the calculated $\Delta H^o(\text{Fe}^{2+}, \text{ao}) - \Delta H^o(\text{Fe}^{3+}, \text{ao})$ are tabulated (Table 3). Also tabulated are the $\Delta (\Delta H^o)$'s derived from the c.m.f. measurements as a function of $T$ for

Fe$^{2+}$(ao) + H$^+$ (ao) $\rightarrow$ Fe$^{3+}$(ao) + $\frac{1}{2}$H$_2$(g)

as well as those values derived from the results of 89EVD/EFI (No. 127), 89EVD/EFI (No. 184) and 90EFI/FUR (Nos. 94, 141, 178, 190) on the calorimetric determinations of $\Delta H^o(\text{FeCl}_2, \text{cr})$, $\Delta H^o(\text{FeCl}_3, \text{cr})$, $\Delta H^o(\text{FeBr}_2, \text{cr})$, $\Delta H^o(\text{FeBr}_3, \text{cr})$ and their $\Delta_{\text{sol}} H^o$s, shown as follows.

From Sec 3.1.2 we have $\Delta_{\text{sol}} H^o(\text{FeCl}_3, \text{cr}) - \Delta_{\text{sol}} H^o(\text{FeCl}_2, \text{cr}) = -54.22 \pm 0.20$ kJ·mol$^{-1}$ from 89EVD/EFI. With the 90EFI/FUR (Nos. 94, 141) measurements of $\Delta_{\text{sol}} H^o$ for FeCl$_3$(cr) and FeCl$_2$(cr) in HClO$_4$ (156.50 ± 1.2 and 03.11 ± 0.42 kJ·mol$^{-1}$, respectively) we obtain

Fe$^{2+}$(ao) $\rightarrow$ Fe$^{3+}$(ao) + Cl$^-$ (ao);

$\Delta H^o$ = 128.02 ± 1.3 kJ·mol$^{-1}$

and

$\Delta_{\text{sol}} H^o(\text{Fe}^{3+}, \text{ao}) - \Delta_{\text{sol}} H^o(\text{Fe}^{2+}, \text{ao}) = 39.06 \pm 1.3$ kJ·mol$^{-1}$.

Similarly from the reaction catalog from the measurements by 89EF/FFTVY (No. 18) we have $\Delta_{\text{sol}} H^o(\text{FeBr}_3, \text{cr}) - \Delta_{\text{sol}} H^o(\text{FeBr}_2, \text{cr}) = -17.90 \pm 0.14$ kJ·mol$^{-1}$, which we may combine with the $\Delta_{\text{sol}} H^o$s for FeBr$_3$(cr) and FeBr$_2$(cr) (150.4 ± 1.3 (No. 178) and 86.85 ± 0.12 kJ·mol$^{-1}$ (No. 190), respectively) to obtain
The enthalpy of oxidation of Fe\(^{2+}\)(ao) by H\(_2\)O\(_2\)(ao) and 
\(\Delta H^\circ\)(Fe\(^{3+}\), ao)−Δ\(H^\circ\)(Fe\(^{2+}\), ao)

| Table 3. The enthalpy of oxidation of Fe\(^{2+}\)(ao) by H\(_2\)O\(_2\)(ao) and 
\(\Delta H^\circ\)(Fe\(^{3+}\), ao)−Δ\(H^\circ\)(Fe\(^{2+}\), ao) |
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\Delta H^\circ)</td>
</tr>
<tr>
<td>68SOU/CHA</td>
<td>−146.13 ± 1.0</td>
</tr>
<tr>
<td>(No. 9)</td>
<td></td>
</tr>
<tr>
<td>71BER/TUM</td>
<td>−148.76 ± 0.10</td>
</tr>
<tr>
<td>(No. 10)</td>
<td></td>
</tr>
<tr>
<td>47FON</td>
<td>−150.16 ± 0.50</td>
</tr>
<tr>
<td>(Nos. 11, 12)</td>
<td></td>
</tr>
<tr>
<td>72WHILAN</td>
<td>38.41 ± 1.5</td>
</tr>
<tr>
<td>(No. 14)</td>
<td></td>
</tr>
<tr>
<td>73NIK/ANT</td>
<td>46.7 ± 2.0m</td>
</tr>
<tr>
<td>(No. 17)</td>
<td></td>
</tr>
<tr>
<td>53MAG/HUI</td>
<td>40.58 ± 0.84</td>
</tr>
<tr>
<td>(No. 22)</td>
<td></td>
</tr>
<tr>
<td>51CON/Mev</td>
<td>41.61 ± 1.0</td>
</tr>
<tr>
<td>(No. 24)</td>
<td></td>
</tr>
<tr>
<td>89EV/LEF/FI and</td>
<td>39.06 ± 1.3</td>
</tr>
<tr>
<td>90EF/FUR</td>
<td></td>
</tr>
<tr>
<td>(chloride system)</td>
<td></td>
</tr>
<tr>
<td>(Nos. 94, 127, 141)</td>
<td></td>
</tr>
<tr>
<td>89EF/LEV and</td>
<td>39.96 ± 1.32</td>
</tr>
<tr>
<td>90EF/FUR (bromide system)</td>
<td></td>
</tr>
<tr>
<td>(Nos. 178, 184, 190)</td>
<td></td>
</tr>
</tbody>
</table>

\(\Delta H^\circ\)(Fe\(^{2+}\), ao) is ill defined. A tabular summary, Table 4, which includes our rejected values follows.

3.4. The Tentative Selected Parameters

It is quite obvious that \(\Delta H^\circ\)(Fe\(^{2+}\), ao) is ill defined. A tabular summary, Table 4, which includes our rejected values follows.

The agreement is not as good as we would like; however, there is a narrow range with some consistency, from 1) the tentative selection of \(-90.0\pm0.5\) kJ\(\cdot\)mol\(^{-1}\) for \(\Delta H^\circ\)(Fe\(^{2+}\), ao) and the \(\Delta(\Delta H^\circ)\) from \(E^\circ\) vs \(T\), the oxidation by the O\(_2\) and from the chloride and bromide systems; 2) the initial selection of \(\Delta H^\circ\)(FeCl\(_3\), cr) = \(-396.02\pm0.14\) kJ\(\cdot\)mol\(^{-1}\) and \(\Delta(\Delta H^\circ) = -156.38\pm0.28\) kJ\(\cdot\)mol\(^{-1}\); and 3) the direct determination of \(\Delta H^\circ\)(Fe\(^{3+}\), ao) = \(-51.00\pm1.3\) kJ\(\cdot\)mol\(^{-1}\). This 'consistent' path narrows the range of values to between \(-51\) and \(-47\) kJ\(\cdot\)mol\(^{-1}\).

We select \(\Delta(\Delta H^\circ) = 41.0\pm1.5\) kJ\(\cdot\)mol\(^{-1}\) and \(\Delta H^\circ\)(Fe\(^{3+}\), ao) = \(-49.0\pm1.5\) kJ\(\cdot\)mol\(^{-1}\) and modify our selection of \(\Delta H^\circ\)(FeCl\(_3\), cr) from \(-396.02\pm0.14\) kJ\(\cdot\)mol\(^{-1}\) to \(-395.66\pm0.50\) kJ\(\cdot\)mol\(^{-1}\). The selected values are given below and become our final recommendations.

\(\Delta H^\circ\)(Fe\(^{2+}\), ao) and \(\Delta H^\circ\)(Fe\(^{3+}\), ao)−Δ\(H^\circ\)(Fe\(^{2+}\), ao)

<table>
<thead>
<tr>
<th>Tentative Selection</th>
<th>(\Delta H^\circ)(Fe(^{2+}), ao)</th>
<th>(\Delta(\Delta H^\circ))</th>
<th>(\Delta H^\circ)(Fe(^{3+}), ao)−Δ(H^\circ)(Fe(^{2+}), ao)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Rejected Value)</td>
<td>(-90.0\pm0.5)</td>
<td>(-95.5)</td>
<td></td>
</tr>
<tr>
<td>(E^\circ) vs (T)</td>
<td>38.41 ± 1.5</td>
<td>(-51.59)</td>
<td>(-57.09)</td>
</tr>
<tr>
<td></td>
<td>42.75 ± 1.5</td>
<td>(-47.25)</td>
<td>(-52.75)</td>
</tr>
<tr>
<td></td>
<td>46.7 ± 2.0</td>
<td>(-43.3)</td>
<td>(-48.8)</td>
</tr>
<tr>
<td></td>
<td>40.58 ± 0.84</td>
<td>(-49.42)</td>
<td>(-54.42)</td>
</tr>
<tr>
<td></td>
<td>41.61 ± 1.0</td>
<td>(-48.39)</td>
<td>(-53.89)</td>
</tr>
<tr>
<td>Calorimetric</td>
<td>44.11 ± 1.0</td>
<td>(-45.89)</td>
<td>(-51.39)</td>
</tr>
<tr>
<td>Oxidation with H(_2)O(_2)</td>
<td>41.48 ± 0.10</td>
<td>(-48.52)</td>
<td>(-54.02)</td>
</tr>
<tr>
<td>40.08 ± 0.5</td>
<td>(-49.42)</td>
<td>(-55.42)</td>
<td></td>
</tr>
<tr>
<td>39.06 ± 1.3</td>
<td>(-50.94)</td>
<td>(-56.44)</td>
<td></td>
</tr>
<tr>
<td>Chloride system</td>
<td>39.96 ± 1.32</td>
<td>(-50.04)</td>
<td>(-55.54)</td>
</tr>
<tr>
<td>Bromide system</td>
<td>39.96 ± 1.32</td>
<td>(-50.04)</td>
<td>(-55.54)</td>
</tr>
</tbody>
</table>

\(\Delta H^\circ\)(FeCl\(_3\), cr) = \(-399.24\) kJ\(\cdot\)mol\(^{-1}\)

\(\Delta(\Delta H^\circ) = 41.0\pm1.5\) kJ\(\cdot\)mol\(^{-1}\)

\(\Delta(\Delta H^\circ) = -44.55\) kJ\(\cdot\)mol\(^{-1}\)

(76NAS/RAS)

(89EV/LEF/FI and 90EF/FUR)

\(\Delta H^\circ\)(Fe\(^{3+}\), ao)−Δ\(H^\circ\)(Fe\(^{2+}\), ao)

\(-51.00\pm1.3\) kJ\(\cdot\)mol\(^{-1}\)

\(\Delta H^\circ\) results with \(\Delta C_\text{P} = 0\).

\(\Delta C_\text{P}\)'s using 88HOV.

\(\Delta H^\circ\)(Fe\(^{3+}\)(aq) + \frac{1}{2} Br\(_2\)(l) = Fe\(^{2+}\)(aq) + Br\(^-\)(aq);

\(\Delta H^\circ = -81.45\pm1.31\) kJ\(\cdot\)mol\(^{-1}\)

from which we obtain 39.96±1.32 kJ\(\cdot\)mol\(^{-1}\) for the tabulated difference given below.

\(\Delta H^\circ\)(Fe\(^{2+}\), ao) + \frac{1}{2} Br\(_2\)(l) = Fe\(^{3+}\)(ao) + Br\(^-\)(ao);

\(\Delta H^\circ = -81.45\pm1.31\) kJ\(\cdot\)mol\(^{-1}\)
4. The Evaluation of the Gibbs Energy of Formation of the Aqueous Ion, Fe$^{2+}$, $\Delta G^\circ$(Fe$^{2+}$, ao)

Some controversy was generated as a result of the selection, made independently by two evaluation groups [69WAG/EVA and 82WAG/EVA, 72MED/BER], for $\Delta G^\circ$(Fe$^{2+}$, ao) = −78.9 kJ mol$^{-1}$ based on the results of 53PAT/THO, a change from the −84.9 kJ mol$^{-1}$ value selected earlier by 52ROS/WAG from the results of 32RAN/FRA2. See comments by 82COB/MUR, for example.

The $\Delta G^\circ$(Fe$^{2+}$, ao) is evaluated from:

1. e.m.f. (Sec. 4.1) and some equilibrium constant measurements (section 4.2.1) that result in values for $\Delta G^\circ$ independent of other Fe species.
2. Equilibrium measurements involving solubilities of Fe$_2$O$_3$(cr, magnetite) (Sec. 4.2.2) and FeSO$_4$·7H$_2$O(cr) (Sec. 4.2.3) and FeCl$_2$·4H$_2$O(cr) (Sec. 4.2.4) which also involves its vapor pressure.

In Sec. 4.3 a tentative selection is made ($p^*=1$ atm).

4.1. The e.m.f. Measurements

We begin with the measurements that had been selected by 52ROS/WAG

32RAN/FRA2 (No. 75) measured the E at 298.15 K for the cell:

Fe(cr)+FeCl$_2$(0.1 mol kg$^{-1}$), Hg$_2$Cl$_2$(cr), Hg(l)

obtaining $E=0.7996\pm 0.0010$ V. Then, using $\gamma_+$ from 79GOL/NUT, $E^0 = 0.7027\pm 0.0010$ V and $\Delta G^\circ = −135.60\pm 0.20$ kJ mol$^{-1}$ for Fe(cr)+Hg$_2$Cl$_2$(cr)=FeCl$_2$(ai)+Hg(l).

Two different samples of Fe(cr) were used, one electrolytically prepared and deposited on Pt electrodes at 1373 K and the second by the reduction of pure Fe$_2$O$_3$(cr) with H$_2$ at temperatures of 1073 to 1123 K. Oxygen was carefully excluded from both as described by 32RAN/FRA. The cell measurements for $E$ using the two differently prepared electrodes are in good agreement, giving 0.7990 V and 0.8002 V respectively leading to the aforementioned $E = 0.7996\pm 0.0010$ V.

32RAN/FRA2 also reviewed the measurements of 96HAM (No. 73) on the same cell. These measurements were made in various concentrations of FeCl$_2$ (m=0.1 mol kg$^{-1}$) and, corrected to the standard state, result in $E^0 = 0.710\pm 0.0014(2s)$ V ($\Delta G^\circ = −137.01\pm 0.30$ kJ mol$^{-1}$), 0.0075 V greater than their measurements. They explained the differences by asserting that electrodes prepared from finely divided iron, used by 26HAM, give too high a value since treatment of the finely divided iron by acid or by prolonged exposure to solutions of FeCl$_2$ reduces the activity of the iron and the measured $E$ approaches their value of $E^0 = −0.70217$ V.

The 26HAM (No. 72) measurements on Fe(cr)+2TICI(cr) = FeCl$_2$(ai)+2TICI(cr) yield $E^0 = −0.1225$ V ($\Delta G^\circ = 23.65\pm 1.0$ kJ mol$^{-1}$) when approached from the left side of equilibrium and are in better agreement since treatment with TICI(ai) removes the finer particles of iron.

For the half cell,

Fe(cr) = Fe$^{2+}$(ao)+2e$^-$,

the values from the Hg$_2$Cl$_2$(cr) cell are $E^0 = 0.4346\pm 0.0010$ V ($\Delta G^\circ$(Fe$^{2+}$, ao) = −83.86 ± 0.20 kJ mol$^{-1}$) from 32RAN/FRA2, and $E^0 = 0.4418\pm 0.0015$ V ($\Delta G^\circ = −85.26\pm 0.30$ kJ mol$^{-1}$) from 26HAM. From the TICI(cr) cell, $E^0 = 0.4340\pm 0.0005$ V ($\Delta G^\circ = −83.75\pm 1.0$ kJ mol$^{-1}$).

Much earlier, 06RIC/BEH conducted measurements on the system FeFeSO$_4$(0.5 mol·dm$^{-3}$)KCl(0.1 mol·dm$^{-3}$)Hg$_2$Cl$_2$−Hg. Although it is not possible to obtain an $E^0$ for this cell because of the unknown liquid potential and the high concentration of FeSO$_4$, these experiments showed that iron prepared electrolytically or by reduction of the oxide with hydrogen gave an average potential 0.02–0.03 V higher than vacuum-fused iron. Since the measurements of 26HAM and 32RAN/FRA were both on iron prepared either electrolytically or by the reduction of the oxide with hydrogen and, according to 53PAT/THO, with some oxygen present, 53PAT/THO undertook a reinvestigation of the standard potential of the Fe(cr), Fe$^{2+}$(ao) half-cell, using hydrogen-free iron prepared by the thermal decomposition of iron pentacarbonyl under vacuum. The powder produced was used directly as the electrode material. Massive iron electrodes prepared by vacuum fused of the metal powder were also used. Special care was taken to remove all traces of oxygen from the cells. This total procedure, it was believed, eliminated all effects due to contamination by atomic hydrogen or molecular oxygen. Their results are as follows.

From the measurements with the Hg(l), Hg$_2$SO$_4$(cr) half cell (No. 206):

Fe(cr)+Hg$_2$SO$_4$(cr)=FeSO$_4$(aq,m)+2Hg(l)

<table>
<thead>
<tr>
<th>cell</th>
<th>$m$ (mol·kg$^{-1}$)</th>
<th>$E$ (V)</th>
<th>$\gamma_+$ (V)</th>
<th>$E^0$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.718</td>
<td>1.1335</td>
<td>0.193</td>
<td>1.02361</td>
</tr>
<tr>
<td>7</td>
<td>0.029 (ah)</td>
<td>1.1845</td>
<td>0.281</td>
<td>1.0249</td>
</tr>
<tr>
<td>0.274</td>
<td>1.1488</td>
<td>0.290</td>
<td>1.02463</td>
<td>0.283</td>
</tr>
<tr>
<td>0.022</td>
<td>1.1522</td>
<td>0.330</td>
<td>1.0257</td>
<td>0.305</td>
</tr>
</tbody>
</table>

$\Delta G^\circ$(TICI, cr)=−184.93 kJ·mol$^{-1}$ [82WAG/EVA] and $\Delta G^\circ=−184.97\pm 3.0$ kJ·mol$^{-1}$ [71MED/BER].

$\gamma_+$ listed by 53PAT/THO from measurements by 411D/H/M/FED.
Thus, $E^o$ for the cell is $1.0247 \pm 0.0003$ V ($\Delta G^o = -197.74 \pm 0.06$ kJ mol$^{-1}$) using $\gamma_{\pm}$s given by 53PAT/THO and $E^o = 1.0236 \pm 0.0003$ V using Pitzer’s (72PIT) $\gamma_{\pm}$s for MgSO$_4$.

The resultant values for $E^o$ for the Fe(cr)–Fe$^{2+}$ (aq) half cell are $0.4119 \pm 0.0003$ V ($\Delta G^o = -79.483 \pm 0.60$ kJ mol$^{-1}$) and $0.4180 \pm 0.0003$ V ($\Delta G^o = -79.263 \pm 0.60$ kJ mol$^{-1}$), respectively.

The above measurements were made with iron powder. For the cell (No. 207)

$$\text{Fe(cr)} + \text{PbSO}_4(cr) = \text{FeSO}_4(aq, x) + \text{Pb}(cr)$$

$E = 0.1654$ V when $m = 0.677$ mol kg$^{-1}$ using massive iron. If $\gamma_+ = 0.198$ as given by 53PAT/THO, $E^o = 0.05461$ V if $\gamma_+ = 0.197$ from 72PIT is used, then $E^o = 0.0538$ V.

If iron powder is used as the electrode, $E = 0.1771$ V when $m = 0.030$ mol kg$^{-1}$ With $\gamma_+ = 0.281$, $E^o = 0.05431$ V. The 72PIT value for $\gamma_+ = 0.274$ leads to $E^o = 0.05374$ V.

It follows with 53PAT/THO $\gamma_{\pm}$s that $E^o = 0.05461$ V (massive iron) and 0.05439 V (iron powder) (with 72PIT’s $\gamma_{\pm}$) $E^o = 0.05380$ and 0.05374 V, respectively. The two different iron electrodes give essentially the same result $E^o = 0.05450 \pm 0.0001$ or 0.05377 $\pm 0.0001$ V ($\Delta G^o = -10.517 \pm 0.020$ kJ mol$^{-1}$ or $-10.376 \pm 0.020$ kJ mol$^{-1}$). The resultant Fe(cr)–Fe$^{2+}$ (aq) standard half cell potential is 0.4121 or 0.4113 V ($\Delta G^o = -79.516$ and $-79.375$ kJ mol$^{-1}$).

The third reference electrode used was the Hg$_2$Cl$_2$–Hg half cell (No. 74) in conjunction with a massive iron electrode and also with an iron powder electrode.

$$\text{Fe(cr)} + \text{Hg}_2\text{Cl}_2(cr) = \text{FeCl}_2(aq) + 2\text{Hg}(l)$$

The measured $E$’s [m(FeCl$_2$,aq) = 0.0760 and 0.0160 mol kg$^{-1}$] are 0.7770 (massive iron) and 0.8298 V (iron powder) which lead to $E^o = 0.6712$ V ($\Delta G^o = -129.522$ kJ mol$^{-1}$) and $E^o = 0.6735$ V ($\Delta G^o = -129.966$ kJ mol$^{-1}$) and for the standard potential of the Fe(cr)–Fe$^{2+}$ (aq) half cell $E^o = 0.4031$ and 0.4055 V ($\Delta G^o = -78.777$ and $-78.221$ kJ mol$^{-1}$, respectively). The $E^o$ values are as follows:

<table>
<thead>
<tr>
<th>E$^o$(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4346 $\pm$ 0.0010</td>
</tr>
<tr>
<td>0.4418</td>
</tr>
<tr>
<td>0.4340</td>
</tr>
<tr>
<td>0.4043</td>
</tr>
<tr>
<td>0.4108</td>
</tr>
<tr>
<td>0.4113</td>
</tr>
</tbody>
</table>

53PAT/THO also made their measurements as a function of time. For all deoxygenated cells using massive iron or iron powder there was a sharp initial rise in potential followed by a general approach to a steady value within a period of 12 to 30 d. The authors note, however, that the presence of small amounts of oxygen in the cells from the carbonyl iron powder affected the manner in which the steady value of 0.4108 V was attained. The potential instead of rising, as is the case with the completely deoxygenated cells, fell regularly to this constant value. They also conducted measurements on two cells using iron reduced from the oxide by hydrogen, one repeating the 32RAN/FRA measurements with a small amount of oxygen intentionally admitted and the second with a completely deoxygenated system.

