

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

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

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Recommended thermochemical property values, $\Delta_f H^\circ$, $\Delta_f G^\circ$, and S° 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: $\Delta_f H^\circ = -90.0 \pm 0.5 \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_f G^\circ = -90.53 \pm 1.0 \text{ kJ} \cdot \text{mol}^{-1}$, $S^\circ = -101.6 \pm 3.7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for $\text{Fe}^{2+}(\text{ao})$ and $\Delta_f H^\circ = -49.0 \pm 1.5 \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_f G^\circ = -16.28 \pm 1.1 \text{ kJ} \cdot \text{mol}^{-1}$, $S^\circ = -278.4 \pm 7.7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for $\text{Fe}^{3+}(\text{ao})$. 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 thermochemical property values is given for $\text{FeOOH}(\text{cr})$, Goethite, $\text{FeCl}_2(\text{cr})$, $\text{FeCl}_3(\text{cr})$, $\text{FeBr}_2(\text{cr})$, $\text{FeBr}_3(\text{cr})$, $\text{FeI}_2(\text{cr})$, and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{cr})$, as well as "reconstituted" recommended process values with uncertainties involving these substances. All recommended values are also given for a standard state of $p^\circ=1 \text{ atm}$. 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; thermochemical measurements.

Contents

1. Introduction.....	1701	2. The Evaluation of the Enthalpy of Formation of the Aqueous Ion Fe^{2+} , $\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao})$	1704
1.1. General.....	1701	2.1. The Chloride System.....	1704
1.2. Conventions and Auxiliary Data.....	1701	2.1.1. $\Delta_f H^\circ(\text{FeCl}_2, \text{cr})$	1704
1.2.1. Definitions and Symbols.....	1701	2.1.1.1. Calorimetric Measurements of $\text{Fe}(\text{cr})$ and $\text{FeCl}_2(\text{cr})$ in HCl Solutions.....	1704
1.2.2. Reference States.....	1702	2.1.1.2. Calorimetric Measurements of $\text{Fe}(\text{cr})$, $\text{FeBr}_2(\text{cr})$, and $\text{FeCl}_2(\text{cr})$ in Aqueous (KBr , Br_2) Solutions.....	1704
1.2.3. Molar Masses.....	1702	2.1.1.3. The High Temperature Reduction of $\text{FeCl}_2(\text{cr})$ by $\text{H}_2(\text{g})$	1705
1.2.4. Units, Fundamental Constants, and Thermochemical Property Values for Auxiliary Data.....	1702	2.1.1.4. Summary.....	1705
1.2.5. Description of Bibliographic References.....	1702	2.1.2. The Standard Enthalpy of Solution of $\text{FeCl}_2(\text{cr})$ in $\text{H}_2\text{O}(\text{l})$ and the $\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao})$	1705
1.2.6. Content and Description of the Reaction Catalog.....	1702	2.2. The Bromide System.....	1705
1.2.7. Uncertainties.....	1702	2.2.1. $\Delta_f H^\circ(\text{FeBr}_2, \text{cr})$	1705
1.3. Acknowledgments.....	1703	2.2.1.1. Calorimetric Measurements of $\text{Fe}(\text{cr})$ and $\text{FeBr}_2(\text{cr})$ in Aqueous (KBr , Br_2) Solutions.....	1705
1.4. Method of Approach.....	1703	2.2.2. The Standard Enthalpy of Solution of $\text{FeBr}_2(\text{cr})$ in $\text{H}_2\text{O}(\text{l})$ and	
1.4.1. General.....	1703		
1.4.2. The Systematic Analysis.....	1703		

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1. Introduction

1.1. General

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

Values are also given for a standard state pressure of 1 atm since the CODATA recommended thermochemical values [89COX/WAG] for S° and $\Delta_f G^\circ$ 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 Fe^{2+} and 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 A1.b (Reaction Catalog) and, unless otherwise specified, reaction energies are to be assumed to be at 298.15 K and are given as $\text{kJ}\cdot\text{mol}^{-1}$; the energy value is for the reaction as written. For convenience to the users, E values and ΔG values given in Secs. 4 and 5 are as originally obtained using $p^\circ=1$ atm, unless otherwise stated; calculation to