The results are as follows:

$$E = 0.8065 \text{ V at } m(\text{FeCl}_2,\text{aq}) = 0.0864 \text{ mol kg}^{-1} \text{ with } \gamma_+ = 0.511 \text{ [79GOL/NEW]} \text{ for the cell containing air, leading to } E^o = 0.7041 \text{ V and } E^o \text{ for the Fe(cr)–Fe}^{2+}(\text{aq}) \text{ half cell is } 0.4361 \text{ V (} \Delta G^o = -84.15 \text{ kJ mol}^{-1} \text{), in excellent agreement with the } 32\text{RAN/FAZ} \text{ measurements, indicating the possibility of air being present in the cells used by } 32\text{RAN/FAZ} \text{.}}$$

The second cell (completely deoxygenated) gave $E = 0.8520$ V with $m = 0.0675$ mol kg$^{-1}$ ($\gamma_+ = 0.511$), so that $E^o$ for the cell is 0.7423 and for the half cell 0.4742 V ($\Delta G^o = -91.51$ kJ mol$^{-1}$), significantly higher than the E$^o$s they obtained from the carbonyl reduced iron half cells that were deoxygenated. The above data appeared to establish $E^o = 0.4088$ V [69WAG/EVA, 72MED/BER], since it would appear that hydrogen contamination and the presence of oxygen caused the higher values. However, other data indicate that this value is also questionable (see 63KO/HOL in Sec. 4.2.3 on $\Delta$mol$G^o$ of FeSO$_4$·H$_2$O(cr) and FeCl$_2$·H$_2$O(cr)). The 60HUR (No. 3) measurements as well as those of 78JOH/BAU (No. 5) on the half cell indicate even greater discrepancies. The o.m.f. measurements of 60HUR at 293 K are indicative of this. He obtained $E^o = 0.467$ V from extrapolation of forward and reverse kinetic data (in acidic FeCl$_2$ solutions). Since correction to 298 K is negligible and the liquid junction potential should be small, possibly about 0.002 V, this supports the 0.47 V value. His electrodes (see catalog entry) were vacuum annealed for 1 h at about 973 K. However, the impurity level is high (~0.3%) and the method of preparation is unknown. The solutions of FeCl$_2$(aq), though, were presaturated with hydrogen in the presence of platinum plated platinum to reduce any Fe$^{3+}$ present and also stored under hydrogen. This is in line with 53PAT/THO’s observation of the hydrogen reduced Fe electrode with solutions completely deoxygenated leading to higher E$^o$s. 78JOH/BAU considered the earlier discordant measurements and measured the cell

$$\text{Fe(cr)}|\text{FeCl}_2(0.02m)||\text{saturated KC}|\text{AgCl(cr)}|\text{Ag(cr)}.$$
the vacuum annealed Fe(cr) cells indicate that the apparent standard potential for the Fe(cr)/Fe²⁺(aq) is strongly dependent on pH in the acidic region but becomes independent at pH≈5.8 and is 0.415±0.001 V (ΔG°(Fe²⁺, ao) = −80.08 ±0.20 kJ·mol⁻¹). If the Fe was not particularly degassed, the potential increased to ~0.435 V (ΔG° = −83.94 kJ·mol⁻¹) in better agreement with 32RAN/FRA2. This supports the supposition that the difference in E is attributable to differences in H content of the metal. Although they do not recommend either value, they have shown that according to theory the potential is experimentally independent of pH.

We now turn to other paths for obtaining ΔG°(Fe²⁺, ao) and E° of the half cell.

4.2. The Equilibrium Constants

4.2.1. The Reaction of Fe(cr) With Aqueous TiCl₄ and NaClO₄

The measurements of 82GAM/REI (No. 4) are considered. Neutral aqueous solutions of TiCl₄ and NaClO₄ were reacted with “ultrapure Fe” in sealed ampoules at 323.15 K. The ionic strength of the NaClO₄ aqueous solution was 1.0 mol·kg⁻¹. Under these conditions lg K = 1.12±0.06 for

Fe(cr)+2Ti⁺(ao)=Fe²⁺(ao)+2Ti(cr).

A plot of log [Fe²⁺] vs log [Ti⁺] gives a straight line with a slope of 2.0 and ΔG° = −6.93±0.4 kJ·mol⁻¹. Correction (see catalog entry) to 298.15 K and I=0 results in ΔG° = −13.51±1.5 kJ·mol⁻¹ (E° = 0.0700 V) and ΔG°(Fe²⁺, ao) = −8.28±4.1 kJ·mol⁻¹ (E° for the Fe(cr)−Fe²⁺(ao) half cell = 0.4057 V), if ΔG°(Ti⁺, ao) = −32.38 kJ·mol⁻¹ [82WAG/EVA and 71MED/BER].

However, 79HEI (a coauthor of the above work) has also measured the e.m.f. of

2Ti⁺(ao)+H₂(g)+Hg(l)=2Ti(sat, in Hg)+2H⁺(ao)

at 323 K under the same conditions and obtained E° = −0.3865 V (I=1.0). Using E° = −0.0031 V from 19RC/DAN and 22GER for

2Ti(sat, in Hg)=2Ti(cr)+Hg(l)

E° = −0.3890 V (I=1.0) at 323.15 K is obtained for

2Ti⁺(ao)+H₂(g)=2Ti(cr)+2H⁺(ao)

and E° = −0.3567 V (I=6) at 79R K. Then for the Fe(cr)/Fe²⁺(ao) half cell E° = 0.4267 V and ΔG°(Fe²⁺, ao) = −8.24 kJ·mol⁻¹. Obviously these measurements could support either the 53PAT/THO or the 32RAN/FRA2 values.

4.2.2. Solubility Measurements of Fe₂O₃(cr)-magnetite

The measurements of 70SWE/BAE (Nos. 36–40) and 80TRE/LEB (Nos. 41–46) on the solubility of magnetite in dilute aqueous solution saturated with H₂ lead to Kₜ values at 298 K for the following process:

1/3Fe₂O₃(cr)+2H⁺(ao)+1/3H₂(g)

=Fe²⁺(ao)+4/3H₂O(l). (No. 36 & No. 41).

Both sets of solubility measurements were conducted in flow systems with varying pH, redox conditions, and temperature (70SWE/BAE temperature range 323 to 573K, 80TRE/LEB 373 to 573K). The solutions used by 70SWE/BAE ranged from m(KOH) = 4 × 10⁻⁴ mol·kg⁻¹ to m(HCl) = 10⁻⁴ mol·kg⁻¹. Solution compositions used by 80TRE/LEB included either HCl or NaOH of molalities up to 1 and 40 mmol·kg⁻¹. The results of both investigations were fitted to a scheme of soluble ferrous Fe(OH)₂⁺ species, Fe²⁺(ao), FeO⁺(ao), Fe²⁺(ao), and Fe(OH)₃(aq). (80TRE/LEB also include ferric species Fe(OH)₃(aq) and Fe(OH)₄(ao)). The reactions for Fe(II) take the following form:

(1/3)Fe₂O₃(cr)+(2−b)H⁺(ao)+1/3H₂(g)

=Fe(OH)(2−b⁻)+(4/3−b)H₂O(l).

For b=0, the extrapolated values at 298.15 K for ΔG° are −68.62±3.0 kJ·mol⁻¹ from 70SWE/BAE and −64.26±2.0 kJ·mol⁻¹ from 80TRE/LEB (b⁺ = 1 atm). With the selected value for ΔG°(Fe₂O₃, cr) from 88HAA = −1013.30±2.15 kJ·mol⁻¹, ΔG° = −90.18±3.1 and −85.82±2.12 kJ·mol⁻¹ respectively. In Table 6 of the 80TRE/LEB paper is given their calculated value for ΔG°(Fe²⁺, ao), obtained from ΔG°(298.15 K) = −66.7 kJ·mol⁻¹ using ΔCₚ = 120 J·K⁻¹·mol⁻¹. This ΔG° results in ΔG° = −88.26 kJ·mol⁻¹. Comparison of their measured values with the 70SWE/BAE measurements shows the following:

<table>
<thead>
<tr>
<th>lg K</th>
<th>70SWE/BAE (No. 36)</th>
<th>80TRE/LEB (No. 41)</th>
<th>Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>373</td>
<td>8.55</td>
<td>8.23±0.08</td>
<td>0.32</td>
</tr>
<tr>
<td>473</td>
<td>5.73</td>
<td>5.92±0.05</td>
<td>−0.19</td>
</tr>
<tr>
<td>573</td>
<td>3.98</td>
<td>4.42±0.05</td>
<td>−0.44</td>
</tr>
</tbody>
</table>

The disagreement is disturbing. However, both sets of measurements indicate a more negative value for ΔG°(Fe²⁺, ao) than that of 53PAT/THO or 32RAN/FRA.

4.2.3. Solution of FeSO₄·7H₂O(cr)

4.2.3.1. Gibbs energy of solution

There have been many measurements of the solubility of FeSO₄·7H₂O(cr) as a function of temperature. Many of them are listed in 58LIN where the smoothed data are tabulated: 100 g of saturated solution contains 22.8 g FeSO₄, so that m=1.944 mol·kg⁻¹. Prior to the isopiestic measurements of 74OYK/BAL, the activity coefficients of FeSO₄(aq) had been estimated from the behavior of similar bivalent sulfate solutions [59ROB/STO, 70ROB/STO, 72PIT]. For 82WAG/EVA and the earlier 69WAG/EVA, γₐ = 0.0344 and φ, the osmotic coefficient, =0.578 from 59ROB/STO were used (reaction No. 209 in 8.2), resulting in ΔmₐG° = 14.12±0.50 kJ·mol⁻¹ for the process

FeSO₄·7H₂O(cr)=FeSO₄(aq)+7H₂O(l).

Values from the 72PIT tabulation are in agreement.
The experimental results of 740YK/BAL require an estimate at $m=0.10$ mol·kg$^{-1}$ for $\gamma_z$. With $\gamma_z = 0.15$ from 59ROB/STO, $\gamma_z$ and $a_w$ at saturation are 0.0423 and 0.952 respectively, leading to $\Delta G^o = 13.24$ kJ·mol$^{-1}$ for the above process. (740YK/BAL use $m=1.964$ mol·kg$^{-1}$ and give $\gamma_z = 0.0423$ and $a_w = 0.951$ resulting in $\Delta G^o = 13.18$ kJ·mol$^{-1}$). However 86REA/BEC point out that reanalysis of the data on the 2.2 type electrolytes by 72PIT indicates that a better value for $\gamma_z$ for FeSO$_4$ at $m=0.10$ mol·kg$^{-1}$, based on 72PIT’s value for MgSO$_4$ (0.161) is 0.161 ± 0.01, resulting in $\gamma_z = 0.048$ and $a_w = 0.952$ so that $\log K_f = -2.205$ and $\Delta_{solv}G^o = 12.58 ± 0.30$ kJ·mol$^{-1}$ (reaction No. 210).

4.2.3.2. The entropy of FeSO$_4$·7H$_2$O(cr) and the calculated $S^o$(Fe$^{2+}$, ao)

The $C_p$ values of 49LYO/UL (No. 208) lead to $S^o = 409.2 ± 1.2$ J·mol$^{-1}$·K$^{-1}$ for FeSO$_4$·7H$_2$O(cr) at 298.15 K.

We have, in Sec. 2.3, accepted, for our first iteration, $\Delta_{solv}H^o = 12.90 ± 0.10$ kJ·mol$^{-1}$. With $\Delta_{solv}G^o = 2.58 ± 0.30$ kJ·mol$^{-1}$, $\Delta_{solv}S^o = 1.07 ± 0.11$ J·mol$^{-1}$·K$^{-1}$. The calculated $S^o$(Fe$^{2+}$, ao) = $97.88 ± 1.4$ J·mol$^{-1}$·K$^{-1}$ and $\Delta_{solv}G^o = 5.37 ± 1.55$ J·mol$^{-1}$·K$^{-1}$ ($S^o$(Fe$^{2+}$, cr) = 27.319 ± 0.002 J·mol$^{-1}$·K$^{-1}$). With our tentative $\Delta_{H}$(Fe$^{2+}$, ao) = $-90.0 ± 0.50$ kJ·mol$^{-1}$ we obtain $\Delta_{solv}G^o = 91.60 ± 0.85$ kJ·mol$^{-1}$.

(E$^o = 0.474 ± 0.004 V), surprisingly more negative than all other values.$^5$ Using 740YK/BAL's original values for $\gamma_{FeSO_4}$ = 13.24 kJ·mol$^{-1}$ and $\Delta_{solv}G^o = -1.14$ J·mol$^{-1}$·K$^{-1}$, so that $S^o$(Fe$^{2+}$, ao) = $100.09 ± 1.14$ J·mol$^{-1}$·K$^{-1}$ and $\Delta_{solv}G^o$(Fe$^{2+}$, ao) = $90.94 ± 0.85$ kJ·mol$^{-1}$.

The earlier $\Delta_{solv}G^o = 14.12 ± 0.50$ kJ·mol$^{-1}$ used in the 69WAG/EVA evaluation (based on an estimated $\gamma_z$) with $\Delta_{solv}G^o$(FeSO$_4$·7H$_2$O(cr)) = $-2509.87$ kJ·mol$^{-1}$ had led to $\Delta_{solv}G^o$(Fe$^{2+}$, ao) = $-91.3$ kJ·mol$^{-1}$ which was rejected because it appeared to be too negative, possibly because the properties of FeSO$_4$(aq) were not sufficiently well established to accept this “very” negative value.

Since then, 86REA/BEC have recalculated the solubility data as a function of temperature using the activity coefficients and the Pitzer equations. Their results are expressed as

$$\log K_f = 1.447 ± 0.04153(T/K) - 21949(T/K)^2$$

The calculated $\Delta_{solv}G^o = 20.54$ kJ·mol$^{-1}$ and with $\Delta_{solv}G^o = 12.58$ kJ·mol$^{-1}$, $\Delta_{solv}S^o = 27.70$ J·mol$^{-1}$·K$^{-1}$, and $S^o$(Fe$^{2+}$, ao) = $-71.3$ kJ·mol$^{-1}$·K$^{-1}$ and $\Delta_{solv}G^o = -100.0$ kJ·mol$^{-1}$.

4.2.4. Measurements on FeCl$_2$·4H$_2$O(cr)

4.2.4.1. Vapor pressure measurements

The catalog lists the various measurements on the hydrates FeCl$_2$·4H$_2$O(cr), FeCl$_2$·2H$_2$O(cr), and FeCl$_2$·H$_2$O(cr). (FeCl$_2$·6H$_2$O(cr) exists below 283 K). The vapor pressure measurements of 49SCH (Nos. 119–121), after correction to 298.15 K show the following:

$^5$Alternatively, since we have tentatively selected $\Delta_{solv}H^o$(FeSO$_4$·7H$_2$O, cr) = $-3013.05 ± 0.65$ kJ·mol$^{-1}$ and $S^o = 409.2 ± 1.2$ J·mol$^{-1}$·K$^{-1}$, $\Delta_{solv}G^o = -2509.61 ± 0.74$ kJ·mol$^{-1}$ and $\Delta_{solv}G^o$(Fe$^{2+}$, ao) = $-91.10 ± 0.8$ kJ·mol$^{-1}$.

1. FeCl$_2$·4H$_2$O(cr) = FeCl$_2$·2H$_2$O(cr) + 2H$_2$O(g) (No. 119),
$$\Delta H^o = 108.04 ± 4.0 \text{ kJ·mol}^{-1}$$
$$\Delta G^o = 23.62 ± 1.0 \text{ kJ·mol}^{-1}$$
$$\Delta S^o = 283.1 \text{ J·K}^{-1}·\text{mol}^{-1}$$

2. FeCl$_2$·2H$_2$O(cr) = FeCl$_2$·H$_2$O(cr) + H$_2$O(g) (No. 120),
$$\Delta H^o = 63.1 ± 5.0 \text{ kJ·mol}^{-1}$$
$$\Delta G^o = 18.57 ± 2.0 \text{ kJ·mol}^{-1}$$
$$\Delta S^o = 149.4 \text{ J·K}^{-1}·\text{mol}^{-1}$$

3. FeCl$_2$·H$_2$O(cr) = FeCl$_2$(cr) + H$_2$O(g) (No. 121),
$$\Delta H^o = 63.1 ± 5.0 \text{ kJ·mol}^{-1}$$
$$\Delta G^o = 24.93 ± 2.0 \text{ kJ·mol}^{-1}$$
$$\Delta S^o = 128.0 \text{ J·K}^{-1}·\text{mol}^{-1}$$

The $\Delta S^o$'s for reactions (1) and (2) are reasonable (a usual contribution is $\Delta S^o/n = 145 ± 10 \text{ J·K}^{-1}·\text{mol}^{-1}$) for nH$_2$O(g), indicating that the $\Delta G^o$'s and $\Delta H^o$'s are acceptable. For reaction (3), the $\Delta S^o$ is low, indicating that either the $\Delta G^o$, or the $\Delta H^o$, or both, are incorrect. We assume that the second law $\Delta H^o$ is the more questionable value and accept the $\Delta G^o$ for our further use.

We now have

$$\text{FeCl}_2·4\text{H}_2\text{O} (\text{cr}) = \text{FeCl}_2·\text{H}_2\text{O} (\text{cr}) + 3\text{H}_2\text{O} (g),}$$
$$\Delta H^o = 171.1 \text{ kJ·mol}^{-1}$$
$$\Delta G^o = 42.19 \text{ kJ·mol}^{-1}$$
$$\Delta S^o = 432.5 \text{ J·mol}^{-1}·\text{K}^{-1}$$

and

$$\text{FeCl}_2·\text{H}_2\text{O} (\text{cr}) = \text{FeCl}_2 (\text{cr}) + \text{H}_2\text{O} (g),}$$
$$\Delta G^o = 24.93 \text{ kJ·mol}^{-1},$$
so that

$$\text{FeCl}_2·4\text{H}_2\text{O} (\text{cr}) = \text{FeCl}_2 (\text{cr}) + 4\text{H}_2\text{O} (g),}$$
$$\Delta G^o = 67.12 ± 3.0 \text{ kJ·mol}^{-1}$$

Using 89COX/WAG for

$$\text{H}_2\text{O} (l) = \text{H}_2\text{O} (g); \quad \Delta G^o = 8.591 ± 0.005 \text{ kJ·mol}^{-1},$$
we obtain

$$\text{FeCl}_2·4\text{H}_2\text{O} (\text{cr}) = \text{FeCl}_2 (\text{cr}) + 4\text{H}_2\text{O} (l),}$$
$$\Delta_{desh}G^o = 32.756 \text{ kJ·mol}^{-1}.$$
the uncertainty of 62KAN/GRO's tabulated $\gamma$-s and $\phi$s to
5% at the saturation point ($m=4.951$ mol·kg$^{-1}$) we obtain,
as indicated in the catalog (reaction No. 118).

$$\Delta G^0 = -16.85 \pm 0.5 \text{ kJ·mol}^{-1}$$

for FeCl$_2$·4H$_2$O(cr)=FeCl$_2$(ai)+4H$_2$O(l).

Combining the $\Delta_	ext{sol} G^0$ with the $\Delta_	ext{dehyd} G^0$ for the tetrahy-
drute, we obtain

$$\text{FeCl}_2\text{(cr)=FeCl}_2\text{(ai); } \Delta G^0 = -16.85 - 32.756$$

$$= -49.61 \pm 3.1 \text{ kJ·mol}^{-1}. $$

In Sec. 2.3 we selected $\Delta_	ext{sol} H^0$ for the above process to be
$-23.00 \pm 0.14$ kJ·mol$^{-1}$. The $\Delta_	ext{sol} G^0$ then is $-112.02 \pm 10$
J·mol$^{-1}$·K$^{-1}$ and $S^0$(FeCl$_2^{2+}$,ao)=-107.212 $\pm$ 10 J·mol$^{-1}$·K$^{-1}$,
resulting in $\Delta G^0$(FeCl$_2^{2+}$,ao) =$-89.46 \pm 3.1$ kJ·mol$^{-1}$ and again
indicating a far more negative value than all the e.m.f. values,
with the exception of 60HUR (No. 6), and the K value from
82GAM/REI (No. 4).

### 4.3. The Tentative Selected Value for $\Delta_r G^0$(Fe$^{2+}$,ao)

The range of values for $\Delta_r G^0$(Fe$^{2+}$,ao) indicates that an
obvious choice is not apparent. On the basis of the e.m.f. measurements,
the most careful work that excluded hydrogen in the preparation of the electrode and from the solution,
as well as oxygen, supports the more positive values from
53PAT/TTHO and 78JOH/BAU. The equilibrium measure-
ments of 82GAM/REI confirm this; however, the values from three other paths (the solubility of Fe$_2$O$_3$(cr), and from the entropies of the Fe$^{2+}$ (ao) from the FeSO$_4$·7H$_2$O(cr) and the FeCl$_2$·4H$_2$O(cr)→FeCl$_2$(cr) systems), indicate a much
more negative value. It is particularly difficult to ascribe a
major error in the $\Delta_	ext{sol} G^0$ for FeSO$_4$·7H$_2$O(cr). See 87REA/BEC
for further discussion. The e.m.f. measurements of
60HUR agree with the very negative values. We hypothe-
sized that kinetic factors are involved and corrected for
them. This may explain the spread in values for all reactions
involving Fe(cr) (e.m.f. measurements and the 82GAM/REI equilibrium measurements with Ti$^2$ (ao)). We therefore base
our initial selection for $\Delta_r G^0$(Fe$^{2+}$,ao) on the values
from the Fe$_2$O$_3$(cr), FeSO$_4$·7H$_2$O(cr), and FeCl$_2$·4H$_2$O(cr)→FeCl$_2$(cr) paths, accepting $\Delta_r G^0$(Fe$^{2+}$,ao)
$=90.5 \pm 1.0$ kJ·mol$^{-1}$ ($\rho^*=1$ atm). Table 6 in Sec. 5.2 shows the measurements. (This initial selection for
$\Delta_r G^0$(Fe$^{2+}$,ao) will become our final recommended value.)

### 5. The Evaluation of the Gibbs Energy of
Formation of the Aqueous Ion
Fe$^{3+}$, $\Delta_r G^0$(Fe$^{3+}$,ao)

The $\Delta_r G^0$(Fe$^{3+}$,ao) is evaluated by:

1. establishing the thermochemical property values of
FeOOH(cr, Goethite) and its $\Delta_	ext{sol} G^0$ (section 5.1.3) to
obtain a value for $\Delta G^{0}$
and
2. obtaining values for $\Delta G^0$(Fe$^{3+}$,ao)$\Delta_r G^0$(Fe$^{2+}$,ao) (Sec.
5.1.4) that are independent of the properties of other iron
compounds, from cell measurements and other equilib-
rium measurements and using our tentative value for
$\Delta_r G^0$(Fe$^{3+}$,ao) to obtain other values for
$\Delta_r G^0$(Fe$^{3+}$,ao).

In Secs. 5.1 and 5.2 we finalize the selections for the $\Delta_r G^0$(Fe$^{3+}$,ao) and for $\Delta_r G^0$(Fe$^{3+}$,ao) ($\rho^*=1$ atm), rationalizing
our selections by reviewing the effect on values for $\Delta_r H^0$
and $\Delta_r H^0$ of substances in the key network.

#### 5.1. The Properties of Goethite, FeOOH(cr, $\alpha$)

##### 5.1.1. $\Delta_r H^0$(FeOOH, cr, $\alpha$)

One path to the $\Delta_r G^0$(Fe$^{3+}$,ao) is from $\Delta_	ext{sol} G^0$(FeOOH, cr, $\alpha$) and $\Delta_	ext{sol} G^0$(tegOHT, cr, $\alpha$). This invokes
the $\Delta_r H^0$(FeOOH, cr, $\alpha$). There are four measurements leading
to $\Delta_r H^0$(FeOOH, cr) from reactions involving Fe$_2$O$_3$(cr) and
Goethite. The reaction is

$$2\text{FeOOH(cr)}=\text{Fe}_2\text{O}_3(cr)+2\text{H}_2\text{O}(l)\text{.}$$

The 59SCH (No. 63) results on the stability regions of
Fe$_2$O$_3$-FeOOH through pressure and temperature measure-
ments (800, 900, and 1000 K at 411 to 453 K) lead to
$\Delta H=\pm 10$ kJ·mol$^{-1}$ (3rd law). The 75KOR/FAD (No. 65)
differential scanning calorimetric measurements (corrected for
$\Delta_	ext{hyp} H^0$(H$_2$O,l)) = 44.004 kJ·mol$^{-1}$ lead to
13.70 kJ·mol$^{-1}$ for $\Delta H$.

Calorimetric measurements of the $\Delta_r H^0$ of FeOOH(cr, $\alpha$) and Fe$_2$O$_3$(cr) in 20.1 wt% aqueous HF at 298.15 K by
65BAR (NO. 51) and in 20.1% aqueous HCl
(HCl+7.6H$_2$O) containing 0.18% FeCl$_3$ at 344 K by
64FER (No. 64) give $\Delta H=7.87 \pm 0.84$ and 4.9±1.2
kJ·mol$^{-1}$, respectively. A summary, Table 5, with $\Delta H^0$(Fe$_2$O$_3$,cr)=$-824.9 \pm 3.2$ kJ·mol$^{-1}$ [88HAA] and
$\Delta H^0$(FeOOH,cr, $\alpha$) = $-559.3 \pm 1.7$ kJ·mol$^{-1}$ based on
65BAR and $\Delta H^0$(Fe$_2$O$_3$,cr)=$-824.9 \pm 3.2$ kJ·mol$^{-1}$.
5.1.2. ΔG°(FeOOH, cr, α)

From the C_p measurements on FeOOH of 70KIN/WET (51 K to 298 K), S°(298.15 K) is tabulated as 60.40±0.60 J·mol⁻¹·K⁻¹ (Nos. 48, 49 in Alb), resulting in ΔS° = -237.250 J·mol⁻¹·K⁻¹ and ΔG° = -488.6±1.7 kJ·mol⁻¹.

5.1.3. Gibbs Energy of Solution of FeOOH(cr, α) and ΔG°(Fe³⁺, ao)

The equilibrium between the solid ferric oxyhydrates and their aqueous solutions is complex. There are various reviews of the stability of the various ferric oxyhydroxide precipitated from Fe³⁺(aq), e.g. 69LAN, 71LAN, 71LAN/WHL, and 85HSU/MAR.

The various naturally occurring ferric oxyhydroxides are amorphous, designated as Fe(OH)₃(am), and the crystalline forms which we write as FeOOH(cr) [α for the Goethite form, β for the Akaganeitite form, and γ for the Lepidocrocite form], as well as Fe₂O₃(cr) [α for hematite and γ for maghemite].

The precipitate in contact with solutions containing Fe⁺³(aq) depends upon the pH of the solution, temperature, time, the presence of Fe²⁺(aq), an oxidizing medium, and various foreign ions. The amorphous (freshly precipitated, after about 2 h), active age to a form considered inactive (after about 2 a) and eventually to Goethite and/or hematite or other crystalline forms with different solubilities. The K_s = a(Fe³⁺)(OH)⁻ is thus difficult to ascribe accurately to a single, well-defined phase. 85HSU/MAR (No. 28) obtained the activity products, a(Fe³⁺)(OH)⁻, of Fe(CIO₃)₃ solutions hydrolyzed and aged at room temperature (298.15 ± 3 K) for 9 to 16 a which contained only well crystallized Goethite as determined by x-ray diffraction. The values determined varied with ionic strength but not with particle size (in contrast to 71LAN/WHL, 71LAN, 74WHL/LAN). The pH was 39.80, 40.32, and 30.83 for ionic strengths of about 0.005, 0.04 and 0.2 mol·dm⁻³ and correspond to the reaction:

FeOOH(cr,α)+H₂O(l)=Fe³⁺(ao)+3OH⁻(ao).

Extrapolation to J=0 results in K_s = 39.5 and ΔG° = 225.46±2.0 kJ·mol⁻¹ and ΔG°(Fe³⁺, ao) = -28.52±2.6 kJ·mol⁻¹.

Earlier 71LAN/WHL had indicated that the "pK" from precipitation, initially at concentration of Fe⁺³(aq) or Fe³⁺(ao) of 10⁻² mol·dm⁻³ varied from 37.3 to 43.3, beginning as amorphous material and that the pK_s of the aged, macroscopic Goethite would be about 43.3 (this includes a calculated 3.2 pK correction for surface area. In addition from the examination of well waters containing 10⁻³ to 10⁻⁴ mol·dm⁻³ Fe⁺³(aq) and suspended oxyhydroxides, "pK" was 37.1 to 43.5. If we adopt 43.4±0.5 as the pK_s from 71LAN/WHL (No. 27) we obtain ΔG° = 247.7±3.0 kJ·mol⁻¹ and ΔG° = -6.3±3.5 kJ·mol⁻¹.

More recently 89KHO reviewed the oxyhydroxy-H₂O system and in a preliminary comunicat indicated that for

0.5Fe₂O₃(cr, hematite)+3H⁺(ao)=Fe³⁺(ao)+1.5H₂O(l),

ΔG° = 3.0±2.5 kJ·mol⁻¹. Since we have accepted ΔH = 3.94±0.42 kJ·mol⁻¹ for the dehydration of Goethite to hematite and ΔS° = 18.27 J·mol⁻¹·K⁻¹ for this process (from Alb, Nos. 47 and 49),

ΔG° = -1.51±0.5 kJ·mol⁻¹, and for

FeOOH(cr, Goethite)+3H⁺(ao)=Fe³⁺(ao)+2H₂O(l),

ΔG° = 1.49±2.6 kJ·mol⁻¹.

89KHO also calculated log K = -0.2±0.5 for the above reaction, from the measurements of 63SCH/MIC.

Converting these to the K_s = a(Fe³⁺)(OH)⁻ for Goethite, using

3H₂O(l)=3H⁺(ao)+3OH⁻(ao); ΔG° = 239.76 kJ·mol⁻¹ and 1.25±2.6 and 240.90±2.0 kJ·mol⁻¹ for the process

FeOOH(cr,α)+H₂O(l)=Fe³⁺(ao)+3OH⁻(ao),

and ΔG° = -12.75±2.6 and -12.45±2.8 kJ·mol⁻¹, respectively. These values are tabulated.

5.1.4. The Direct Relationship Between ΔG°(Fe²⁺, ao) and ΔG°(Fe³⁺, ao)

5.1.4.1. The cell measurements

72WHL/LAN (No. 14) measured the E°'s (using a silver-silver chloride reference electrode with a saturated KCl solution) in perchloric acid solutions from 278 K to 308 K. At 298.15 K, E° = -0.7698±0.002 V for

Fe²⁺(ao)+2H⁺(ao)=Fe³⁺(ao)+2H₂(g),

resulting in ΔG° = 74.274±0.20 kJ·mol⁻¹. 73NIK/ANT (No. 16) also measured the E°'s (using Ti/Hg, TiCl(cr) reference electrode with saturated KCl solution). At 298.15 K, E° = -0.770±0.005 V and ΔG° = 74.30±0.50 kJ·mol⁻¹, in excellent agreement with 72WHL/LAN although the values diverge above 298 K resulting in ΔH°(298 K) values that differ by 4 kJ·mol⁻¹. (See Nos. 17 and 15.)

The earlier measurements of 37SCH/SHE (No. 19) (E° = -0.770±0.010 V) and 51CON/MCV (No. 25) (E° = -0.771±0.005 V) are in agreement. Other measurements are listed in the reaction catalog.

5.1.4.2. The equilibrium constants

34BRA/HER (No. 20) have recalculated the equilibrium constant of

Fe³⁺(ao)+Ag(cr)=Fe²⁺(ao)+Ag⁺(ao)

to be K = 0.363±0.015 (measurements of 12NOY/BRA) or ΔG° = 2.512±0.25 kJ·mol⁻¹ and K = 0.137±0.010 for

2Fe³⁺(ao)+2Hg(l)=2Fe²⁺(ao)+2H₂(g),

(measurements of 31POP/PLE) or ΔG° = 4.927±0.50 kJ·mol⁻¹ (No. 21).

The resultant ΔG for

Fe²⁺(ao)+H⁺(ao)=Fe³⁺(ao)+0.5H₂(g)

Table 6. The Gibbs energies of formation of Fe$^{2+}$(ao) and Fe$^{3+}$(ao) and $\Delta G^\circ$(Fe$^{3+}$(ao))
$\Delta G^\circ$(Fe$^{2+}$(ao))(p$^\circ$=1 atm)

<table>
<thead>
<tr>
<th>Source</th>
<th>$\Delta G^\circ$(Fe$^{3+}$(ao)) kJ mol$^{-1}$</th>
<th>$\Delta G^\circ$(Fe$^{2+}$(ao)) kJ mol$^{-1}$</th>
<th>$\Delta G^\circ$(Fe$^{3+}$(ao)) kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>e.m.f. measurements</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26HAM</td>
<td>−85.26±0.30</td>
<td>−83.75±1.0</td>
<td></td>
</tr>
<tr>
<td>32RAN/FRA and 32RRA2</td>
<td>−83.86±0.20</td>
<td>−78.95±0.5</td>
<td></td>
</tr>
<tr>
<td>53PAT/THO</td>
<td>−90.11±0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>78JOH/BAU</td>
<td>−80.08±0.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>72WHI/LAN (Selected Value)</td>
<td></td>
<td></td>
<td>74.27±0.20</td>
</tr>
<tr>
<td>73NIK/ANT</td>
<td></td>
<td></td>
<td>74.30±0.50</td>
</tr>
<tr>
<td>Equilibrium Constants</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>82GAM/REI</td>
<td>−78.28±1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Fe$^{3+}$) and Ti$^{4+}$(ao))</td>
<td>or</td>
<td></td>
<td></td>
</tr>
<tr>
<td>34BRA/HER</td>
<td>−82.34±1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Hg, ag reduction)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe$\text{O}_3$(cr) solubility</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70SWE/RAF</td>
<td>−90.18±3.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80TRE/LEB</td>
<td>−88.26±2.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe$\text{SO}_4$·7H$_2$O (cr), solubility</td>
<td>−91.60±0.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeCl$\text{2}$·4H$_2$O (cr)</td>
<td>−89.4±3.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>vapor pressure and solubility FeOOH (cr, Goethite), solubility</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>84HUS/MAR (pK = 39.5)</td>
<td></td>
<td>−28.5±2.6</td>
<td></td>
</tr>
<tr>
<td>71LAM/WHI (pK = 43.4)</td>
<td></td>
<td>−6.3±4.4</td>
<td></td>
</tr>
<tr>
<td>Fe$_{2}$O$_3$(cr, hematite), solubility</td>
<td></td>
<td>−12.6±2.8</td>
<td></td>
</tr>
<tr>
<td>89KHO re-analysis of data (calculated pK$_{sp}$(Goethite) = 42.3)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\Delta H^\circ$, $\Delta G^\circ$(p$^\circ$=1 atm), $S^\circ$ for Fe$_\text{O}_3$(cr, magnetite) = −1116.72±2.2 kJ mol$^{-1}$, −1010.30±2.15 kJ mol$^{-1}$, and $\log K$=3.5±0.4 k J mol$^{-1}$, respectively.

5.1.5. The Selected Value for the Relationship Between $\Delta G^\circ$(Fe$^{3+}$(ao)) and $\Delta G^\circ$(Fe$^{2+}$(ao))

The e.m.f. measurements and the equilibrium measurements are in good agreement and it would appear that the $\Delta G^\circ$(Fe$^{3+}$(ao))−$\Delta G^\circ$(Fe$^{2+}$(ao)) = 74.27±0.20 kJ mol$^{-1}$ and $E^\circ$ = −0.769±0.002 V.

5.2. The Selection of $\Delta G^\circ$(Fe$^{3+}$(ao))

The values obtained for $\Delta G^\circ$(Fe$^{3+}$(ao)) and $\Delta G^\circ$(Fe$^{2+}$(ao)) as well as the values for the $\Delta(\Delta G^\circ)$ are summarized in Table 6. The selected value for the $\Delta(\Delta G^\circ)$ is indicated. This value must be maintained within the stated uncertainty.

It is quite obvious that if we accept $\Delta G^\circ$(Fe$^{2+}$(ao)) = −90.5±1.0 kJ mol$^{-1}$ and we maintain $\Delta(\Delta G^\circ)$ = 74.27±0.20 kJ mol$^{-1}$ our value for $\Delta G^\circ$(Fe$^{3+}$(ao)) must be −16.2±1.1 kJ mol$^{-1}$, in marginal agreement with the 89KHO value obtained from the solubility of Fe$_3$O$_4$(cr, hematite). It is also obvious that the more positive value of −6.3 kJ mol$^{-1}$ for $\Delta G^\circ$(Fe$^{2+}$(ao)) would support the more positive values for $\Delta G^\circ$(Fe$^{3+}$(ao)) from the measurements of 82GAM/REI, 53PAT/THO, 78JOH/BAU, as well as those from 32RAN/FRA and 32RAN/FRA2. However, this would require complete rejection of the values from three paths for $\Delta G^\circ$(Fe$^{3+}$(ao)), from the solubility of Fe$_3$O$_4$(cr, hematite), the solubility of Fe$\text{SO}_4$·7H$_2$O(cr), and the solubility of FeCl$\text{2}$·4H$_2$O(cr) and the decomposition of the tetrahydrate. Although the uncertainties on the values from Fe$_3$O$_4$ and FeCl$\text{2}$·4H$_2$O are large and some adjustments could be made in the interpretations of the Gibbs energies of reaction, a 6 to 10 kJ mol$^{-1}$ adjustment is not possible. If we attempt to go the other way, that is, to select a value of −81 kJ mol$^{-1}$ (or even 84 kJ mol$^{-1}$) for $\Delta G^\circ$(Fe$^{2+}$(ao)) and use the Gibbs energies of reaction of the three above mentioned paths we would obtain calculated values for the enthalpies of formation of Fe$_3$O$_4$(cr), Fe$\text{SO}_4$·7H$_2$O(cr), and FeCl$\text{2}$·4H$_2$O(cr) and FeCl$\text{2}$(cr) that are incompatible with the selected values for these substances and their $\Delta_m H^\circ$'s. (See sections on $\Delta H^\circ$(Fe$\text{SO}_4$·7H$_2$O(cr), $\Delta H^\circ$(FeCl$\text{2}$(cr), and $\Delta H^\circ$(Fe$^{3+}$(ao))). We therefore accept:

$\Delta G^\circ$(Fe$^{3+}$(ao)) = −1673±71 k J mol$^{-1}$

and our previous "tentative" value for $\Delta G^\circ$(Fe$^{2+}$(ao)) = −90.5±1.0 kJ mol$^{-1}$.
6. Summary

All final recommended property values and uncertainties are tabulated ($p^* = 1$ atm and $p^* = 1$ bar). Predicted (calculated) process values and uncertainties for many of the reactions used in this evaluation are also tabulated ($p^* = 1$ bar). In addition, a list of reactions (contained in the reaction catalogue) pertinent to this evaluation but not definitive are given (Sec. 6.2).

6.1. The Final Recommended Values

It is disturbing that firmer values for these important ions cannot be offered. At present we accept the following:

For Fe$^{2+}$(ao)
\[
\Delta H^\circ = -90.0 \pm 0.5 \text{ kJ mol}^{-1}
\]
\[
\Delta G^\circ = -90.5 \pm 1.0 \text{ kJ mol}^{-1} \quad (p^* = 1 \text{ atm})
\]
\[
\Delta G^\circ = -90.53 \pm 1.0 \text{ kJ mol}^{-1} \quad (p^* = 1 \text{ bar}),
\]
\[
S^\circ = 101.6 \pm 3.7 \text{ J mol}^{-1} \cdot \text{K}^{-1}
\]

For Fe$^{3+}$(ao)
\[
\Delta H^\circ = -49.0 \pm 1.5 \text{ kJ mol}^{-1}
\]
\[
\Delta G^\circ = -162.3 \pm 1.1 \text{ kJ mol}^{-1} \quad (p^* = 1 \text{ atm})
\]
\[
= -162.28 \pm 1.1 \text{ kJ mol}^{-1} \quad (p^* = 1 \text{ bar}),
\]
\[
S^\circ = -276.44 \pm 7.7 \text{ J mol}^{-1} \cdot \text{K}^{-1}
\]

This requires a small modification in the values for \(\Delta H^\circ\) and/or \(\Delta G^\circ\) for FeSO$_4$-$7\text{H}_2\text{O}$(cr). We have chosen to adjust \(\Delta G^\circ = 13.2 \text{ kJ mol}^{-1}\) by returning to the 740K Y/BAL yields values with \(y_p = 0.15\) at \(m = 0.1 \text{ mol kg}^{-1}\). This results in an adjustment to \(\Delta H^\circ(\text{FeSO}_4$-$7\text{H}_2\text{O}$(cr) from the tentative value of \(-3013.05 \pm 0.85 \text{ kJ mol}^{-1}\) given in Sec. 2.5 to \(-3012.6 \pm 0.9 \text{ kJ mol}^{-1}\). The equation for the enthalpy of solution is adjusted for this so that

\[
\Delta H_{(T)} - \Delta H_{(298K)} / \text{kJ mol}^{-1} = (12.45 \pm 0.12)(x + (64.16 \pm 2.83)(x - 382.55 \pm 57.07))^2.
\]

Recommended values for the thermodynamic property values for all substances considered are given in Tables 7 and 8. In addition “reconstituted” process values are given in Table 9.
6.2. Other Cycles in the Fe Network

In addition to the cycles used here, there are others which we initially considered and rejected from further consideration because they are too indirect and the values we would obtain for the thermodynamic properties of FeCl₃(μ) and FeCl₃(μ) would not be weighted highly. A better approach would be to use the better defined "key compounds" to help define the properties of those compounds in the greater network. Reaction numbers follow those given in Appendixes A, b, and c. Those involving FeCl₃(μ) are contained in 89EFL. The reactions are as follows:

FeOCl(μ)+2HCl(aq)=FeCl₃(μ)+H₂O(l)

(Appendix A, b, Nos. 159 and 160),

6FeOCl(μ)=2Fe₂O₃(μ)+6FeCl₆(μ)

(Appendix A, b, No. 161),

Fe₂O₃(μ)+6HCl(aq)=2FeCl₃(μ)+3H₂O(l)

(Appendix A, b, No. 162),

2FeCl₃(μ)+Cl₂(g)=2FeCl₅(g)

(Appendix A, b, No. 163 and 164),

2FeCl₃(μ)=Fe₃Cl₆(g) (Appendix A, c, Nos. 19–33).

Fe₂Cl₆(μ)=2FeCl₅(g),

Fe₂O₃(μ)+6HCl(aq)=2FeCl₃(μ)+3H₂O(l),

2Fe₂O₃(μ)+6Cl₂(g)=4FeCl₃(μ)+3O₂(g).

6.3. Effect of values on other networks

The values given here for some iron compounds, particularly for ΔG°(Fe₂⁺,μo) and for ΔH°(μ,FeCl₃), differ from those given in 82WAG/EVA, 69WAG/EVA, and 71MED/BER, and should not be combined with values from those sources. These new values are not only on the CODATA scale, but indicate that a reanalysis of other key networks are needed. In particular, the thermochemical relationships in the uranium key network (see 83FUG/PAR and 92GRE/FUG) involve ΔH°(μ,FeCl₃) from 82WAG/EVA in the analysis of the UCl₄(μ)–UO₂Cl₂(μ) relationship. Some of these reactions may be necessary not only for ΔH°(μ,FeCl₃,μ), ΔH°(μ,FeCl₅,μ), and ΔH°(μ,FeCl₃,μ) (see 85O'H and 92FUG), but also for ΔH°(μ,FeCl₅,μ), ΔH°(μ,FeCl₅,μ), ΔH°(μ,FeCl₃,μ), and ΔH°(μ,FeCl₅,μ). The latter two have also been defined by CODATA (see 89COX/WAG) from 83FUG/PAR.

7. Bibliography on Selected Fe Compounds

[References are provided for each sub-section.]

THE THERMODYNAMIC PROPERTIES OF THE AQUEOUS IONS OF IRON


THE THERMODYNAMIC PROPERTIES OF THE AQUEOUS IONS OF IRON

Appendix I: Reaction Catalogs for Selected Fe Compounds

* Chemical Thermodynamics Data Center
* National Institute of Standards and Technology
* Computer Readable Reaction Catalog
* For Selected Fe Compounds 3/91
* Vivian D. Parker (VDP) with the cooperation of Vadim Medvedev (VM) and M. Efimov (EME) IVTAN, I. Khodakovskii (IKh.) and O. Devina (O.D.) VIGAC

Al.a. Descriptive Information

The reaction catalog is constructed as a database in a format developed for input of the information into a form more suitable for storage and calculation [83NEU]. This format was used as input for the calcium reaction catalog output which was published in 87GAR/PAR. For convenience, we repeat the pertinent information given in Secs. 1.2.1, 1.2.5, 1.2.6, and 1.2.7.

Z: The reference code described in Sec. 1.2.5. The final two digits of the year (nineteenth century citations carry the four digits) preceded the first three letters of the first two author’s last names (separated by a slash) in upper case letters. A number at the end of the code indicated that there is more than one reference having the same first two authors codes and year of publication. The bibliography in Sec. 7 is arranged chronologically by this reference code and alphabetically by the first author within each year.

R: The reaction studied, or the substance studied. If it is for a substance studied, the substance formula will be preceded by an “=” sign. This is primarily used for the entropy of a substance.

DV: The thermodynamic property measured for the reaction listed, the temperature, the value and its uncertainty, and the units. The uncertainties in the values for reactions listed in the reaction catalog and used in the text are initial uncertainties assumed by the evaluator, as discussed in 87PAR/EVA and may not agree with the experimentalist’s appraisal.