$\Delta_f G^\circ(\text{Fe}^{+2}, \text{ao})$ and $\Delta_f G^\circ(\text{Fe}^{+3}, \text{ao})$ is also made at $p^\circ=1$ atm. Final conversion is made to $p^\circ=1$ 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 [82IUP] 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 (A1.b), the following are used:

ai = 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:

Φ_L = the relative apparent molal enthalpy = the integral enthalpy of dilution of the solute to infinite dilution

\bar{L}_2 = the relative partial molal enthalpy of the solute in the given solution

$$= \Phi_L + \frac{1}{2}m^{1/2}(d\Phi_L/dm^{1/2})$$

$\Phi_{L(D-H)}$ = the Debye-Hückel (see 58HAR/OWE) limiting law contribution to Φ_L .

One of us (I.K.) in 75KHO proposed an equation for calculating the thermal effects to infinite dilution derived from the Debye-Hückel relation which was modified in 1986 to:

$$\Phi_{L(D-H)} = \Delta z^2 \left[\frac{S_H}{4B} y_1 + \frac{W_H}{(4B)^2} y_2 \right],$$

where

$$y_1 = 1 - \frac{2}{4BI^{1/2}} + \frac{2 \ln(1 + 4BI^{1/2})}{(4B)^2 I},$$

$$y_2 = 1 - \frac{4}{4BI^{1/2}} + \frac{2}{(4B)^2 I} \left[\frac{1}{1 + 4BI^{1/2}} + 3 \ln(1 + 4BI^{1/2}) - 1 \right],$$

$\Delta z^2 = \sum (z^2 \text{ ions, products} - z^2 \text{ ions, reactants})$,

z = charge on the ion,

at 298.15 K $B=0.3285$,

$S_H=1.4703 \text{ kJ}\cdot\text{mol}^{-1}$,

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

So that

^aThis 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 A1.a.

$$\Phi_{L(D-H)} = \Delta z^2(267.428y_1 - 75.003y_2).$$

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 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. 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 \pm .

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

$\text{kJ} = \text{kJ} \cdot \text{mol}^{-1}$ for H,G, and $\text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for S, C_p

$\text{kC} = \text{kcal} \cdot \text{mol}^{-1}$ for H,G, and $\text{kcal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for S, C_p

$\text{J} = \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for S, C_p

$\text{C} = \text{cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for S, C_p

K, $^\circ\text{C}$ = 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 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, $\Delta_f H^\circ$, $\Delta_f G^\circ$, and S° 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 $\text{Fe}^{2+}(\text{ao})$ and $\text{Fe}^{3+}(\text{ao})$ are:

$\text{Fe}_3\text{O}_4(\text{cr})$, $\text{FeOOH}(\text{cr})$, Goethite, $\text{FeCl}_2(\text{cr})$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}(\text{cr})$, $\text{FeCl}_3(\text{cr})$, $\text{FeBr}_2(\text{cr})$, $\text{FeBr}_3(\text{cr})$, $\text{FeI}_2(\text{cr})$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{cr})$, and $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}(\text{cr})$.

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 $\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao})$ beginning with:

- (1) the determinations of $\Delta_f H^\circ(\text{FeCl}_2, \text{cr})$, independent of other Fe compounds, and the $\Delta_{\text{sol}} H^\circ$ of $\text{FeCl}_2(\text{cr})$ in $\text{H}_2\text{O}(\text{l})$; an initial selection is made for $\Delta_f H^\circ(\text{FeCl}_2, \text{cr})$;
- (2) the determinations of $\Delta_f H^\circ(\text{FeBr}_2, \text{cr})$, independent of other Fe compounds, and the $\Delta_{\text{sol}} H^\circ$ of $\text{FeBr}_2(\text{cr})$ in $\text{H}_2\text{O}(\text{l})$; this also requires an initial selection for $\Delta_f H^\circ(\text{FeBr}_2, \text{cr})$;
- (3) the measurements of $\Delta_f H^\circ(\text{FeI}_2, \text{cr})$; those independent of other Fe compounds, and then that dependent upon $\Delta_f H^\circ(\text{FeBr}_2, \text{cr})$; an initial selection is also made for $\Delta_f H^\circ(\text{FeI}_2, \text{cr})$, as well as $\Delta_{\text{sol}} H^\circ$;
- (4) the independently determined $\Delta_f H^\circ(\text{FeSO}_4 \cdot 7\text{H}_2\text{O}, \text{cr})$ and the $\Delta_{\text{sol}} H^\circ$ in $\text{H}_2\text{O}(\text{l})$;
- (5) the independently arrived at $\Delta_f H^\circ((\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2, \text{cr})$ and its $\Delta_{\text{sol}} H^\circ$ in $\text{H}_2\text{O}(\text{l})$.

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

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

- (1) the determinations for $\Delta_f H^\circ(\text{FeCl}_3, \text{cr})$, those independent of other Fe compounds as well as those linked to $\text{FeCl}_2(\text{cr})$, combined with a selection for $\Delta_{\text{sol}} H^\circ(\text{FeCl}_3, \text{cr})$ which in itself requires a working value;
- (2) the direct determination of $\Delta_f H^\circ(\text{Fe}^{3+}, \text{ao})$ through oxidation of $\text{Fe}(\text{cr})$;
- (3) the enthalpy relationship between $\text{Fe}^{3+}(\text{ao})$ and $\text{Fe}^{2+}(\text{ao})$.

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

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

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

In Sec. 4.3 a tentative selection is made ($p^\circ = 1 \text{ atm}$).

Section 5—The $\Delta_f G^\circ(\text{Fe}^{3+}, \text{ao})$ is evaluated by:

- (1) establishing the thermochemical property values of $\text{FeOOH}(\text{cr}, \text{Goethite})$ and its $\Delta_{\text{sol}}G^\circ$ (Sec. 5.1.3) to obtain a value for $\Delta_f G^\circ$ and
- (2) by obtaining values for $\Delta_f G^\circ(\text{Fe}^{3+}, \text{ao}) - \Delta_f G^\circ(\text{Fe}^{2+}, \text{ao})$ (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 $\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao})$ to obtain other values for $\Delta_f G^\circ(\text{Fe}^{3+}, \text{ao})$.

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

Section 6—All final recommended property values and uncertainties are tabulated ($p^\circ = 1 \text{ atm}$ and $p^\circ = 1 \text{ bar}$). 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 catalogs) pertinent to this evaluation but not definitive are given (Sec. 6.2).

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

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

- (1) the determinations of $\Delta_f H^\circ(\text{FeCl}_2, \text{cr})$, independent of other Fe compounds, and the $\Delta_{\text{sol}} H^\circ$ of $\text{FeCl}_2(\text{cr})$ in $\text{H}_2\text{O}(\text{l})$; an initial selection is made for $\Delta_f H^\circ(\text{FeCl}_2, \text{cr})$;
- (2) the determinations of $\Delta_f H^\circ(\text{FeBr}_2, \text{cr})$, independent of other Fe compounds, and the $\Delta_{\text{sol}} H^\circ$ of $\text{FeBr}_2(\text{cr})$ in $\text{H}_2\text{O}(\text{l})$; this also requires an initial selection for $\Delta_f H^\circ(\text{FeBr}_2, \text{cr})$;
- (3) the measurements of $\Delta_f H^\circ(\text{FeI}_2, \text{cr})$; those values independent of other Fe compounds, and then that dependent upon $\Delta_f H^\circ(\text{FeBr}_2, \text{cr})$; an initial selection is also made for $\Delta_f H^\circ(\text{FeI}_2, \text{cr})$, as well as $\Delta_{\text{sol}} H^\circ$;
- (4) the independently determined $\Delta_f H^\circ(\text{FeSO}_4 \cdot 7\text{H}_2\text{O}, \text{cr})$ and the $\Delta_{\text{sol}} H^\circ$ in $\text{H}_2\text{O}(\text{l})$;
- (5) the independently arrived at $\Delta_f H^\circ((\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2, \text{cr})$ and its $\Delta_{\text{sol}} H^\circ$ in $\text{H}_2\text{O}(\text{l})$.