F: A flag to indicate special features such as a subcatalog. Here it is used with TN (Technical Note Series) to indicate that the reaction was used in the 69WAG/ EVA evaluation. However, the absence of this flag does not indicate that it was not considered for the 1969 evaluation.

W: This is a weighting code. If it followed by “-1,” it is a constraint to accept the value with no modification; if it is followed by a “99,” it is for information only (i.e., the measurement is not given any weight in the evaluation).

C: Comments pertaining to the reaction or other pertinent information.

*: Private comments and working notes

S: Name or initials of the evaluator and the date of the preparation, or modification of the entries.

The thermochemical property designation for reactions is: H for ΔH; G for ΔG; S for ΔS; and S for S° (if the R: entry is for a substance, the formula is preceded by an “=”).
The temperature is given in degrees Kelvin or Celsius units. If the temperature is not specified, the measurement is assumed to refer to 298.15 K. The pressure can be assumed to be either one bar or one atmosphere. For $\Delta G$'s (where needed) or $S^\circ$'s of gases, the pressure is stated in the comments. The thermochemical value and uncertainty are given as decimal numbers. The currency symbol (in the U.S., the "$\$" is used to separate the value and its uncertainty and represents "$\pm$".

The shorthand abbreviations for the units used in the catalog are dependent on the property so that:

- $\text{kJ}=\text{kJ mol}^{-1}$ for H, G, and $\text{kJ mol}^{-1}$ for S, C_P
- $\text{kC}=$cal mol$^{-1}$ for H, G, and kcal mol$^{-1}$ for S, C_P
- $J=$mol$^{-1}$K$^{-1}$ for S, C_P
- $C=$cal mol$^{-1}$K$^{-1}$ for S, C_P

K, °C=degrees Kelvin, Celsius temperature.

All values are for the reaction as given.

The recommendations of the Division of Physical Chemistry of the International Union of Pure and Applied Chemistry [82UP] are followed for thermodynamic conventions, standard states, terminology, nomenclature, symbols, and units. The symbols used here are also given in 89COX/WAG. In addition, the following are used:

- $a_i=$hypothetical standard state, $m=1$ mol kg$^{-1}$ for an electrolyte in aqueous solution
- $a_0=$hypothetical standard state, undiss sociated
- $a_q=$aqueous, unspecified concentration, usually dilute
- $250\text{H}_2\text{O}$ etc. = solution of specified composition
- $D=$differential (partial molar property).

### Al.b. Reaction Catalog

The following information is a duplicate of the actual computer file, which is in an ASCII format, thus, in this published document, upper and lower case, super- and subscripted, and Greek and math characters are not used. As mentioned in Al.a, for example, the "$\bullet$" character in the computer file is actually the "$\pm$" mathematical symbol; "$\text{C}_p$" is actually "$\text{C}^\circ_p$", "$\text{dH}$" is "$\text{dH}^\circ$".

<table>
<thead>
<tr>
<th></th>
<th>Z:</th>
<th>89CTT</th>
</tr>
</thead>
<tbody>
<tr>
<td>R:</td>
<td>=Fe($\text{cr}$)</td>
<td></td>
</tr>
<tr>
<td>DV:</td>
<td>S, 27.319 ± 0.002 J</td>
<td></td>
</tr>
<tr>
<td>C:</td>
<td>bcc phase; $C_p=25.154 \pm 0.065$ J mol K$^{-1}$ at 200 K, $H(H(298))=2.317 \text{ kJ}$, $S=17.9417$ J/mol K and $C_p=21.6054$ J/(mol K). From 90HAA/CHA. Using $H(H(0))=2.192$ kJ/mol at 200 K from 85CHA/DAV, $H(H(0))=4.509$ kJ/mol at 298 K.</td>
<td></td>
</tr>
<tr>
<td>S:</td>
<td>8/89 VBP, 8/90 VBP</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Z:</th>
<th>89CTT</th>
</tr>
</thead>
<tbody>
<tr>
<td>R:</td>
<td>=Fe($\text{cr}$)</td>
<td></td>
</tr>
<tr>
<td>DV:</td>
<td>S, 180.489 $\pm 0.010$ J</td>
<td></td>
</tr>
<tr>
<td>C:</td>
<td>$1$ bar, $C_p=25.675 $ $0.010$ J/(mol.K), $H(H(0))=-6.850 $ $0.005$ kJ/mol</td>
<td></td>
</tr>
<tr>
<td>S:</td>
<td>8/89 VBP, 4/90 VBP</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Z:</th>
<th>82GAM/REI</th>
</tr>
</thead>
<tbody>
<tr>
<td>R:</td>
<td>Fe$^2+$(aq)+2$\text{H}$(aq)=Fe$^3+$(aq)+2$\text{H}$(aq)</td>
<td></td>
</tr>
<tr>
<td>DV:</td>
<td>G, $+13.51 $ $1.5$ kJ</td>
<td></td>
</tr>
<tr>
<td>C:</td>
<td>$K^+$ at 323K and concentration $NaClO_4=1.0$ mol/($kg H_2O$) is 0.07592 $\pm 0.06$ kJ/mol at 298.15 K and to 1=0 ($-0.33k$). Note: Authors use co-author's half cell value for $2H^+=Fe^{2+}+2H_2O=2H^+(aq)+2H_2O$ at $dG=68.826$ kJ/mol at 298.15 K. NIST and IVTAN evaluations give 64.852 kJ/mol.</td>
<td></td>
</tr>
<tr>
<td>S:</td>
<td>VBP Aug 85, 11-87</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Z:</th>
<th>78OH/BAU</th>
</tr>
</thead>
<tbody>
<tr>
<td>R:</td>
<td>Fe($\text{cr}$)+$2\text{H}$(aq)=Fe$^2+$(aq)+$H_2$(g)</td>
<td></td>
</tr>
<tr>
<td>DV:</td>
<td>G, $-80.08 $ $0.20$ kJ</td>
<td></td>
</tr>
<tr>
<td>C:</td>
<td>From cell Fe($\text{cr}$)[FeCl$_2$(0.02mM)][Fe$^2+$(aq)][Cl$^-$][Fe$^3+$(aq)] $E_0$ constant when pH is over 5.8. Fe($\text{cr}$) was used as spectroscopic grade with less than 10 ppm total spectroscopically detectable impurities and 10 ppm H. This Fe was specially vacuum-annealed to remove H2. If not specially degassed, potential becomes greater, from 0.415 V to $-0.435$ V. p=1 atm.</td>
<td></td>
</tr>
<tr>
<td>S:</td>
<td>5/86 VBP</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Z:</th>
<th>60HUR</th>
</tr>
</thead>
<tbody>
<tr>
<td>R:</td>
<td>Fe($\text{cr}$)+$2\text{H}$(aq)=Fe$^2+$(aq)+$H_2$(g)</td>
<td></td>
</tr>
<tr>
<td>DV:</td>
<td>G, $-90.115$ 80.80 kJ</td>
<td></td>
</tr>
<tr>
<td>C:</td>
<td>From $E_0=+0.467$ V at 203 K which includes a (probably small) liquid junction potential. Measurements in aqueous acid chloride solutions. Author corrects data for all activities. Iron used for electrolytes contain $0.03$ C, $0.01$ Si, $0.19$ Mn, $0.027$ P, and $0.030$ S. Electrodes vacuum annealed for one hour at about 973 K. Rate of reaction is proportional to $OH$ activity. Mechanism proposed is 2Fe($\text{cr}$)+OH$^-$=2Fe$^2+$(aq)+OH$^-$4e. Correction to 298 K is negligible. p=1 atm.</td>
<td></td>
</tr>
<tr>
<td>S:</td>
<td>5/86 VBP</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Z:</th>
<th>78NAS/RAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>R:</td>
<td>Fe($\text{cr}$)+$3/2\text{H}$(aq)+3$\text{Cl}$(aq)=Fe$^2+$(aq)+3$\text{H}$(aq)</td>
<td></td>
</tr>
<tr>
<td>DV:</td>
<td>H, $-617.349$ 0.84 kJ</td>
<td></td>
</tr>
<tr>
<td>W:</td>
<td>99</td>
<td></td>
</tr>
</tbody>
</table>

|   | Linear extrapolation to 1=0 from measurements in 1, 2, 3 and 4 mol dm$^{-3}$ $\text{HClO}_4$ aqueous solutions containing 1% and 1.5% $\text{H}_2\text{O}_2$ using thermal corrections given by 78VNAS/ YAS3. From 1% $\text{H}_2\text{O}_2$, $d$sof$=10.616.89$ kJ/mol. From 1.5% $\text{H}_2\text{O}_2$, $d$sof$=167.81$ kJ/mol. Using 67VNAS corrections, extrapolated values are $-615.51$ and $-616.14$ kJ/mol, re- |
spectively. Solutions corrected from molarity to molality. See revision.

8. S: VBP Aug 85
Z: 76VAS/RAS
R: Fe(cr)+3/2 H2O2(aq)+3HClO4(ai)
   =Fe(ClO4)3(ai)+3H2O(l)
DV: H, -617.2150.3 k J
C: Reextrapolation to I=0 using Khodakovskii’s '86 equation and constants. Individual experimental val- ues are: For m Fe+3(ao)=0.012 mol/(kg H2O) in 1.058, 2.220, 3.501, 4.920 molal HClO4 solns containing 1.0% H2O2, dH = -618.43, -618.27, -621.24 and -623.08 kJ/mol, respectively, in solns containing 1.5% H2O2, dH= -616.51, -618.65, -620.61 and -622.45 kJ/mol respectively. dhd-H corrections for extrapolation are 2.67, 3.08, 3.326, and 3.50 kJ/mol.
S: O.D., I.Kh. with VBP 5/87

9. Z: 6830OU/CIIA
R: Fe+2(ao)+1/2 H2O2(aq)+H+(ao)=Fe+3(ao)+H2O(l)
DV: H, -146.1381.0 k J
C: Oxidation of (NH4)2Fe(SO4)2 soln (0.1 molal) in .05m H2SO4; final concentration Fe+3(ao) is 5E-04 molal with dH= -146.650.84 kJ/mol, and oxidation of Fe(ClO4)2 soln (0.2 molal) in 0.1 HClO4 soln); final concentration Fe+3 is 5E-04 molal with dH= -145.601.3 kJ/mol.
S: 6/86 VBP

10. Z: 71BER/TUM
R: Fe+2(ao)+1/2 H2O2(aq)+H+(ao)=Fe+3(ao)+H2O(l)
DV: H, -148.7650.10 k J
C: Used FeSO4 solutions, m=.003 to .009 mol/(kg H2O) with about 0.01 m H2SO4.
S: 6/86 VBP

11. Z: 47FON
R: Fe+2(ao)+1/2 H2O2(aq)+H+(ao)=Fe+3(ao)+H2O(l)
DV: H, -150.160.50 k J
C: In 0.5 mol dm-3 HClO4
S: 6/86 VBP

12. Z: 47FON
R: Fe+3(ao)+1/2 H2(g)=Fe+2(ao)+H+(ao)
DV: H, -40.080.50 k J
S: 6/86 VBP

13. Z: 35CHSW/SWE
R: Fe+2(ao)+Ag+(ao)=Fe+3(ao)+Ag(cr)
DV: G, -1.7250.2 k J
C: K meas. from Fe+3(ao) reduction in HClO4 aqueous solutions, m=0.9255 to 0.07404= mol/(kg H2O). Ionic strength solution 1.4 to 0.1. Extrapolation to zero using Davies equation for activity coefficients.
S: 6/86, 10/90 VBP

14. Z: 72WHI/LAN
R: Fe+2(ao)+H+(ao)=Fe+3(ao)+1/2 H2(g)
DV: G, +74.274.00 k J

15. Z: 72WHI/LAN
R: Fe+2(ao)+H+(ao)=Fe+3(ao)+1/2 H2(g)
DV: H, 42.75 $ 1.5 k J
C: See G reaction. E's measured 278.15 to 308.15 K. 2nd law; authors give 42.67 $ 1.7 kJ/mol.
C: Calculated dS= +105.9 J/(mol.K); See 73NIK/ANT for use of this dS and 88HOV Cp data.
S: 8/88 VBP, 3/90 VBP

16. Z: 73NIK/ANT
R: Fe+2(ao)+H+(ao)=Fe+3(ao)+1/2 H2(g)
DV: G, +74.30 $ 0.50 k J
C: E measured in 0.125 to 1.913 mol dm-3 HClO4 (10 concentrations). Fe+2(ao), Fe+3(ao) concentrations are less than 0.01 M. Corrected for ionic strength of solution. Used Ti(Hg).
C: TICI(cr) sat'd KCl solution half cell. p=1 atm.
S: 3/90 VBP

17. Z: 73NIK/ANT
R: Fe+2(ao)+H+(ao)=Fe+3(ao)+1/2 H2(g)
DV: H, 46.7 $ 2.0 k J
C: E measured in 0.125 to 1.913 mol dm-3 HClO4 (10 concentrations). Fe+2(ao), Fe+3(ao) concentrations are less than 0.01 M. Corrected for ionic strength of solution. Used Ti(Hg), TICI(cr) sat'd KCl solution half cell. Second Law value, based on E measurements 298 to 343 K; If use E values at higher temperatures Second Law value is 47.4 $ 5.0 kJ/mol. dH(-H298.15)
C: at mean $13.49 K=1.2 kJ/mol, taken from Cp measurements Fe+2(ao) and Fe+3(ao) by 88HOV. Third Law value, using dS= -105.9 J/(mol.K) is 42.27 $ 1.4 kJ/mol. dS over range 298 to 323 K is $ 57.9 J/(mol.K). Over entho range dS= -72.2 J/(mol.K).
S: 3/90 VBP

C: Effect of pH in the range from 1.5 to 11.0 on oxid-red'n potential of Fe+3(ao)-Fe+2(ao)-SO4-2(ao) aqueous system. Obtains E0
V. B. PARKER AND I. L. KHODAKOVSKI

(Chemical equations and calculations are presented.

Section 19:

Z: 37SCH/SHE
R: Fe(2+)(aq) + H+(aq) = Fe(3+)(aq) + 1/2 H2(g)
DV: G = +74.303 kJ
C: From cell measurements (H2 electrode) in HClO4, m = 0.273 to 0.259 mol/kg H2O-1.
Ratio of [Fe+] to [Fe2+] maintained at 1.0
Correct for activity coeff. and extrap. to m = 0.
Correct for hydrolysis of Fe(3+)(aq) to Fe(OH)+2(aq), p = 1 atm.
S: 6/86 VBP

Section 20:

Z: 34BRA/HER
R: Fe(2+)(aq) + Ag+(aq) = Fe(3+)(aq) + Ag(cr)
DV: G = -2.512 kJ
C: Corrected data of 12NOV/BRA. Measurements in acidic nitrate salt solutions at high ionic strength
S: 6/86, 10/60 VBP

Section 21:

Z: 34BRA/HRI
R: Fe(2+)(aq) + H2(g) = Fe(3+)(aq) + Hg(l)
DV: G = -2.46 kJ
C: Corrected data of 31POP/FLE. Measurements in acidic perchlorate salt solutions at low ionic strength.
S: 6/86, 10/90 VBP

Section 22:

Z: 53MAG/HU
R: Fe(CIO4)2(HClO4 + 5.5H2O:au)
DV: G = -2.512 kJ
C: From e.m.f. meas. at 288, 298 and 623 K, p = 1 atm.
S: 6/86 VBP

Section 23:

Z: 53MAG/HUI
R: Fe(2+)(aq) + H+(aq) = Fe(3+)(aq) + 1/2 H2(g)
DV: G = 7.344 kJ
W: 99
C: E = -0.7375 V in 1 mol dm-3 HClO4. Davies eqn. used to correct for activity coefficients. p = 1 atm.
S: 6/86 VBP

Section 24:

Z: 51CON/MCV
R: Fe(CIO4)2(HClO4 + 110H2O:au)
DV: G = -7.11 kJ
C: From e.m.f. meas. 283–308 K. Initial concentration Fe(2+)(aq) = 0.025 moles (kg H2O)-1.
S: 6/86 VBP

Section 25:

Z: 51CON/MCVC
R: Fe(2+)(aq) + H+(aq) = Fe(3+)(aq) + 1/2 H2(g)
DV: G = +7.375 kJ
C: E = -0.7394 V in 0.3 pmol dm-3 HClO4 (corrected to unit concentration H+). Ionic strength solution = 0.55 mol/kg H2O). Corrected to activities using Davies eqn. p = 1 atm.
S: 6/86 VBP

Section 26:

Z: 60MAT
R: Fe(2+)(aq) + H+(aq) = Fe(3+)(aq) + 1/2 H2(g)
DV: G = 7.344 kJ
C: E = -0.7375 V. Calculation of results of 58LAP; corrects for Fe(3+)-SO4-2 complexing. Uses Davies equation. p = 1 atm.
S: 6/86 VBP

Section 27:

Z: 71LAN/WHI
R: FeOOH(cr, a) + H2O(l) = Fe(3+)(aq) + 3OH-(aq)
DV: G = +247.7 kJ
C: From laboratory solution containing crystalline Goethite and ground waters for beds containing iron minerals.
S: 8/87, 10/90 VBP

Section 28:

Z: 85HSU/MAR
R: FeOOH(cr, a) + H2O(l) = Fe(3+)(aq) + 3 OH-(aq)
DV: G = 225.6 kJ
C: Aged Fe(CIO4)2 solutions, nine to sixteen a, at 99.8 ± 3 K. Solid phase determined by X-ray diffraction. Only solutions containing well characterised Goethite were used to calculate pK's of 39.80, 40.32 and 40.83 for iron strength solutions of 0.005, 0.04 and 0.2 M. Corrections for hydrolysis were made.
S: 10/90 VBP

Section 29:

Z: 90CTT
R: Fe(OH)3(cr) = Fe(3+)(aq) + 3 OH-(aq)
DV: G = +223.7 kJ
C: Log K = -39.15. Recalculation of results of 58LAP; corrects for Fe(3+)-SO4-2 complexing. Uses Davies equation.
S: 6/86 VBP

Section 30:

Z: 89CTT
R: Fe(OH)2(g)
DV: S = 286.9 kJ
C: One Bar. H = H0 = 17.816 ± 2.00 $/mol, Cp = 84.444 ± 6.0 $/mol(K) = 98/79
S: 8/87 VBP

Section 31:

Z: 1882THO
R: FeCl3(300H2O) + 3NaOH(100H2O)
DV: H = -104.438 $/mol
C: pH = 102.51 $/mol at 293 K; estimated dCp = +380 $/mol(K)
S: 8/87 VBP

Section 32:

Z: 1873BER
R: Fe2(SO4)3(aq) + 6KOH(200H2O)
DV: H = -246.960 $/mol
C: pH = -251.0 $/mol at 291 K; estimated dCp = -600 $/mol(K)
S: 6/87 VBP

Section 33:

Z: 60MAT
R: 3Fe(2+)(aq) + 4H2O(l) = Fe3O4(cr) + 8H+(aq) + 2e
DV: G = 237.238 $/mol
C: Recalculation of results of 58LAP; corrects for Fe+3—SO4-2 complexing. Uses Davies equation. p=1 atm.

S: 6/86 VBP

34. Z: 58LAP
R: Fe+2(aq)+3H2O(l)=Fe(OH)3(cr)+3H(aq)+2e
DV: G, 87.61 S20.0 kj
W: 99
C: Effect of pH in the range from 1.5 to 11.0 on oxid-red' potential of Fe+3(aq)-Fe+2(aq)-SO4-2(aq) aqueous system. Obtains E0 Fe +2(aq)-Fe+3(aq)=0.738 V and log Kso Fe(OH)3(cr)=-39.43. Reference electrode was a saturated calomel half cell. Concentration of SO4-2(aq)=0.04 mol dm-3. Corrects for aFe +3/4Fe+2 using Debye-Huckel equation; no extrapolation to I=0. See recalculations by 60MAT. p=1 atm.

S: 6/86 VBP

35. Z: 58LAP
R: 3Fe+2(aq)+4H2O(l)=Fe3O4(cr)+8H(aq)+2e
DV: G, 232.72 S20.0
W: 99
C: Effect of pH in the range from 1.5 to 11.0 on oxid-red' potential of Fe+3(aq)-Fe+2(aq)-SO4-2(aq) aqueous system. Obtains E0 Fe +2(aq)-Fe+3(aq)=0.738 V and log Kso Fe(OH)3(cr)=-39.43. Reference electrode was a saturated calomel half cell. Concentration of SO4-2(aq)=0.04 mol dm-3. Corrects for aFe +3/4Fe+2 using Debye-Huckel equation; no extrapolation to I=0. See recalculations by 60MAT. p=1 atm.

S: 6/86 VBP

36. Z: 70SWE/BAE
R: 1/3Fe3O4(cr)+2H2(g)+3H2O(l)=Fe+2(aq)+4/3H2O(l)
DV: G, -68.68 S10.1 kj
C: Solubility Fe3O4(cr) in dilute aqueous solns satsd with H2 at 1 atm at 298 K measured at temperatures between 323 K and 573 K. Solutions ranged from KOH molality 4E-04 mol/kg to HCL molality 1E-04 mol/kg. Measurements were made by continuous flow of solution over bed of pure Fe3O4. Solubilities have been combined to calculate K's and extrapolate to 298 K for processes leading to formation of Fe+2(aq), FeOH+(aq), Fe(OH)2(aq), and Fe(OH)3-1(aq). dS(298) for reaction forming Fe+2(aq) was restricted to -25.3 cal/(mol.K) using S0(Fe+2, ao) from 68LAR/CER. Used dCp=42 J/(mol.K). p=1 atm.

S: 5/86 VBP

37. Z: 70SWE/BAE
R: 1/3Fe3O4(cr)+H+(ao)+1/3H2(g)-FeOH +2(aq)+1/3H2O(l)
DV: G, -15.43 S 5.0 kj
C: Solubility Fe3O4(cr) in dilute aqueous solns satsd with H2 at 1 atm at 298 K measured at temperatures between 323 K and 573 K. Solutions ranged from KOH molality 4E-04 mol/kg to HCL molality 1E-04 mol/kg. Measurements were made by continuous flow of solution over bed of pure Fe3O4. Solubilities have been combined to calculate K's and extrapolate to 298 K for processes leading to formation of Fe+2(aq), FeOH+(aq), Fe(OH)2(aq), and Fe(OH)3-1(aq). dS(298) for reaction forming Fe+2(aq) was restricted to -25.3 cal/(mol.K) using S0(Fe+2, ao) from 68LAR/CER. p=1 atm.

S: 5/86 VBP

38. Z: 70SWE/BAE
R: 1/3Fe3O4(cr)+1/3H2(g)+2/3H2O(l)=Fe(OH)2(aq)+H+(ao)
DV: G, 48.71 S10.0 kj
C: Solubility Fe3O4(cr) in dilute aqueous solns satsd with H2 at 1 atm at 298 K measured at temperatures between 323 K and 573 K. Solutions ranged from KOH molality 4E-04 mol/kg to HCL molality 1E-04 mol/kg. Measurements were made by continuous flow of solution over bed of pure Fe3O4. Solubilities have been combined to calculate K's and extrapolate to 298 K for processes leading to formation of Fe+2(aq), FeOH+(aq), Fe(OH)2(aq), and Fe(OH)3-1(aq). dS(298) for reaction forming Fe+2(aq) was restricted to -25.3 cal/(mol.K) using S0(Fe+2, ao) from 68LAR/CER. p=1 atm.

S: 5/86 VBP

39. Z: 70SWE/BAE
R: 1/3Fe3O4(cr)+5/3H2(g)+1/3H2O(l)=Fe(OH)3-1(aq)+H+(ao)
DV: G, +99.42 S10.0
C: Solubility Fe3O4(cr) in dilute aqueous solns satsd with H2 at 1 atm at 298 K measured at temperatures between 323 K and 573 K. Solutions ranged from KOH molality 4E-04 mol/kg to HCL molality 1E-04 mol/kg. Measurements were made by continuous flow of solution over bed of pure Fe3O4. Solubilities have been combined to calculate K's and extrapolate to 298 K for processes leading to formation of Fe+2(aq), FeOH+(aq), Fe(OH)2(aq), and Fe(OH)3-1(aq). dS(298) for reaction forming Fe+2(aq) was restricted to -25.3 cal/(mol.K) using S0(Fe+2, ao) from 68LAR/CER. p=1 atm.

S: 5/86 VBP

40. Z: 70SWE/BAE
R: Fe+2(aq)+H2O(l)=FeOH+(ao)+H+(ao)
DV: G, +53.1 S2.9
C: Difference in 2 extrapolated K's.
S: 5/86 VBP

41. Z: 60TRE/LED
V. B. PARKER AND I. L. KHODAKOVSKII

D:
\[
\begin{align*}
1/3\text{Fe}_3\text{O}_4(cr) + 7/3 \text{H}^+(aq) + 1/3 \text{H}^+(g) &= \\
\text{Fe}^2+2(ao) + 4/3\text{H}_2\text{O}(l)
\end{align*}
\]

DV: 
H: -85.4454 kJ
DV: 
G: -64.265 2.0 kJ
C: 
\[
\begin{align*}
\text{d} \text{H} (473 \text{ K}) &= -78.09 \text{ kJ/mol and } \text{dS} (473 \text{ K}) = -51.63 \text{ J/(mol.K)}, \text{Evaluator used } \text{dCp}=42 \\
\text{J/(mol.K)} \text{ from } 70 \text{SW/EBAE}
\end{align*}
\]

C: 
**Solubility of carefully characterized Fe\text{SO}_4(cr)** in dilute aqueous solutions satd with H\text{2}(g) measured from 373 to 573 K in flow apparatus. Solution compositions included either HCl molettes of up to 1 mmole (kg H\text{2}O)-1 or NaOH molettes of up to 40 mmole (kg H\text{2}O)-1. The dependence of the equilibrium solubility on the pH and reduction potential were fitted to a scheme of soluble ferrous and ferric species. Solubility products were used to derive thermodynamic constants in the species \text{Fe}^2+(ao), \text{FeOH}^+(ao), \text{Fe(OH)}_2(cr), \text{Fe(OH)}_3(ao), \text{Fe(OH)}_3(cr) and \text{Fe(OH)}_4(ao). Values extrapolated by authors to 298.15 K. S0(FeOH^+, ao)=80(Fe^{1,2}, ao) was constrained to be 12.6 J/(K.mol) from 78OH/BAU, p=1 atm.

S: 586 VBP, 588 VBP

44. Z: 80TRE/LEB
R: 
\[
1/3\text{Fe}_3\text{O}_4(cr) + 1/3\text{H}^2(g) + 2/3\text{H}_2\text{O}(l)
\]

DV: 
H: -58.9860 kJ
DV: 
G: -9.115 2.5 kJ
C: 
Authors established dCp=125 J/(mol.K) used. dH(473 K)=-36.78 kJ/mol with dS (473 K)= -108.96 J/(mol.K). If use dCp=14 J/mol from 70 SWE/BP, dH and dG are -39.23 and -4.8 kJ/mol respectively.

C: 
**Solubility of carefully characterized Fe\text{SO}_4(cr)** in dilute aqueous solutions satd with H\text{2}(g) measured from 373 to 573 K in flow apparatus. Solution compositions included either HCl molettes of up to 1 mmole (kg H\text{2}O)-1 or NaOH molettes of up to 40 mmole (kg H\text{2}O)-1. The dependence of the equilibrium solubility on the pH and reduction potential were fitted to a scheme of soluble ferrous and ferric species. Solubility products were used to derive thermodynamic constants in the species \text{Fe}^2+(ao), \text{FeOH}^+(ao), \text{Fe(OH)}_2(cr), \text{Fe(OH)}_3(ao), \text{Fe(OH)}_3(cr) and \text{Fe(OH)}_4(ao). Values extrapolated by authors to 298.15 K. S0(FeOH^+, ao)=80(Fe^{1,2}, ao) was constrained to be 12.6 J/(K.mol) from 78OH/BAU, p=1 atm.

S: 586 VBP, 588 VBP

45. Z: 80TRE/LEB
R: 
\[
1/3\text{Fe}_3\text{O}_4(cr) + 5/3\text{H}_2\text{O}(l)=\text{Fe(OH)}_3(ao)+1/6\text{H}_2\text{O}(g)
\]

DV: 
H: 72.8880 kJ
DV: 
G: 127.783 0 kJ
C: 
Authors est'd dCp=-10.6 J/(mol.K) used. dH (473 K)=71.58 kJ/mol and dS (473 K)= -188.71 J/(mol.K).

C: 
**Solubility of carefully characterized Fe\text{SO}_4(cr)** in dilute aqueous solutions satd with H\text{2}(g) measured from 373 to 573 K in flow apparatus. Solution compositions included either HCl molettes of up to 1 mmole (kg H\text{2}O)-1 or NaOH molettes of up to 40 mmole (kg H\text{2}O)-1. The dependence of the equilibrium solubility on the pH and reduction potential were fitted to a scheme of soluble ferrous and ferric species. Solubility products were used to derive thermodynamic constants in the species \text{Fe}^2+(ao),
FeOH+(aq), Fe(OH)2(cr), Fe(OH)3(aq), Fe(OH)3(cr) and Fe(OH)4(aq). Values extrapolated by authors to 298.15 K. So(FeOH+
+aq)-So(Fe2+2aq) was constrained to be 12.6
J/(K.mol) from 78JOH/BAU. p=1 atm.

S: 5/86 VBP, 3/88 VBP

46. Z: 80TRE/LEB
R: 1/3Fe3O4(cr)+8/3H2O(l)=Fe(OH)4-1(aq) 
+1/6H2(g)+H+ (aq)
DV: S, -192.658.8
C: Authors dCp=10.5 J/(mol.K). used. dS (473 K) 
= 197.76 J/(mol.K).
C: Solubility of carefully characterized Fe3O4(cr)
in dilute aqueous solutions saturated with H2(g) 
measured from 373 to 573 K in flow apparatus.
Solution compositions indicated either HCl mole-
ratios of up to 1 mole/kg H2O)-1 or NaOH 
molarities of up to 40 mole/kg H2O)-1. The depen-
dence of the equilibrium solubility on the 
PH and reduction potential were fitted to a 
scheme of soluble ferrous and ferric species.
Solubility products were used to derive thermo-
dynamic constants in the species Fe2+2(aq), 
FeOH+(aq), Fe(OH)2(cr), Fe3O4(cr) and Fe(OH)4(aq). Values 
eextrapolated by authors to 298.15 K. So(FeOH+
+aq)-So(Fe2+2aq) was constrained to be 12.6
J/(K.mol) from 78JOH/BAU. p=1 atm.

S: 5/86 VBP

47. Z: 89CTT
R: =Fe2O3 (cr)
DV: S, 87.483 $ 0.06 J
C: Evaluation of J. Haas
S: 10/89 VBP

48. Z: 7JKIN/WEL
R: =FeOOH(cr)
DV: S, 60.3800.63 J
C: low temp Cp measurements 51 to 298 K.
S: 6/86 VBP

49. Z: 90CTT
R: =FeOOH(cr)
DV: S, 60.40 $ 0.6 J
C: Work of 70JKIN/WEL. H-HO=10.820 $ 0.08 
kJ, Cp=74.480 $ 0.07 J/(mol.K).
S: 5/86 VBP

50. Z: 90TCC
R: =FeO2H2 (cr)
DV: S, 93.00 $ 6.0 J
C: Est'd by IVTAN
S: 3/90 VBP

51. Z: 65BAR
R: 2FeOOH(cr)=Fe2O3(cr)+H2O(l)
F: TN
DV: H, 7.8750 8.4 KJ
C: Also IVTAN Equation 367, with additional 
decimal of H2O(cr) to 20.1 wt% HF= 
-82.2650.60 KJ/mol combined with dsoH 
Fe2O3(cr)=-175.900 60.60 KJ/mol and ddinH 
= +1.76 KJ/mol.
S: 5/86 VBP

52. Z: 53LEU/KOL
R: Fe(OH)2(cr)=Fe+2(aq)+2OH-(aq)
DV: G, 86.1781.0 KJ

53. Z: 53LEU/KOL
R: Fe(OH)2(cr)=Fe(OH)+2(aq)+OH-(aq)
F: TN
DV: G, 53.750.6 KJ
C: K=3.9 $(1.0)E-10. Used activity coefficients 
from 37KIE
S: 5/86 VBP

54. Z: 80DIB/CHE
R: Fe(cr)+Cd(OH)2(ce)Fe(OH)2(ce)+Cd(ce)
DV: H, -10.6151.0KJ
C: Electrochem. measurements anodic enthalpy 
plateau.
S: 5/86 VBP

55. Z: 43FR/RHI
R: Fe(OH)2(cr)+1/4O2(g)=FeO2(cr)+H2O(l)
DV: H, -125.352.5 KJ
C: dhE/296 K=-124.68 KJ/mol used as dH in 
IVTAN catalog equation 372
S: 5/86 VBP

56. Z: 78JHJ/BAU
R: Fe+2(aq)+H2O(l)=FeOH+1(aq)+H+(aq)
DV: G, 52.6950.57 KJ
DV: H, 35.655.0 KJ
C: From FeCl2 (aq) or FeCl4O2 (aq), ionic 
strength less than 0.1. Activity coef. for all spe-
cies from Debye-Hückel relationship.
S: 5/86 VBP

57. Z: 78JHJ/BAU
R: Fe(OH)2(2am)=Fe+2(aq)+2OH-(aq)
DV: H, 19.6651.7 KJ
DV: G, 82.148 0.21 KJ
C: Freshly pptd.
S: 5/86 VBP

58. Z: 32RAN/FRA
R: Fe(cr)+HgO(cr)+H2O(l)=Hg(l) 
+Fe(OH)2(cr)
DV: G, -187.765KJ
F: TN
W: 99
C: See combined reaction, linking Fe(OH)2(cr) to 
Fe+2(aq) or FeCl2(aq). E=0.97350.005 V. 
IVTAN equation 374 assigned value to dH0 in-
correctly.
S: 5/86 VBP

59. Z: 33KRI/AWS
R: Fe(OH)2(cr)=Fe+2(aq)+2OH-(aq)
DV: G, 82.75 KJ
C: Potentiometric
S: 7/86 VM

60. Z: 50AIB
R: Fe(OH)2(2cr)=Fe+2(aq)+2OH-(aq)
DV: G, 77.75 KJ
C: Potentiometric
S: 7/86 VM

61. Z: 51QUI
R: Fe(OH)2(cr)=Fe+2(aq)+2OH-(aq)
DV: G, 84.45 KJ
C: Potentiometric
S: 7/86 VM

62. Z: 63BER/KOV
R: 3Fe(OH)2(cr)=Fe3O4(cr)+2H2O(g)+H2(g)
C: Third law value. Second law value = 308 kJ/mol DTA, 422-465 K. Graph only.
S: 7/86 VM

63. Z: 939CH
R: 2FeOOH (cr) = Fe₂O₃ (cr) + H₂O(l)
DV: H, 14.7 $\pm$ 10 kJ
F: TN
C: $\Delta G^{\circ}(400\ K)$ = 0; 3rd law value. PVT, 411-453 K.
S: VM 7/86, 8/89 VBP

64. Z: 6AER
R: 2FeOOH (cr) = Fe₂O₃ (cr) + H₂O(l)
DV: H, 4.9 $\pm$ 1.2 kJ
F: TN
C: Also IVTAN 3-85 eq. 366; from differences in enthalpies of soln. in 20.1% HCl (m = 7.30) at 344 K (dH = 5.2 kJ/mol); corrected to 298.15 K and H₂O(l) using d(H-H₂98) = 1.37 kJ/mol H₂O(l)
S: VM 7/86, 5/89 VBP

65. Z: 75KOR/FAD
R: 2FeOOH (cr) = Fe₂O₃ (cr) + H₂O(g)
DV: H, 57.75kJ
F: IVTAN 7.85 eq. 368; corrected from 57.9 kJ/mol; differential scan. calorimetry
S: VM 7/86

66. Z: 1882THO
R: Fe₂O₃ (cr) + H₂SO₄(200H₂O) = 2HCl(100H₂O) + K₂SO₄(200H₂O) + Fe(OH)₂(cr)
DV: H, $-116.35$k J/mol
C: IVTAN 3-85 eq. 369; summation of dsoH of FeCl₂, cr = $-74.89$ kJ/mol, dmixH (FeCl₂200H₂O) with H₂SO₄(200H₂O) = $-15.06$ kJ/mol and dottedH = $-26.53$ kJ/mol.
S: VM 7/86, 5/87 VBP

67. Z: 1882THO
R: BaSO₄(200H₂O) + Ba(OH)₂(200H₂O) = BaSO₄(cr) + Fe(OH)₂(cr)
DV: H, $-47.65$k J/mol
C: dH meas at 292 K = $-50.2$ kJ/mol. dCp = 440 J/(mol.K) used by VBP. IVTAN 3-85 eq. 370
S: VM 7/86, 6/87 VBP

68. Z: 1882THO
R: Fe(OH)₂(cr) + 0.5Fe₂O₃(cr) + H₂O(l)
DV: H, $-114.25$kJ/mol
C: IVTAN 3-85 eq. 371, Combustion calorimetry.
S: VM 7/86

69. Z: 75KOR/FAD
R: FeOOH (cr) = Fe₂O₃ (cr)
DV: H, 21.01$k J/mol
C: FeOOH (cr) is alpha form (Goethite); cr2 is gamma form (lepidocrite). From differences in dH dehydration.
S: 6/87 VBP

70. Z: 37FRI/ZER
R: FeOOH (cr) = FeOOH (cr)
C: Enthalpy messy of alpha and gamma forms in 40% HF solutions at 293.6 K corrected for moisture content of samples.

71. Z: 6/87 VBP
R: Fe(OH)₂(cr) + H₂C₂O₄(cr) = Fe₂O₃(cr) + H₂O(l) + Fe₂O₃(cr)
DV: G, $+52.16$k J/mol
C: Combined reaction. Measured Fe(cr) - Fe(OH)₂(cr). E₀ combined with 32RAN/FRA2 Fe(cr) - Fe₂O₃(cr). E₀ = $-0.27$ V.
S: 5/86 VBP

72. Z: 26HAM
R: Fe₃O₄ + 2TiCl₄ = Fe₂C₂O₄ + 2TiCl₄
DV: G, $+23.65$k J/mol
C: From left side of equilibrium. Molality FeCl₂ = 0.0453 mol/kg H₂O and TiCl₄ = 0.0042 mol/kg H₂O. gamma from 79GOL/NUT. 32RAN/FRA2 say better agreement with their results is because the 26HAM treatment with TiCl₄(aq) removes the finer particles of iron.
S: 5/86 VBP

73. Z: 26HAM
R: Fe(cr) + 2H₂C₂O₄(cr) = 2Fe₂O₃(cr) + 2H₂O(l)
DV: G, $137.06$k J/mol
C: Used electrodes prepared from finely divided Fe(cr). Fe₂O₃(cr) was reduced with H₂ which was O₂ and H₂O free. Mean of 4 meas. with m = 0.11, 0.1805, 0.1805, and 0.1805. Used gamma from 79GOL/NUT. 32RAN/FRA say that these meas. were not true equilibrium values and that the finely divided iron gives values for E which are too high, prolonged exposure to solutions of FeCl₂ makes activity of the finely divided iron approach those of 32RAN/FRA2.
S: 5/86 VBP

74. Z: 53PAT/THO
R: Fe(cr) + 2H₂C₂O₄(cr) = Fe₂O₃(cr) + 2H₂O(l)
DV: G, $-129.73$k J/mol
F: TN
C: E₀ = 0.673200.025 V; mean of measurements: m FeCl₂(aq) = 0.0760 and 0.0160; gamma = 0.5324 and 0.6857 from 79GOL/NUT. H₂ free Fe was prepd. by thermal decomposition of Fe(CO)₅ under vacuume (powder obtained used directly as electrode material.) Also massive iron electrodes were prepd by vacuum fusion of Fe powder. Also special care to remove all traces of O₂ from cells. Authors indicate that variations from their values in E₀ for FeFe₂O₃(aq) such as such as 32RAN/FRA are due to presence of atomic H in metal. This dE was measured to be $-0.054$ V.
S: 5/86 VBP

75. Z: 32RAN/FRA
R: Fe(cr) + 2H₂C₂O₄(cr) = Fe₂O₃(cr) + 2H₂O(l)
DV: G, $-135.65$k J/mol
F: TN
C: E = 0.7996 V for 0.1 m FeCl₂ solution; gamma = 0.5093 from 79GOL/NUT. E₀ = 0.7027 V. Used two differently prepd samples Fe(cr), electrolytic iron deposited on Pt electrodes and Fe produced by reduction of FeO with H₂. O₂
THE THERMODYNAMIC PROPERTIES OF THE AQUEOUS IONS OF IRON

S: 5/71 VBP

1731

DV: H, 159.87$1.5$kJ
F: TN
C: IVTAN 3-8 EQ. 231, values readjusted (vbp) using S(298.15 K) = 118.0 J/(mol.K) from JANAF and 86ARI/BER text calculations. Static; Temp. range 759–935 K, 18 pts, 3rd law. 2nd law 155.855.2 kJ/mol
S: VM 5/71 and 10/87, 7/88 VBP

84. Z: 52NOV/ORA
R: FeCl2(cr)+H2(g)=2HCl(g)+Fe(cr)
DV: H, 155.02$1.6$kJ

85. Z: 60NOV/MAK
R: FeCl2(cr)+H2(g)=2HCl(g)+Fe(cr)
DV: H, 158.01$1.8$kJ

86. Z: 38SAN
R: FeCl2(cr)+H2(g)=2HCl(g)+Fe(cr)
DV: H, 154.8$1.7$kJ

87. Z: 76BUR/GER
R: FeCl2(cr)+H2(g)=2HCl(g)+Fe(cr)
DV: H, 146.2$3.1$kJ
W: 99
C: e.m.f.; Temp. range 973–1093 K, equation, third law, second law 92.0 kJ/mol. Values readjusted (vbp) using S(298.15 K) = 118.0 J/(mol.K) from JANAF and 86ARI/BER text calculations.
S: VM 5/71 and 10/87, 7/88 VBP

88. Z: 43WAG/STE
R: FeCl2(cr)+H2(g)=Fe(cr)+2HCl(g)
DV: H, 157.66$62.0$kJ
F: TN
C: 3rd law, 2 points, 1152 and 1203 K
S: 7/88 VBP

89. Z: 1882THO
R: FeCl2(cr)=FeCl2(400 H2O)
DV: H, −76.69$0.50$kJ
F: TN
C: Measured at 292K, dH=−74.89 kJ/mol in HCl solns. dCp=236 J/(mol.K). Original measurement Fe(cr) dH=−90.91 kJ/mol in HCl(50 H2O) corrected to HCl(20012O).
S: 3/86 VBP

90. Z: 59KOE/COU
R: Fe(cr)+2HCl(12.731H2O)=FeCl2(cr)+H2(g)
DV: H, −117.0$0.21$kJ
F: TN
C: Summation of 4 reactions at 303 K, corrected using \( \Delta C_p = 236 \, J/(mol \cdot K) \). Dissolv H Fe(cr) and FeCl₂(cr) at 303 K = 87.11 \( \$0.17 \) and =\( -62.76 \, \$0.09 \) kJ/mol respectively. Same reaction as IVTAN Eq. 389.

S: 3/86 VBP

91. Z: 88CTT
R: \( FeCl₂(cr) \)
DV: S, 118.0 \$0.40 J
C: \( H - H(0) = 16.27 \, kJ/mol, C_p = 76.66 \, J/mol \cdot K \)
**See updated 89CTT value below.

**Change in values for S and H-H(0) at 298 K results in small differences in third law and sec-
second law dH values for all entries for FeCl₂(cr); dependent upon T correction. Comments spell out values used.

S: 8/88 VBP

92. Z: 89CTT
R: \( FeCl₂(cr) \)
DV: S, 118.060 \$0.20 J
C: \( H - H(0) = 16.10 \, kJ/mol, C_p = 76.60 \, J/mol \cdot K \)
S: 11/89 VBP

93. Z: 82COB/MUR
R: FeCl₂(cr) = FeCl₂(ai)
DV: H, -82.906 \$0.32 kJ
C: Debye Hückel extrapol. from measurements in 0.005 molal HClO₄. Molality salt at 2E-03 to 0.01; nine points. AH adjusted from 688 to 710 cal/mol.
S: VBP Aug. 85

94. Z: 90E8F/FUR
R: FeCl₂(cr) = Fe + 2(ao) + 2Cl⁻(ao)
DV: H, -83.11 \$0.42 kJ
C: Authors' extrapolation after correction for phiL D-H from measurements in 0.001 m HClO₄. Measured values are -82.680, -82.639, -82.502 and -81.925 kJ/mol for m FeCl₂(aq) =0.00459, 0.00422, 0.00550 and 0.00849. PhiL corrections are 0.623, 0.602, 0.673 and 0.793 kJ/mol, respectively. This is really an average.
S: 5/89 VBP

95. Z: 90E8F/FUR
R: FeCl₂(cr) = FeCl₂(1115(HClO₄ + 55500H₂O))
DV: H, -82.437 \$0.45 kJ
C: Average of 4 experimental measurements in 0.001 m HClO₄. See above for individual measurements.
S: 5/89 VBP

96. Z: 77CER/HEP
R: FeCl₂(cr) = FeCl₂(ai)
DV: H, -83.05 \$0.42 kJ
C: Measurements on FeCl₂.0082 H₂O(cr), dH = -82.97 kJ/mol and FeCl₂.0228(cr), dH = -82.38 kJ/mol, at infinite dilution. These measurements were corrected to anhydrous FeCl₂(cr) assuming presence of FeCl₂.0228H₂O(cr) or FeCl₂.2H₂O(cr) in samples with dH = -62.8 kJ/mol and -41.8 kJ/mol respectively. This reaction is also in IVTAN catalog, reaction 390.

S: 3/86, 6/87 VBP

97. Z: 52LI/GER
R: FeCl₂(cr) = FeCl₂(8000H₂O)
DV: H, -81.84 \$0.84 kJ
F: TN
C: Mean of 5 measurements. Molality range 0.00139 to 0.0117 mols/kg H₂O. In IVTAN catalog, reaction 386 as dH = -81.5 \$0.2 kJ/mol at infinite dilute. If phi(L) = 860 J/mol, dH0 = -82.70 kJ/mol.
S: 3/86 VBP

98. Z: 10R1C/BUR
R: Fe(cr) + 2HClO₄D = FeCl₂(HClO₄ + 6.3H₂O) + H₂(g)
DV: H, -85.78 kJ
C: dH meas at 293 K; Estimated dCp = +40 J/(mol.K)
S: 4/87 VBP

99. Z: 47FON2
R: FeCl₂(cr) = FeCl₂(72.7HClO₄ + 8000H₂O)
DV: H, -79.50 \$0.42 kJ
S: 4/87 VBP

100. Z: 62A/H/KOP
R: Fe(cr) + 2HClO₄D = FeCl₂(10.6HClO₄ + 700H₂O) + H₂(g)
DV: H, -84.94 \$0.10 kJ
F: TN
S: 4/87 VBP

101. Z: 10R1C/ROW
R: Fe(cr) + 2HCl(200H₂O) = FeCl₂(400H₂O) + H₂(g)
DV: H, -86.28 \$2.0 kJ
F: TN
C: Measurement at 293.2 K, in concentrated HCl corrected by authors for HCl dil. to obtain value, dH = -87.03 kJ/mol for product free of excess acid. Estimated dCp = +40 J/(mol.K)
S: 5/87 VBP

102. Z: 87NBS
R: FeCl₂(12.54H₂O) = FeCl₂(1100H₂O)
DV: H, -15.5 kJ
C: Extrapolated from 41PER measurements at 285.7 K of dsoln HClO₂:4H₂O(cr) in nH₂O from n=12.8 to 1100; dCp corrections using phi Cp from 79BER/MOR.
S: 4/87 VBP

103. Z: 87NBS
R: FeCl₂(13H₂O) = FeCl₂(1100H₂O)
DV: H, -15.65 kJ
C: From measurements by 41PER on dsoln HClO₂:4H₂O(cr) in nH₂O from n=12.8 to 1100; dCp corrections using phi Cp from 79BER/MOR.
S: 4/87 VBP

104. Z: 87NRS
R: FeCl₂(15H₂O) = FeCl₂(1100H₂O)
DV: H, -14.20 kJ
C: From measurements by 41PER on dsoln HClO₂:4H₂O(cr) in nH₂O from n=12.8 to 1100; dCp corrections using phi Cp from 79BER/MOR.
S: 4/87 VBP
THE THERMODYNAMIC PROPERTIES OF THE AQUEOUS IONS OF IRON

105. Z: 87NBS
R: FeCl₂(2H₂O) = FeCl₂(1100H₂O)
DV: H, -11.00 kJ
C: From measurements by 41PER on dsoInH
FeCl₂·4H₂O(cr) in nH₂O from n=12.8 to 1100; dCp corrections using phi Cp from 79BER/MOR
S: 4/87 VBP

106. Z: 87NBS
R: FeCl₂(30H₂O) = FeCl₂(1100H₂O)
DV: H, -7.90 kJ
C: From measurements by 41PER on dsoInH
FeCl₂·4H₂O(cr) in nH₂O from n=12.8 to 1100; dCp corrections using phi Cp from 79BER/MOR
S: 4/87 VBP

107. Z: 87NBS
R: FeCl₂(40H₂O) = FeCl₂(1100H₂O)
DV: H, -6.20 kJ
C: From measurements by 41PER on dsoInH
FeCl₂·4H₂O(cr) in nH₂O from n=12.8 to 1100; dCp corrections using phi Cp from 79BER/MOR
S: 4/87 VBP

108. Z: 87NBS
R: FeCl₂(50H₂O) = FeCl₂(1100H₂O)
DV: H, -5.10 kJ
C: From measurements by 41PER on dsoInH
FeCl₂·4H₂O(cr) in nH₂O from n=12.8 to 1100; dCp corrections using phi Cp from 79BER/MOR
S: 4/87 VBP

109. Z: 87NBS
R: FeCl₂(75H₂O) = FeCl₂(1100H₂O)
DV: H, -3.60 kJ
C: From measurements by 41PER on dsoInH
FeCl₂·4H₂O(cr) in nH₂O from n=12.8 to 1100; dCp corrections using phi Cp from 79BER/MOR
S: 4/87 VBP

110. Z: 87NBS
R: FeCl₂(100H₂O) = FeCl₂(1100H₂O)
DV: H, -2.80 kJ
C: From measurements by 41PER on dsoInH
FeCl₂·4H₂O(cr) in nH₂O from n=12.8 to 1100; dCp corrections using phi Cp from 79BER/MOR
S: 4/87 VBP

111. Z: 87NBS
R: FeCl₂(200H₂O) = FeCl₂(1100H₂O)
DV: H, -1.33 kJ
C: From measurements by 41PER on dsoInH
FeCl₂·4H₂O(cr) in nH₂O from n=12.8 to 1100; dCp corrections using phi Cp from 79BER/MOR
S: 4/87 VBP

112. Z: 87NBS
R: FeCl₂(500H₂O) = FeCl₂(1100H₂O)
DV: H, -0.40 kJ
C: From measurements by 41PER on dsoInH
FeCl₂·4H₂O(cr) in nH₂O from n=12.8 to 1100; dCp corrections using phi Cp from 79BER/MOR
S: 4/87 VBP

113. Z: 87NBS
R: FeCl₂(1000H₂O) = FeCl₂(1100H₂O)
DV: H, -0.10 kJ
C: From measurements by 41PER on dsoInH
FeCl₂·4H₂O(cr) in nH₂O from n=12.8 to 1100; dCp corrections using phi Cp from 79BER/MOR
S: 4/87 VBP

114. Z: 1882THO
R: FeCl₂·4H₂O(cr) = FeCl₂(cr) + 4H₂O(l)
DV: H, +64.31 & 0.0 kJ
F: TN
C: dsoInH tetrhydrate = -11.51 $1.0$ kJ/mol at 292 K combined with dsoInH anhydrous = -74.89 kJ/mol. Estimated dCp = +151 J/(mol·K)
* Check Khodakovskii value
S: 4/87 VBP

115. Z: 1941PER
R: FeCl₂·4H₂O(cr) = FeCl₂(400H₂O) + 4H₂O(l)
DV: H, -11.96 & 0.0 kJ
F: TN
C: Measurement at 285.7 K, dH = -10.21 kJ/mol. Estimated dCp = -130 J/(mol·K)
79BER/MOR measured phi Cp for FeCl₂ (12.54 H₂O) to be -37 J/(mol·K) and phi Cp₀ = -256 30 J/K·mol
S: 4/87 VBP

R: FeCl₂(12.54H₂O) = FeCl₂(ai)
DV: H, -20.55 & 0.176 kJ
DV: H, 288.15 K, -17.938 & 0.079 kJ
DV: H, 308.15 K, -22.353 & 0.109 kJ
C: Also measured phi Cp at 288, 298 and 308 K of solution (12.54H₂O). Calculates phi Cp₀ = -256 30 J/(mol·K) at 298.15 K
S: 4/87 VBP

117. Z: 1889SA
R: FeCl₂·2H₂O(cr) = FeCl₂(450H₂O) + 2H₂O(l)
DV: H, 293 K, -96 & 2.0 kJ
DV: H, -37.5 & 2.2 kJ
F: TN
C: Measurement at 293 K in 300 to 600 H₂O; dCp extrapolated = -229 J/(mol·K)
S: 4/87 VBP

118. Z: 87NBS
R: FeCl₂·4H₂O(cr) = FeCl₂(ai) + 4H₂O(l)
DV: G, -16.65 & 0.3 kJ
C: Saturation m=4.951 from 85CHO/PH; activity coefficient = 2.46 & 0.10 and ln aw = -0.522 & 0.10
from 62KAN/GRO.
* Khodakovskii titration gives -17.3 $1.0$ kJ/mol. These values need to be reconciled.
S: 4/87 VBP

119. Z: 1949SCH
R: FeCl₂·4H₂O(cr) = FeCl₂·3H₂O(cr) + 2H₂O(g)
DV: H, 108.0 & 4.0 kJ
DV: G, +23.62 & 1.0 kJ
F: TN
C: Vapor pressure measurements 293–338 K. 
log P atm=7.389−2.820/T. dcP assumed to be 0. Calculated dS=33.8 cal/(molH2O) K is slightly low.
S: 487 VBP

120. Z: 1949SCH
R: FeCl2·2H2O(cr)=FeCl2·H2O(cr)+H2O(g)
DV: H, 63.1 $5.0$ kJ
DV: G, 18.57 $2.0$ kJ
F: 'IN
S: 487 VBP

121. Z: 1949SCH
R: FeCl2·H2O(cr)=FeCl2(cr)+H2O(g)
DV: H, 63.1 $5.0$ kJ
DV: G, 24.03 $2.0$ kJ
S: 487 VBP

122. Z: 88C11
R: =FeCl3(cr)
DV: S, 147.80 $0.3$ J
C: From the low temp. Cp measurements (4.7–307.6K) by 80STU/FER. Cp=96.942 J/(mol.K) and H-HO=19.440 kJ/mol at 298.15 K. Low temp. results of STOD/COU rejected
S: 486 VBP, 10/88 VBP

123. Z: 71STU/PRO
R: =FeCl3(cr)
DV: S, 142.335 $2.0$ J
F: TN
W: 99
C: From low temp. measurements (51–298 K) by STOD/COU who report S0 (21K)=10.626 $1.26$ J/(mol.K) and S0 (298.15)−S0 (51K) = 115.855 $0.38$ J/(mol.K). 71STU/PRO adjusts S0 (51K) to 76.72 J/(mol.K) in order to reconcile 2nd and 3rd law dHr for FeCl2(cr) =FeCl3(cr) equilibrium and considers difference to be the remaining magnetic entropy at 51K. Dated evaluation June 1965.
S: 486 VBP

124. Z: 59KOE/COU
R: Fe(cr)+3HCl(12.731H2O)+0.5H2O(12.58 H2O)=FeCl3(cr)+H2(g)+H2O(l)
DV: H, −102.59 $0.30$ kJ
F: TN
C: Measured dH(303K)=−100.75 $0.29$ kJ/mol; dCp=368 J/(mol.K). Same reaction as IVTAN equation 393 without dCp corrections.
S: 3/86 VBP

125. Z: 82LAV/TIM
R: Fe(cr)+1.5Cl2(g)=FeCl3(cr)
DV: H, −396.02 $0.14$ kJ
C: IVTAN 3-85 EQ. 394
Two different samples used; one, NIST electrolytic grade SRM#797-2 and 2nd from Central Res. Inst. of Ferrous Metallurgy, Moscow which had been prep. by vacuum meeting of Fe(CO)5 and then refined in H2 in presence of ZrH2. Corrected for impurities.
S: VM, VBP 7/87

126. Z: 84LAV/TIM
R: Fe(cr)+1.5Cl2(g)=FeCl3(cr)
DV: H, −396.02 $0.14$ kJ
C: See 82LAV/TIM
S: VBP 7/87

127. Z: 89EVD/EFI
R: FeCl2(cr)+1/2Br2(l)+KCl(cr)=FeCl3(cr) +KBr(cr)
DV: H, −11.386 $0.18$ kJ
C: Calorimetric measurements at 298.15 K of all chloride components in solution of (KBr, 0.43 Br2, 112 HBr, 50.78 H2O) combined with reactions from 89EVP/EVD. dH FeCl3(cr)=−146.523 kJ/mol. Reported earlier as 88EVP/EVD.
S: 88/89 VBP, 9/91 VBP

128. Z: 96BAG/*R: 2FeCl3(cr)+H2(g)=2FeCl2(cr)+2HCl(g)
DV: H, 130.866 $10.00$ kJ
W: 99
C: IVTAN 3-85 EQ. 98; One pt 564 K, third law: not to be cited.
S: VM 4/87

129. Z: 25MAI
R: 2FeCl3(cr)=2FeCl2(cr)+Cl2(g)
DV: H, 107.02 $3.6$ kJ
C: IVTAN 3-85 EQ. 99, readjusted (vbp) in agreement with 86AR/BER text calculations and returning to S(FeCl2, cr)=118.0 J/(mol.K) at 298.15 K. Static; third law, two points, 567 K and 525 K
S: VM 4/87 and 10/87, 8/88 VBP

130. Z: 50KAN/PET
R: 2FeCl3(cr)=2FeCl2(cr)+Cl2(g)
DV: H, 104.98 $2.3$ kJ
C: IVTAN 3-85 EQ. 100, readjusted (vbp) in agreement with 86AR/BER text calculations and returning to S(FeCl2, cr)=118.0 J/(mol.K) at 298.15 K. Transpiration: third law, 12 pts, 526–574 K
S: VM 4/87 and 10/87, 8/88 VBP

131. Z: 55SCH/OEH
R: 2FeCl3(cr)=2FeCl2(cr)+Cl2(g)
DV: H, 108.54 $1.6$ kJ
C: IVTAN 3-85 EQ. 101, readjusted (vbp) in agreement with 86AR/BER text calculations and returning to S(FeCl2, cr)=118.0 J/(mol.K) at 298.15 K. Transpiration; third law, 19 pts, 435–482 K; second law 112.0 $4.2$ kJ/mol
S: VM 4/87 and 10/87, 10/88 VBP

132. Z: 58WIL/GRE
R: 2FeCl3(cr)=2FeCl2(cr)+Cl2(g)
DV: H, 108.75 $1.6$ kJ
THE THERMODYNAMIC PROPERTIES OF THE AQUEOUS IONS OF IRON

133. Z: 521/L/GRE
R: FeCl₃(cr) = Fe³⁺ + 3Cl⁻(aq)
DV: H: -158.99 $0.84$ kJ
C: IVTAN 3-85 EQ. 102, readjusted (vbp) in agreement with 86ARI/BER text calculations and returning to S(FeCl₃, cr) = 118.0 J/(mol·K) at 298.15 K. Transpiration; third law, equation, 433–493 K; second law 109.1 kJ/mol
S: VM 4/87 and 10/87, 8/88 VBP

134. Z: 87/86
R: FeCl₃(cr) = FeCl₃(HCl + 11.10 H₂O:au)
DV: H: -138.78 $1.0$ kJ
C: Extrapolation from results as a function of concentration of HCl of 35KAN/FLU at 293 K and measurements of 76COR/OI1W and 80STU/FER at 298 K and 59KOE/COU at 303 K. Used 86KHO corrections to extrapolate to I=0.
S: 4/86 VBP, 7/87 VBP

135. Z: 87/86
R: FeCl₃(cr) = FeCl₃(HCl + 55.51 H₂O:au)
DV: H: -132.85 $1.0$ kJ
C: Smoothed curve from measurements as a function of concentration of HCl of 35KAN/FLU at 293 K and measurements of 76COR/OI1W and 80STU/FER at 298 K and 59KOE/COU at 303 K. Used 86KHO corrections to extrapolate to I=0.
S: 3/90 VBP

136. Z: 87/86
R: FeCl₃(cr) = FeCl₃(HCl + 27.75 H₂O:au)
DV: H: -123.77 $1.0$ kJ
C: Smoothed curve from measurements as a function of concentration of HCl of 35KAN/FLU at 293 K and measurements of 76COR/OI1W and 80STU/FER at 298 K and 59KOE/COU at 303 K. Used 86KHO corrections to extrapolate to I=0.
S: 3/90 VBP

137. Z: 87/86
R: FeCl₃(cr) = FeCl₃(HCl + 18.50 H₂O:au)
DV: H: -115.12 $1.0$ kJ
C: Smoothed curve from measurements as a function of concentration of HCl of 35KAN/FLU at 293 K and measurements of 76COR/OI1W and 80STU/FER at 298 K and 59KOE/COU at 303 K. Used 86KHO corrections to extrapolate to I=0.
S: 3/90 VBP

138. Z: 87/86
R: FeCl₃(cr) = FeCl₃(HCl + 13.88 H₂O:au)
DV: H: -106.62 $1.0$ kJ
C: Smoothed curve from measurements as a function of concentration of HCl of 35KAN/FLU at 293 K and measurements of 76COR/OI1W and 80STU/FER at 298 K and 59KOE/COU at 303 K. Used 86KHO corrections to extrapolate to I=0.
S: 3/90 VBP

139. Z: 87/86
R: FeCl₃(cr) = FeCl₃(HCl + 11.10 H₂O:au)
DV: H: -98.22 $1.0$ kJ
C: Smoothed curve from measurements as a function of concentration of HCl of 35KAN/FLU at 293 K and measurements of 76COR/OI1W and 80STU/FER at 298 K and 59KOE/COU at 303 K. Used 86KHO corrections to extrapolate to I=0.
S: 3/90 VBP

140. Z: 87/86
R: FeCl₃(cr) = FeCl₃(HCl + 55.51 H₂O:au)
DV: H: -138.78 $1.0$ kJ
C: Extrapolation to I=0 from measurements in m HClO₄ = 4.769, 3.61 and 1.085 after correction for phi(L)-D-H. See reactions listed separately. Authors' uncertainty of 0.28 kJ/mol increased.
S: 6/89 VBP, 3/90 VBP

141. Z: 87/86
R: FeCl₃(cr) = FeCl₃(HCl + 27.75 H₂O:au)
DV: H: -123.77 $1.0$ kJ
C: Smoothed curve from measurements as a function of concentration of HCl of 35KAN/FLU at 293 K and measurements of 76COR/OI1W and 80STU/FER at 298 K and 59KOE/COU at 303 K. Used 86KHO corrections to extrapolate to I=0.
S: 3/90 VBP

142. Z: 87/86
R: FeCl₃(cr) = FeCl₃(HCl + 18.50 H₂O:au)
DV: H: -115.12 $1.0$ kJ
C: Smoothed curve from measurements as a function of concentration of HCl of 35KAN/FLU at 293 K and measurements of 76COR/OI1W and 80STU/FER at 298 K and 59KOE/COU at 303 K. Used 86KHO corrections to extrapolate to I=0.
S: 3/90 VBP
C: Mean of four experimental measurements in 1.0257 mol dm-3 HClO4 (m FeCl3=0.00474, 0.00444, 0.00381, and 0.00304 moles/kg H2O) with \( \Delta H = -144.743, -144.885, -144.136, \) and \(-144.879 \text{ kJ/mol, respectively. PhiL D-H correction at 1.097 is 5.36 kJ.} \)
S: 6/89 VBP

154. Z: 84NOV/BEL
R: FeCl3(cr)→FeCl3(42.4(HClO4+82.24 H2O))
C: Mean of measurements. Used isothermal calorimetry. Also measured dsoH of FeCl3:6H2O(cr), FeCl3:3.5H2O(cr), FeCl3:2.5H2O(cr), and FeCl3:2H2O(cr) in 0.65 mol dm-3 HClO4. PhiL D-H correction at 1=0.072 (4.37 kJ/mol) resulted in -142.50 kJ/mol for inclusion in extrapolation of dH to 1=0. See 90EFU/FUR measurements. Interpolation of 90EFU/FUR measurements at 1=0.72 gives dH= -152.5 kJ/mol, 10 kJ more negative.
S: 5/92 VBP

155. Z: 84NOV/BEL
R: FeCl3:3.5 H2O(cr)=FeCl3(42.4(HClO4+82.24 H2O))+6.5 H2O(l)
C: Used isothermal calorimeter. Mean of 6 measurements. Also measured dsoH FeCl3(cr), FeCl3:2 H2O(cr), FeCl3:3.5 H2O(cr), and FeCl3:6 H2O(cr) in 0.65 mol dm-3 HClO4. Dihor correction considered negligible.
S: 5/92 VBP

156. Z: 84NOV/BEL
R: FeCl3:6H2O(cr)=FeCl3(42.4(HClO4+82.24 H2O))+6 H2O(l)
C: Used isothermal calorimeter. Mean of 8 measurements. Also measured dsoH FeCl3(cr), FeCl3:2 H2O(cr), FeCl3:2.5 H2O(cr), and FeCl3:3.5 H2O(cr) in 0.65 mol dm-3 HClO4. Dihor correction considered negligible.
S: 5/92 VBP

157. Z: 1881SAB
R: FeCl3:6H2O(cr)=FeCl3(1200H2O)+6H2O(l)
C: dH for soin of FeCl3:6H2O(cr) in 435 H2O(l) at 297 K= -21.42 kJ/mol
S: VBP 4/86

158. Z: 89CDD
R: FeCl3:6H2O(cr)=FeCl3(1200H2O)+6H2O(l)
C: dH for soin of FeCl3:6H2O(cr) in 435 H2O(l) at 297 K= -21.42 kJ/mol
S: VBP 4/86

159. Z: 56SCH/WIT
R: FeCl3(600 H2O)
C: Based on measurements by 80STU/FER in T range 6 to 305 K. H(H2O)+H2O=12.940 kJ, Cpk=70.50 J/(mol.k).
S: 7/89 VBP
THE THERMODYNAMIC PROPERTIES OF THE AQUEOUS IONS OF IRON

160. Z: 80STU/FER
R: FeCl₃ (cr) + H₂O (l) = FeOCl (cr) + 2 HCl (3.221 H₂O)
DV: H° = −24.31 5 kJ/mol
C: dS(H₂O) = 0.098 kJ/mol
S: 10/87, 789 VBP

161. Z: 85GRE
R: 2FeOCl (cr) + 2H₂O (l) = Fe₂O₂Cl₂ (cr) + 2HCl (cr) + 2H₂O (g)
DV: H° = −4.15 5 kJ/mol
C: c₁ = 0.098 kJ/mol
S: 7/87 VBP

162. Z: 49SCH
R: Fe₂O₃ (cr) + 2HCl (g) = Fe₂Cl₆ (g) + 3H₂O (g)
DV: H° = −27.17 5 kJ/mol
C: Transpiration, 523–623 K; first equation; second law; standard state; second law value 5.1 kJ/mol.
S: 5/89 EME, 10/89 and 1/90 VBP

163. Z: 50KAN/PET
R: 2FeCl₂(cr) + Cl₂(g) = Fe₂Cl₆(g)
DV: H° = 23 5 kJ/mol
C: Static; 606–970 K; 11 points; third law; second law 54 5 kJ/mol.
S: 5/89 EME, 11/89 VBP

164. Z: 58WIL/GRE
R: 2FeCl₂(cr) + Cl₂(g) = Fe₂Cl₆(g)
DV: H° = 23 5 kJ/mol
C: Transpiration, 500–673 K; equation; third law; second law 33.0 kJ/mol.
S: 5/89 EME, 11/89 VBP

165. Z: 89EFI/EVID
R: Fe(cr) + Br₂(l) = FeBr₂(cr)
DV: H° = −24.13 5 kJ/mol
C: Calorimetric measurements at 298.15 K of all components in solution of (KBr, 0.43 Br₂, 112 HBr, 0.78 H₂O). Fe(cr) dH° = −395.43 5 kJ/mol; Br₂(l) = −7.77 5 kJ/mol; FeBr₂(cr) = −158.47 5 kJ/mol. Reported earlier as 89EFI/EVID.
S: 8/88 VBP, 9/91 VBP

166. Z: 89EDV/EFI
R: FeBr₂(cr) + 2KCl(cr) = FeCl₂(cr) + 2KBr(cr)
DV: H° = −10.03 5 kJ/mol
C: Calorimetric measurements at 298.15 K of all components in solution of (KBr, 0.43 Br₂, 112 HBr, 0.78 H₂O) combined with measurements from 89EFI/EVID. KBr(cr) dH° = 18.12 5 kJ/mol; KCl(cr) = 16.26 5 kJ/mol; FeCl₂(cr) = −152.16 5 kJ/mol. See other 89EFI/EVID and 89 EVID/EVI reactions on FeBr₂(cr), FeCl₃(cr), FeBr₃(cr), and Fe₂(cr). Reported earlier as 89EFI/EVID.
S: 8/88 VBP, 9/91 VBP

167. Z: 34HIE/WE
R: Fe(cr) + Br₂(l) = FeBr₂(cr)
DV: H° = −251.44 5 kJ/mol
C: Enthalpies of reaction of all components in Br₂(KBr) solutions at 273 K. dCP correction = −21 J/mol. Enthalpies for components at 273 K are Fe(cr) = −408.86, Br₂(l) = −7.74, and FeBr₂(cr) = −165.69 kJ/mol respectively.
S: 6/89 VBP

168. Z: 34HIE/APP
R: FeCl₂(cr) + FeBr₂(D: HCl + 27 H₂O) = FeBr₂(cr) + FeCl₂(D: HCl + 27 H₂O)
DV: H° = 273.15 K, 4.69 kJ/mol
C: Measurements of enthalpies of solution of FeCl₂(cr) (−68.20 kJ/mol) and FeBr₂(cr) (−72.89 kJ/mol) in 2 N HCl at 273 K. dCP =12 J/mol.
S: 6/89 VBP

169. Z: 89NBS
R: FeCl₂(D: HCl + 27 H₂O) + 2HBr = FeBr₂(D: HCl + 27 H₂O) + 2 HCl
DV: H° = −1.96 5 kJ/mol
C: Correction to standard state based on L2 HCl and HBr from 89PAR
W: −1
S: 7/89 VBP

170. Z: 34HIE/APP
R: FeBr₂(cr) = FeBr₂(1650 H₂O)
DV: H° = −86.86 5 kJ/mol
DV: H° = 293.15 K, −85.19 5 kJ/mol
C: Estimated dCP correction = −334 J/mol used to correct measurements from 293.15 K. Also measured dH solution in 2N HCl.
S: 7/89 VBP

171. Z: 89PAR
R: FeBr₂(1650 H₂O) = FeBr₂(ai)
DV: H° = −1.44 ± 0.2 5 kJ/mol
C: Estimated.
S: 7/89 VBP

172. Z: 52LJ/GRE
R: FeBr₂(cr) = FeBr₂(11,500 H₂O)
DV: H° = −84.1 5 kJ/mol
C: Average of five measurements at m = 0.000828, 0.00652, 0.00386, 0.00316, 0.00247 mol/kg H₂O with experimental enthalpies = −19.7, −20.2, −20.3, −20.3 and −20.4 kcal/mol respectively.
S: 7/89 VBP

173. Z: 52LJ/GRE
R: FeBr₂(cr) = FeBr₂(ai)
V. B. PARKER AND I. L. KHODAKOVSKI

DV: \( H = -86.53 \) $2.0$ kJ
C: Extrapolation of five measurements (corrected for phiL. D-H). phiL D-H at 1 = 0.025 is 543 J/mol.
S: 7/89 VBP

174 Z: 65PAO
R: FeBr(2(cr)=FeBr(2)(2000 H2O))
DV: H = -84.35 $0.5$ kJ
C: Earlier paper 64PAO/VAC gives concentration and temperature. dh value reported as - 26.16 kcal/mol is typographical error. With Table 3 values -20.06 $0.06$ kcal/mol (- 83.93 kJ) is obtained which is in good agreement with value given in Errata 66PAO. -20.16 kcal.
S: 7/89 VBP

175 Z: 89PAR
R: FeBr(2(2000 H2O)=FeBr(2)(2111)
DV: H = -1.4 $0.2$ kJ
C: Estimated; based on phiL D-H = 1.21 kJ and phiL m = 0.2 kJ/mol.
S: 7/89 VBP

176 Z: 89PAR
R: FeBr(2 (2000 H2O))=FeBr(2) (4000 H2O)
DV: H = -0.20 = 0.20 kJ
C: Estimated from comparison of divalent bromides
S: 7/89 VBP

177 Z: 67CHR/CRE
R: Fe2O3(cr)+6 HBr(g)=2 FeBr(2(cr)+3 H2O(g)+Br(2)(g)
DV: H = -150.5 $8$ kJ
C: Third law, thermodynamic study. T range 488 - 598 K; second law dH = -150.8 kJ/mol. Used thermal functions for FeBr(2) from 85CHA/DAY which gives S (FeBr2, cr) = 140.7 $1.3$ J at 298.15 K from a private communication (Westrum).
S: 7/89 VBP

178 Z: 90EFE/FUR
R: FeBr(2(cr)=Fe+2(aq)+2 Br(aq)
DV: H = -86.85 $0.12$ kJ
C: Author's extrapolation after correction for Phi L D-H from measurements in 0.001 mol dm-3 HClO4. Measured values are -86.803, -86.442, and -86.116 kJ/mol for m = 0.004958, 0.004273, and 0.007588 moles/(kg H2O) respectively. PhiL D-H corrections made are 0.665, 0.613, and 0.771 kJ/mol for I = 0.01587, 0.01382, and 0.002475. Measurements were also made in 1.0257, 0.1026 and 0.0105 mol dm-3 HClO4 solutions. See other reactions.

---

This is really an average of the three measurements. A plot of dh vs
*** I or (1/2) using measurements in 0.01, 0.1, and 1.0 mol dm-3 HClO4 (corrected for phiL D-H) shows high curvature.
S: 5/89 VBP, 11/89 VBP

179 Z: 90EFE/FUR
R: FeBr(2(cr)=FeBr(2(0.18(HClO4+55.500 H2O)))
DV: H = -86.214 $0.20$ kJ
C: Average of three measurements in 0.001 mol dm-3 HClO4. See extrapolated value.

---

S: 5/89 VBP
Z: 90EFE/FUR
R: FeBr(2(cr)=FeBr(2)(182(HClO4+51.16 H2O)))
DV: H = -82.611 $0.01$ kJ
C: Average of two measurements in 1.085 molal HClO4. m FEBr2 = 0.00567 and 0.00618 mol/(kg H2O). PhiL D-H correction would be 2.674 kJ/mol for extrapolation.
S: 5/89 VBP

180 Z: 90EFE/FUR
R: FeBr(2(cr)=FeBr(2)(28.7(HClO4+512 H2O)))
DV: H = -84.522 kJ
C: Experimental measurements in 0.1085 molal HClO4. m FEBr2 = 0.003777. PhiL D-H correction would be 1.28 kJ/mol for extrapolation.
S: 5/89 VBP

181 Z: 90EFE/FUR
R: FeBr(2(cr)=FeBr(2)(2.13(HClO4+5290 H2O)))
DV: H = -85.960 kJ
C: Experimental measurements in 0.0105 molal HClO4. m FEBr2 = 0.004918. PhiL D-H correction would be 0.776 kJ/mol for extrapolation.
S: 5/89 VBP

182 Z: 89WES
R: =FeBr2(cry)
DV: S, 140.67 $0.20$ J
C: Calorimetric Cp measurements 4-303 K. H-H0 (298.15 K) = 18.092 $???$ kJ/mol and Cp = 79.747 $0.20$ J/mol(K).
S: 7/89 VBP

183 Z: 89EFE/EVD
R: Fe2+D(2(aq)+1/2D2(2)+2Br(2)(aq) 
DV: H = -17.8955 $0.14$ kJ
C: Calorimetric measurements at 298.15 K of all components in solution of (KBr, 0.43 Br2, 112 HBr, 50.78 H2O). dH FEBr3(cr) = -144.463 kJ/mol, see other 89EFE/EVD reaction. Reported earlier as 88EFE/EVD.
S: 8/88 VBP, 9/91 VBP

184 Z: 50GRT/THA
R: 2FeBr3(cr)=2FeBr2(cr)+Br2(g)
DV: H = 67.1 $2.0$ kJ
DV: S, 161.8 $7.7$ J
C: TN

185 Z: 50GRT/THA
R: 2FeBr3(cr)=2FeBr2(cr)+Br2(g)
DV: H = 67.1 $2.0$ kJ
DV: S, 161.8 $7.7$ J
C: TN

186 Z: 52LIGRE
R: FeBr3(cr)=FeBr3(40,000 H2O)
DV: H = -104.0 kJ
C: From smoothed experimental curve. Measurements at 7 concentrations, 0.0074 to 0.00098 mol/(kg H2O). dh varies from -121.3 to -101.7 kJ/mol. See other reactions.
S: 7/89 VBP

187 Z: 52LIGRE
R: FeBr3(cr)=FeBr3(20,000 H2O)
DV: H = -119.7 kJ
C: From smoothed experimental curve. Measurements at 7 concentrations, 0.0074 to 0.00098 mol/(kg H2O). dh varies from -121.3 to -101.7 kJ/mol. See other reactions.

---

THE THERMODYNAMIC PROPERTIES OF THE AQUEOUS IONS OF IRON

188. Z: 52LI/GRE
R: FeBr₃(cr) = FeBr₃(10,000 H₂O)
DV: H, -122.3 kJ
C: From smoothed experimental curve. Measurements at 7 concentrations, 0.0074 to 0.00098 mol/kg H₂O. ΔH varies from -121.3 to -101.7 kJ/mol. See other reactions.

190. Z: 90EFE/LEU
R: FeBr₃(cr) = FeBr₃(183(HClO₄+51.16 H₂O))
DV: H, -139.342 $0.08$ kJ
C: Mean of three experimental measurements in 1.0257 mol dm⁻³ HClO₄ (m = 1.085), m FeBr₃ is 0.00504, 0.00431, and 0.00841 mol/kg H₂O. ΔH = -139.301, -139.360, and -139.312 kJ/mol, respectively. Phil.D-H at 1=1.12 is 5.376 kJ.

192. Z: 52LI/GRE
R: FeBr₃(cr) = FeBr₃(530(HClO₄+15.76 H₂O))
DV: H, -128.238 $0.2$ kJ
C: Mean of two experimental measurements in 3.11 mol dm⁻³ HClO₄ (m = 3.651), m FeBr₃ = 0.00659 and 0.00710 mol/kg H₂O. ΔH = -128.230 and -128.246 kJ/mol, respectively. Phil.D-H correction at 1=3.672 is 6.70 kJ.

199. Z: 34HIF/WEF
R: FeCl₂(cr) + H₂O = FeCl₂(D) + HCl + $1/2$ H₂(g)
DV: H, -99.2 $0.0$ kJ
C: From measurements of dH in 2 mol dm⁻³ HCl at 273 K of FeCl₂(cr) (-68.20 kJ; corrected to -68.78 kJ at 293 K) and FeCl₂(cr) (-77.86 kJ) at 293 K. dCp = -20 J/mol K.

200. Z: 34HIF/WEF
R: FeH₂ + $1/2$ H₂O = FeH₂(D) + H₂(g)
DV: H, -4.68 kJ
C: Correction to standard state based on L2's for HCl and H₂ from 34HIF/WEF.

201. Z: 65PAO/SAB
R: FeCl₂(D) = FeCl₂(4000 H₂O)
DV: H, -81.42 $0.25$ kJ
C: Sample prepared from elements at 773 K. Analysis indicated 82.03% Iodine (calculated 81.97%).

202. Z: 34NAE
R: Fe(aq) + K₂O(aq) = Fe₂O(aq) + K₂O(aq)
DV: H, -217.0 $10$ kJ
S: 7/89 VBP

203. Z: 97MOS
R: Fe(aq) + H₂O = Fe(OH)₂(aq) + H₂(g)
DV: H, -103.7 $10$ kJ

S: 8/88 VBP, 9/91 VBP

R: FeI2(cr)=FeI2(au)
DV: H= -97.1 kJ
S: 7/89 VBP

204. Z: 42MOO/KEL
R: =FeSO4(cr)
DV: S, 25.70 $0.30$ cal
F: TN
C: Low temp Cp measurements (53–295 K). S(298.15 K)=S(0.12 K)=23.60 cal/(mol.K) and S(0.12 K)=2.10 (extrapolated). Also reported in 61KEL/KIN.
S: 5/86 VBP

205. Z: 71STU/PRO
R: =FeSO4(cr)
DV: S, 28.91 $0.30$ cal
C: Reanalysis of work of 42MOO/KEL; Magnetic entropy contribution of 3.2 cal/(mol.K) (R ln 5) added to S(298.15)=25.71 cal/(mol.K) helps reconcile second and third law dH's of decomposition.
S: 5/86 VBP

206. Z: 53PAT/THO
R: Fe(cr)+HgSO4(cr)=FeSO4(aq)+2Hg(l)
DV: G= -197.740 $0.060$ kJ
C: E0=1.0247 $0.0003$ V. See reaction with Hg2Cl2 for comments. Mean of 4 meas. Concentration FeSO4 solution, $m=0.022$ w 0.0718. Activity coef. used are given by above authors from meas. by 41DEM/FED. Comparison with activity coefficients of CuSO4 by 80MII/MAR in dilute region indicates values are reasonable.
S: 5/86 VBP

207. Z: 53PAT/THO
R: Fe(cr)+PbSO4(cr)=FeSO4(aq)+2Pb(cr)
DV: G= -10.520 $0.038$ kJ
C: E0=0.05452 $0.0002$ V mean of 2 meas. m FeSO4=0.0677 and 0.030 mol/kg H2O. gamma=0.198 and 0.281 used to correct. See reaction with Hg2SO4 and Hg2Cl2.
S: 5/86 VBP

208. Z: 49LYO/GIA
R: =FeSO4:7H2O(cr)
DV: S, 97.8 $0.3$ C
F: TN
C: From low temp. Cp measurements (13–307 K and 0.9 and 20 K). Assumed S(1 K)=0.2 cal/(mol.K); S(1–10 K)=1.4 $0.07$; S(10–20 K)=17 $0.08$ and S(298.15 K)=94 $81.15$ S associated with magnetic system from integration (Cp total–Cp lattice)=2.8 cal/(mol.K)
S: VBP 5/86

209. Z: 86NBS
R: FeSO4:7H2O(cr)=FeSO4(aq)+7H2O(l)
DV: G=+14.116 $0.50$ kJ
F: TN
C: Calculated from solubility=1.944 $0.007$ mol/kg H2O from 58LIN and estimated gamma =0.0344 and phi=0.578 on basis of NiSO4 from 59ROB/STO. IVTAN evaluation used dG0=14.07 $0.51$ kJ.
S: 3/86 VBP

210. Z: 87REA/BEC
R: FeSO4:7H2O(cr)=FeSO4(aq)+7H2O(l)
DV: G, +12.58 $0.30$ kJ
C: Reanalysis of isopiestic meas. of 74OYK/BA1. activity coefficients; uses gamma at 0.1 m=0.161 and phi=0.556. Uses mstat=1.94 $0.02$, gamma=0.048, aw=0.952 $0.003$.
S: i87 VBP

211. Z: 63ADA/KEL
R: Fe(cr)+H2SO4(7.068 H2O)+7H2O(l)=FeSO4:7H2O(cr)+H2(g)
DV: H= -137.09 $0.40$ kJ
F: TN
C: Measurements on FeSO4:6.952 H2O(cr) at 303.15 K combined with measurement by 59KOE/COU on Fe(cr); Composite dH= -137.737 $0.25$ kJ/mol corrected to 298.15 K (dCp= -184 J/(mol.K)) and to stoichiometric FeSO4:7H2O(cr) assuming presence of 0.008 FeSO4:2H2O(cr). Correction for this= -0.46 kJ/mol.
S: 3/86 VBP

212. Z: 63ADA/KEL
R: Fe(cr)+H2SO4(7.068 H2O)+H2O(l)=FeSO4: H2O(cr)+H2(g)
DV: H= -79.72 $0.40$ kJ
F: TN
C: Measurements on FeSO4:1.008 H2O(cr) at 303.15 K combined with measurements by 59KOE/COU on Fe(cr); Composite dH= -81.714 $0.29$ kJ/mol. corrected to 298.15 K (dCp= -5.7 J/(mol.K)) and to stoichiometric FeSO4:7H2O(cr) assuming presence of 0.0013 FeSO4:7H2O(cr) (correction= +1.68 kJ/mol).
S: 3/86 VBP

213. Z: 64KOH/ZAS
R: FeSO4:4H2O(cr)=FeSO4:4H2O(cr)+3H2O(g)
DV: H, 140.7 $2.0$ kJ
F: TN
DV: G, 21.44 $1.0$ kJ
F: TN
C: Vapor pressure meas: log P (in mm)= -2, 450T -1+9.49 (40–52 °C) Calculated dS=30.2 cal/(mol.H2O) is low. dG at p=1 bar.
S: 3/86 VBP

214. Z: 64KOH/ZAS
R: FeSO4:4H2O(cr)=FeSO4:4H2O(cr)+3H2O(g)
DV: H, 156.2 $2.0$ kJ
F: TN
DV: G, 29.02 $0.5$ kJ
F: TN
C: Vapor pressure meas: equations only log P (in mm)= -27197T–1+10.30 (40–54 °C) for dehydration to tetrahydrate. Calculated dS=34.0 cal/(K.mol.H2O). dG at p=1 bar.
S: 3/86 VBP

215. Z: 79MAL/DRA
R: FeSO4:7H2O(cr)=FeSO4:4H2O(cr)+3H2O(g)
DV: H, 156.0 $2.0$ kJ
DV: G, 29.31 $0.25$ kJ
C: Isopiestic procedure. p=1 bar.
S: 3/86 VBP

216. Z: 14BIL
R: FeSO4:7H2O(cr)=FeSO4:4H2O(cr)+3H2O(g)
DV: H, 166.4 $6.0$ kJ
THE THERMODYNAMIC PROPERTIES OF THE AQUEOUS IONS OF IRON

F:  217. Z: 14FOR
C:  Data of 01COH/VIS.
S:  3/86 VBP

217. Z: 14FOR
R:  FeSO4:7H2O(cr)=FeSO4(aq)+7H2O(l)
DV:  H, +18.0 $2.5$ kJ
F:  TN
C:  Measurements at 286 K; dH=18.13 kJ/mol
(dCp= -8 J/(mol.K))
S:  3/86 VBP

225. Z: 78VAS/VAS
R:  (NH4)2 SO4(cr)+Fe(cr)+H2O2 (4.95H2O)
+H2SO4(0.43H2O)+4H2O(l)=(NH4)2
Fe(SO4)2:6H2O(cr)
DV:  H, -579.78 $0.87$ kJ
W:  99

226. Z: 03DMI
R:  (NH4)2 Fe(SO4)2:6H2O(cr)+2H++(aq)=
2NH4++(aq)+Fe+2(aq)+2H2SO4-(aq)
+6H2O(l)
DV:  H, 69.40 $0.20$ kJ
C:  Extrapol from dsoInH meas. in 2.0, 3.0, 4.0 mol
dm-3 HClO4 aqueous solutions. m salt=0.01 to
0.04. Correct for SO4--in HClO4 soln., and to
ionic strength=0 using Khodakovskii equation
with 1986 constants. Supersedes 78VAS/
VAS.
S:  VBP Aug. 85, 3/87 VBP

227. Z: 83DMI
R:  FeSO4:7H2O(cr)=FeSO4(aq)+7H2O(l)
DV:  H, 12.90 $0.10$ kJ
C:  Experimental points ref to Khodakovskii
equation with extrapolation to m=0. dH(0)
= dH0(DH)/kJ/mol=-(12.895 $0.096$)+
(35.572 $2.372$) I
S:  83DMI

228. Z: 83VD
R:  FeSO4:7H2O(cr)+H++(aq)=Fe+2(aq)+H2SO4
-(aq)+7H2O(l)
DV:  H, +33.58 $0.50$ kJ
W:  99
C:  Extrapolation of enthalpies of solution of
FeSO4:1H2O(cr) in 2N, 3N and 4N HClO4 as
a function of m(1/2) to m(Fe+2(aq))=0 and to
ionic strength solution=0 using corrections
from 78VAS/VAS. See 83DMI.
S:  6/86 VBP

229. Z: 68LAR/CER
R:  FeSO4:7H2O(cr)=FeSO4(aq)+7H2O(l)
DV:  H, +11.80 $0.42$ kJ
C:  From melt of dsoInH of hydrated salts with
compositions FeSO4:6.92 H2O, FeSO4:6.78
H2O, FeSO4:5.32 H2O, FeSO4:3.98 H2O, and
FeSO4:2.46 H2O. Measured concentrations
0.005 to 0.05 m. Authors correct to std state
using phil from 56LAN/MIE for NiSO4. More
details in 68LAR.
S:  8/85 VBP

230. Z: 68LAR/CER
R:  FeSO4:4H2O(cr)=FeSO4(aq)+4H2O(l)
DV:  H, -13.81 $0.42$ kJ
From the analysis of solutions of hydrated salts with compositions FeSO₄·6.92 H₂O, FeSO₄·6.78 H₂O, FeSO₄·5.32 H₂O, FeSO₄·3.98 H₂O, and FeSO₄·2.46 H₂O. Measured concentrations 0.005 to 0.05 m. Authors correct to standard state using pH from 56LAN/MIE for NiSO₄. More details in 68LAR.

**231. Z:** 68LAR/CER
**R:** FeSO₄·H₂O(cr)=FeSO₄·7H₂O(l)
**DV:** H, $-4.35$ S° 84 kJ
**C:** From the analysis of solutions of hydrated salts with compositions FeSO₄·6.92 H₂O, FeSO₄·6.78 H₂O, FeSO₄·5.32 H₂O, FeSO₄·3.98 H₂O, and FeSO₄·2.46 H₂O. Measured concentrations 0.005 to 0.05 m. Authors correct to standard state using pH from 56LAN/MIE for NiSO₄. More details in 68LAR.

**S:** VBP Aug. 85

**232. Z:** 41PER
**R:** FeSO₄·7H₂O(cr)=FeSO₄·1500 H₂O+7 H₂O(l)
**DV:** H, $17.10$ S° 1.0 kJ
**C:** Measurements at 282–293 K over range 1550 H₂O to 32.7 H₂O. Corrected to 298 K using 41PER Cp measurements of aqueous solutions at 293 K.

**S:** 10/90 VBP

**233. Z:** 41PER
**R:** FeSO₄·7H₂O(cr)=FeSO₄·1000 H₂O+7 H₂O(l)
**DV:** H, $17.35$ S° 1.0 kJ
**C:** Measurements at 282–293 K over range 1550 H₂O to 32.7 H₂O. Corrected to 298 K using 41PER Cp measurements of aqueous solutions at 293 K.

**S:** 10/90 VBP

**234. Z:** 41PER
**R:** FeSO₄·7H₂O(cr)=FeSO₄·300 H₂O+7 H₂O(l)
**DV:** H, $18.30$ S° 1.0 kJ
**C:** Measurements at 282–293 K over range 1550 H₂O to 32.7 H₂O. Corrected to 298 K using 41PER Cp measurements of aqueous solutions at 293 K.

**S:** 10/90 VBP

**235. Z:** 41PER
**R:** FeSO₄·7H₂O(cr)=FeSO₄·200 H₂O+7 H₂O(l)
**DV:** H, $18.70$ S° 1.0 kJ
**C:** Measurements at 282–293 K over range 1550 H₂O to 32.7 H₂O. Corrected to 298 K using 41PER Cp measurements of aqueous solutions at 293 K.

**S:** 10/90 VBP

**236. Z:** 41PER
**R:** FeSO₄·7H₂O(cr)=FeSO₄·100 H₂O+7 H₂O(l)
**DV:** H, $19.35$ S° 1.0 kJ
**C:** Measurements at 282–293 K over range 1550 H₂O to 32.7 H₂O. Corrected to 298 K using 41PER Cp measurements of aqueous solutions at 293 K.

**S:** 10/90 VBP

**237. Z:** 41PER
**R:** FeSO₄·7H₂O(cr)=FeSO₄·75 H₂O+7 H₂O(l)
**DV:** H, $19.65$ S° 1.0 kJ
**C:** Measurements at 282–293 K over range 1550 H₂O to 32.7 H₂O. Corrected to 298 K using 41PER Cp measurements of aqueous solutions at 293 K.

**S:** 10/90 VBP

**238. Z:** 41PER
**R:** FeSO₄·7H₂O(cr)=FeSO₄·50 H₂O+7 H₂O(l)
**DV:** H, $20.05$ S° 1.0 kJ
**C:** Measurements at 282–293 K over range 1550 H₂O to 32.7 H₂O. Corrected to 298 K using 41PER Cp measurements of aqueous solutions at 293 K.

**S:** 10/90 VBP

**239. Z:** 41PER
**R:** FeSO₄·7H₂O(cr)=FeSO₄·40 H₂O+7 H₂O(l)
**DV:** H, $20.30$ S° 1.0 kJ
**C:** Measurements at 282–293 K over range 1550 H₂O to 32.7 H₂O. Corrected to 298 K using 41PER Cp measurements of aqueous solutions at 293 K.

**S:** 10/90 VBP

**240. Z:** 41PER
**R:** FeSO₄·7H₂O(cr)=FeSO₄·35 H₂O+7 H₂O(l)
**DV:** H, $20.45$ S° 1.0 kJ
**C:** Measurements at 282–293 K over range 1550 H₂O to 32.7 H₂O. Corrected to 298 K using 41PER Cp measurements of aqueous solutions at 293 K.

**S:** 10/90 VBP

**241. Z:** 61KEL/KIN
**B:** 34AND
**R:** =FeCO₃(cr)
**DV:** S, $22.25$ S° 0.4 C
**F:** TN
**C:** measured by 34AND, 54–297 K. Cp=19.63 cal/(mol·K) at 298.15

**S:** VBP Aug. 85

**242. Z:** 64KOS/KAL
**R:** =FeCO₃(cr)
**DV:** S, $96.1$ S° 0.4J
**C:** measured Cp 70–298 K and combines results with meas. of 62KAL, 1.6 to 70 K. Estimated purity 97%. Individual Cp meas. not given. $S(0–70 K)=16.8 J/(mol·K)$

**S:** VBP Aug. 85

**243. Z:** 35KRU
**R:** FeCO₃(cr)=FeO(cr)+CO₂(g)
**DV:** H, $127$ S° 20 kJ
**F:** TN
**W:** 99
**C:** Third law value. Decomp. to FeO occurs at approx. 710 K. Not considered. Mechanism of decompression complex. See 71FRE

**S:** VBP Aug. 85

**244. Z:** 81REI/JOH
**R:** FeCO₃(cr)+2H⁺(aq)=Fe⁺(aq)+CO₂(g)+H₂O
**DV:** G, $323.15$ K, $-45.84$ S° 0.5 kJ
**DV:** G, $-44.75$ S° 1.0 kJ
THE THERMODYNAMIC PROPERTIES OF THE AQUEOUS IONS OF IRON

C: meas. at 323.15 K, I=1.0 mol dm⁻³ NaClO₄, corrected to I=0 using Davies eqn and to 298.15 K using est'd dS=44 J/(mol·K). p=1 atm.
S: VBP Aug. 85

245. Z: 29ROT
R: 3FeCO₃(cr)+1/2 O₂(g)=Fe₃O₄(cr)+3CO₂(g)
DV: H, 291.15 K, -133.7 $8J$
DV: H, -133.8 $15 K$
F: TN
W: 99
C: Corrected from 18 C; no analysis of products. Assumed oxidation goes completely to Fe₃O₄(cr). Same as 29ROT11. Rejected in TN evaluation.
S: VBP Aug. 85

246. Z: 1875FR
R: FeSO₄(220 H₂O)+K₂CO₃(220 H₂O)
   =FeCO₃(cr)+K₂SO₄(440 H₂O)
DV: H, 4.36 $0.5 K$
C: 16 C measurement, est'd dCp=100 cal/(mol·K)
S: 8/85 VBP

247. Z: 1875ER
R: FeSO₄(220 H₂O)+Na₂CO₃(220 H₂O)
   =FeCO₃(cr)+Na₂SO₄(440 H₂O)
DV: H, 4.64 $0.5 K$
C: 16 C measurement, est'd dCp=100 cal/(mol·K)
S: VBP Aug. 85

248. Z: 18SMI
R: FeCO₃(cr)+H₂CO₃(aq)=Fe(HCO₃)₂(aq)
DV: G, 14.01 $0.5 K$
C: meas. at 303 K; corrected for ionic strength =0.01 and to 298.15 K; uncorrected K =4.50E-03 at 303.15 K
S: VBP Aug. 85

249. Z: 18SMI
R: FeCO₃(cr)=Fe₂O₃+3CO(g)
DV: G, 59.96 $0.84 K$
F: TN
W: 99
C: author's calculated value from meas at 303 K in CO₂ solns. See revised reaction.
S: VBP Aug. 85

250. Z: 69LAN
R: FeCO₃(cr)=Fe₂O₃(aq)+CO(g)
DV: G, 60.22 $0.60 K$
C: pK=10.55 $0.03 based on three measurements.
S: 3/89 VBP

251. Z: 78JOH/BAU
R: Fe₂O₃(aq)+H₂O(aq)=Fe(HCO₃)₂(aq)
DV: G, -7.4 $1.1 K$
C: K lies between 10 and 30 at 298 K
S: 5/86 VBP

Al.c. Reaction Catalog Provided by IVTAN

This catalog is part of the original catalog provided by Dr. V. Medvedev (IVTAN) in 1986 and 1987. Since that time it has been updated and corrected by V. B. Parker and M. Efimov (IVTAN). The following references are not cited in this paper and do not appear in A1.b (Reaction Catalog).

1. Z: 52SCH/KRE
R: 2HCl(g)+Fe(cr)=FeCl₂(g)+H₂(g)
DV: H, 41.3 $6.0 K$
C: IVTAN 3-85 EQ. 229
Corrected for S(FeCl₂, g)=293.803 J/mol (1 atm)
C: Transpiration; third law, 1205–1373 K, 22 pts
S: VM 4/87, 10/88 VBP

2. Z: 25MAI
R: FeCl₂(cr)=FeCl₂(g)
DV: H, 195.2 $6.0$
C: IVTAN 3-85 EQ. 234
Corrected for S(FeCl₂, g)=293.803 (1 atm) and FeCl₂(cr), S₀=118.0 and H-H(0)=16.27
C: Static; 3rd law, 22 pts, 972–1268 K; second law 196 $6$
S: VM 4/87, 10/88 VBP

3. Z: 52SCH/KRE
R: FeCl₂(cr)=FeCl₂(g)
DV: H, 194.15 $5.0 K$
C: IVTAN 3-85 EQ. 235
Corrected for S(FeCl₂, g)=293.803 (1 atm) and FeCl₂(cr), S₀=118.0 and H-H(0)=16.27
C: Transpiration, third law, 6 pts, 961–1107 K, second law 201 $18$
S: VM 4/87, 10/88 VBP

4. Z: 55SCI/DAY
R: FeCl₂(cr)=FeCl₂(g)
DV: H, 194 $8.26 K$
W: 99
C: IVTAN 3-85 EQ. 236
Corrected for S(FeCl₂, g)=293.803 (1 atm) and FeCl₂(cr), S₀=118.0 and H-H(0)=16.27
S: VM 4/87, 10/88 VBP

5. Z: 58SCH/POOR
R: FeCl₂(cr)=FeCl₂(g)
DV: H, 199.17 $4.0 K$
W: 99
C: IVTAN 3-85 EQ. 237
Corrected for S(FeCl₂, g)=293.803 (1 atm) and FeCl₂(cr), S₀=118.0 and H-H(0)=16.27
C: Effusion, third law, 2 pts 671 K and 701 K
S: VM 4/87, 10/88 VBP

6. Z: 58SCH/POOR
R: FeCl₂(cr)=FeCl₂(g)
DV: H, 196.73 $4.0$
C: IVTAN 3-85 EQ. 238
Corrected for S(FeCl₂, g)=293.803 (1 atm) and FeCl₂(cr), S₀=118.0 and H-H(0)=16.27
C: Mass spectroscopy, third law, 7 pts, 621–701 K; Second law 172 $15 K$
S: VM 4/87, 10/88 VBP

7. Z: 60SIM/GRE
R: FeCl₂(cr)=FeCl₂(g)
DV: H, 199.03 $4.0 K$
C: IVTAN 3-85 EQ. 239
Corrected for S(FeCl₂, g)=293.803 (1 atm) and FeCl₂(cr), S₀=118.0 and H-H(0)=16.27
C: Torsion; third law, 670–740 K equation only, second law 196 K
S: VM 4/87, 10/88 VBP
V. B. PARKER AND I. L. KHODAKOVSKII

8. Z: 69KAN/MCC
   R: FeCl2(cr) = FeCl2(g)
   DV: H, 198.81 $4.0$ kJ
   C: IVTAN 3-85 EQ. 240
      Corrected for S0(FeCl2, g)=293.803 (1 atm) and
      FeCl2(cr), S0=118.0 and H-H(0)=16.27
   C: Effusion; third law, 725–825 equation only, second
      law 210 kJ
   S: VM 4/87, 10/88 VBP

9. Z: 69KAN/MCC
   R: FeCl2(cr) = FeCl2(g)
   DV: H, 198.31 $4.0$
   C: IVTAN 3-85 EQ. 241
      Corrected for S0(FeCl2, g)=293.803 (1 atm) and
      FeCl2(cr), S0=118.0 and H-H(0)=16.27
   C: Torsion; third law 725–825 K equation only, second
      law 209 kJ
   S: VM 4/87, 10/88 VBP

10. Z: 75BUR/MIR
    R: FeCl2(cr) = FeCl2(g)
    DV: H, 198.68 $6.0$ kJ
    C: IVTAN 3-85 EQ. 242
       Corrected for S0(FeCl2, g)=293.803 (1 atm) and
       FeCl2(cr), S0=118.0 and H-H(0)=16.27
    C: Torsion, third law, 1000–1300 K equation only;
       second law 185 kJ
    S: VM 4/87, 10/88 VBP

11. Z: 76RAT/NOV
     R: FeCl2(cr) = FeCl2(g)
     DV: H, 199.75 $4.0$
     C: IVTAN 3-85 EQ. 244
        Corrected for S0(FeCl2, g)=293.803 (1 atm) and
        FeCl2(cr), S0=118.0 and H-H(0)=16.27
     C: Mass spectroscopy; third law, 668–766 K equation
        only; second law 204 kJ
     S: VM 4/87, 10/88 VBP

12. Z: 77LAN/ADA
     R: FeCl2(cr) = FeCl2(g)
     DV: H, 193.23 $4.0$ kJ
     C: IVTAN 3-85 EQ. 245
        Corrected for S0(FeCl2, g)=293.803 (1 atm) and
        FeCl2(cr), S0=118.0 and H-H(0)=16.27
     C: Torsion, third law, 711–887 K equation only; second
        law 207 kJ
     S: VM 4/87, 10/88 VBP

13. Z: 77LAN/ADA
     R: FeCl2(cr) = FeCl2(g)
     DV: H, 196.41 $4.0$
     C: IVTAN 3-85 EQ. 246
        Corrected for S0(FeCl2, g)=293.803 (1 atm) and
        FeCl2(cr), S0=118.0 and H-H(0)=16.27
     C: Effusion; third law, 624–952 K equation only;
        second law 215 kJ
     S: VM 4/87, 10/88 VBP

14. Z: 78NOV
     R: FeCl2(cr) = FeCl2(g)
     DV: H, 202.419 $4.14$ kJ
     W: 99
     C: IVTAN 3-85 EQ. 246
        Corrected for S0(FeCl2, g)=293.803 (1 atm) and
        FeCl2(cr), S0=118.0 and H-H(0)=16.27
     S: VM 4/87, 10/88 VBP

15. Z: 88CTT
     R: =FeCl2(g)
     DV: S, 293.915 $4.0$ J
     C: at 1 bar, S0(1 atm)=293.806 kJ/mol
     ** or 293.912 and 293.803 (6/90 EME)
     S: 8/88 VBP

16. Z: 88CTT
     R: =Fe2Cl4(g)
     DV: S, 439.872 $10.0$
     C: at 1 bar
     ** or 439.868 (6/90 EME)
     S: 10/88 VBP

17. Z: 89CTT
     R: =Fe2Cl6(g)
     DV: g, 520.0668
     C: at 1 bar, H-H(0)=37.30 kJ/mol
     S: 10/88 VBP

18. Z: 89CTT
     R: FeCl3(g)
     DV: S, 344.8275
     C: at 1 bar, H-H(0)=17.815 kJ/mol
     S: 10/88 VBP

19. Z: 25MAI
     R: 2FeCl3(cr)=Fe2Cl6(g)
     DV: H, 133.36 $6.7$ kJ
     C: Revisited from IVTAN 3-85 EQ.103 and 86ARI/BER
        values (at 0 K)
     C: Static, 490–558 K, 6 pts, 3rd law; 2nd law value
        134.4 $4.5$ kJ
     S: 10/87 VM, 10/88 VBP, 12/89 EME and VBP

20. Z: 25STI
     R: 2FeCl3(cr)=Fe2Cl6(g)
     DV: H, 132.67 $6.8$ kJ
     C: Revisited from IVTAN 3-85 EQ.104 and 86ARI/BER
        values (at 0 K), Static: 526–598 K, 9 pts,
        third law; second law value 111.3 $8$ kJ/mol
     S: 10/87 VM, 10/88 VBP, 12/89 EME and VBP

     R: 2FeCl3(cr)=Fe2Cl6(g)
     DV: H, 130.1 $7.1$ kJ
     C: Revisited from IVTAN 3-85 EQ.105 and 86ARI/BER
        values (at 0 K)
     C: Transpiration, 473–553 K, 4 pts, third law;
        second law 111.4 $8$ kJ. Author’s assumed reaction was 2
        FeCl3(cr)=2FeCl3(g). Measurements were recalculated
        for Fe2Cl6(g) as a reaction product.
     S: VM 10/87, 10/88 VBP, 12/89 EME and VBP

22. Z: 38SANZ
     R: 2FeCl3(cr)=Fe2Cl6(g)
     DV: H, 134.6 $6.8$ kJ
     C: Revisited from IVTAN 3-85 EQ.107 and 86ARI/BER
        values (at 0 K)
     C: Static, 501–577 K, 20 pts, third law; second law
        134.5 $4.0$ kJ
THE THERMODYNAMIC PROPERTIES OF THE AQUEOUS IONS OF IRON

23. Z: 42JOH/WEI
R: 2FeCl₃(cr)=Fe₂Cl₆(g)
DV: H, 132.7 $6.7 \text{ kJ}$
C: Revised from IVTAN 3-85 EQ.108 and 86ARI/BER values (at 0 K)
C: Static, 505–562 K, 6 pts, third law; second law 151.25 $6.3 \text{ kJ}$
S: VM 10/87, 10/88 VBP, 12/89 EME and VBP

24. Z: 58WIL/GRE
R: 2FeCl₃(cr)=Fe₂Cl₆(g)
DV: H, 134 $11 \text{ kJ}$
C: Revised from IVTAN 3-85 EQ.109 and 86ARI/BER values (at 0 K)
C: Static and transpiration, 423–503 K, equation, third law; second law 143.0 $4.3 \text{ kJ}$
S: VM 10/87, 10/88 VBP

25. Z: 62HAM/GRE
K: 2FeCl₃(cr)=Fe₂Cl₆(g)
DV: H, 155.0 $4.2 \text{ kJ}$
C: Revised from IVTAN 3-85 EQ.110 and 86ARI/BER values (at 0 K)
C: Effusion, 393–413 K, 4 pts, third law; second law 137.2 $4.3 \text{ kJ}$
S: VM 10/87, 10/88 VBP, 12/89 EME and VBP

26. Z: 62COO
R: 2FeCl₃(cr)=Fe₂Cl₆(g)
DV: H, 127.6 $11.00 \text{ kJ}$
C: Revised from IVTAN 3-85 EQ.112. and 86ARI/BER values (at 0 K)
C: Transpiration, 588–710 K, equation, third law; second law 166.7 $9.7 \text{ kJ}$
S: VM 10/87, 10/88 VBP, 12/89 EME and VBP

27. Z: 65CHR
R: 2FeCl₃(cr)=Fe₂Cl₆(g)
DV: H, 120.8 $8.3 \text{ kJ}$
W: 99
C: Spectrophotometric, only vsH₂O(440 K)=115.5 $2.5 \text{ kJ} calculated by the 2nd law is known.
S: VM 10/87, 10/88 VBP, 12/89 EME and VBP

28. Z: 68GAL
R: 2FeCl₃(cr)=Fe₂Cl₆(g)
DV: H, 132.1 $6.8 \text{ kJ}$
C: Revised from IVTAN 3-85 EQ.114 and 86ARI/BER values (at 0 K)
C: Static, 483–560 K, equation, third law; second law 170 $9 \text{ kJ}$
S: VM 10/87, 11/88 VBP, 12/89 EME and VBP

29. Z: 68MAP/GRE
R: 2FeCl₃(cr)=Fe₂Cl₆(g)
DV: H, 139.3 $6.3 \text{ kJ}$
DV: H, 550 K, 128.0 $5.4 \text{ kJ}$
C: Calorimetric dsH₀(550 K)=128.0 $5.4 \text{ kJ}$. Five measurements.
S: VM 10/87, 11/88 VBP, 12/89 VBP

30. Z: 68MAP/GRE
R: 2FeCl₃(cr)=Fe₂Cl₆(g)
DV: H, 151.5 $7.6 \text{ kJ}$
C: Calorimetric dsH₀(583 K)=51.8 $2.5 \text{ kJ}$. Three measurements.
S: VM 10/87, 11/88 VBP, 12/89

31. Z: 68MAP/GRE
R: 2FeCl₃(cr)=Fe₂Cl₆(g)
DV: H, 583 K, 51.8 $2.5 \text{ kJ}$
C: Calorimetric, three measurements
S: VM 10/87, 11/88 VBP

32. Z: 69POL/KOM
R: 2FeCl₃(cr)=Fe₂Cl₆(g)
DV: H, 131.9 $7.2 \text{ kJ}$
C: Revised from IVTAN 3-85 EQ.115 and 86ARI/BER values (at 0 K)
C: Static, 503–563 K, equation, third law; second law 135.4 $9 \text{ kJ}$
S: VM 10/87, 11/88 VBP, 12/89 EME and VBP

33. Z: 77LAN/ADA
R: 2FeCl₃(cr)=Fe₂Cl₆(g)
DV: H, 139.8 $5.0 \text{ kJ}$
C: Revised from IVTAN 3-85 EQ.117 and 86ARI/BER values (at 0 K)
C: Torsion, 403–442 K, equation, third law; second law 125 $9 \text{ kJ}$
S: VM 10/87, 11/88 VBP, 12/89 EME and VBP

34. Z: 7714N/ADA
R: 2FeCl₃(cr)=Fe₂Cl₆(g)
DV: H, 133.6 $6.1 \text{ kJ}$
C: Revised from IVTAN 3-85 EQ.116 and 86ARI/BER values (at 0 K)
C: Effusion, 369–463 K, equation third law; second law 136.5 $9 \text{ kJ}$
S: VM 10/87, 11/88 VBP, 12/89 EME and VBP

35. Z: 83RUS/GRE
R: 2FeCl₃(cr)=Fe₂Cl₆(g)
DV: H, 154.1 $9 \text{ kJ}$
W: 99
C: Spectrophotometric, dsH₀(550 K)=147.2 $9 \text{ kJ}$, second law
S: VM 10/87, 11/88 VBP, 12/89 VBP