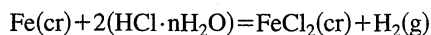
In Sec. 2.5 we tabulate the various values obtained for $\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao})$ from our initial selections for the $\Delta_f H^\circ$'s of the ferrous halides and sulfates and make our tentative selection for $\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao})$ and also make adjustments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

2.1. The Chloride System

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

2.1.1.1. *Calorimetric measurements of the enthalpies of the reaction of $\text{Fe}(\text{cr})$ and $\text{FeCl}_2(\text{cr})$ in HCl solutions*

There are two determinations for the enthalpy of the reaction:

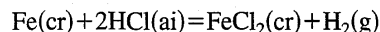


$$\Delta_r H = -17.04 \pm 0.21 \text{ kJ} \cdot \text{mol}^{-1} \quad (n = 12.731) [59\text{KOE/COU (No. 90)}]$$

and

$$\Delta_r H = -12.85 \pm 2.0 \text{ kJ} \cdot \text{mol}^{-1} \quad (n = 200) [1882\text{THO (No. 89)}].$$

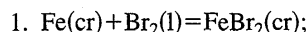
Correction to the standard state of $\text{HCl}(\text{aq})$, using ϕ_L from 65PAR, results in $\Delta_r H^\circ = -7.50 \pm 0.21$ and $-11.08 \pm 2.0 \text{ kJ} \cdot \text{mol}^{-1}$, respectively, for



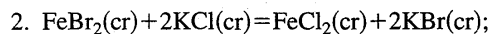
$$\text{and } \Delta_f H^\circ(\text{FeCl}_2, \text{cr}) = -341.66 \pm 0.25 \text{ and } -345.24 \pm 2.0 \text{ kJ} \cdot \text{mol}^{-1}, \text{ respectively.}$$

2.1.1.2. *Calorimetric measurements of the enthalpies of the reaction of $\text{Fe}(\text{cr})$, $\text{FeBr}_2(\text{cr})$ and $\text{FeCl}_2(\text{cr})$ in aqueous (KBr , Br_2) solutions.*

Recently, 89EFI/EVD and 89EVD/EFI (Nos. 115 and 166) measured the enthalpies of reaction of $\text{Fe}(\text{cr})$, $\text{FeBr}_2(\text{cr})$, and $\text{FeCl}_2(\text{cr})$ in (KBr , Br_2) solutions, as well as the enthalpies of solution of $\text{KCl}(\text{cr})$ and $\text{KBr}(\text{cr})$ in the same medium to result in the following summations:

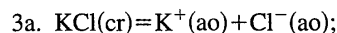


$$\Delta_r H^\circ = -244.737 \pm 0.22 \text{ kJ} \cdot \text{mol}^{-1}$$



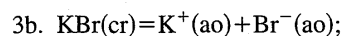
$$\Delta_r H^\circ = -10.032 \pm 0.21 \text{ kJ} \cdot \text{mol}^{-1}$$

Using the following:



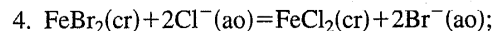
$$\Delta_r H^\circ = 17.245 \pm 0.045 \text{ kJ} \cdot \text{mol}^{-1} [87\text{GAR/PAR}]$$

and



$$\Delta_r H^\circ = 19.75 \pm 0.05 \text{ kJ} \cdot \text{mol}^{-1} [89\text{PAR}]^b$$

we obtain



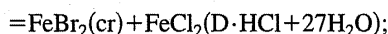
$$\Delta_r H^\circ = -5.032 \pm 0.22 \text{ kJ} \cdot \text{mol}^{-1}.$$

Thus, $\Delta_f H^\circ(\text{FeCl}_2, \text{cr}) - \Delta_f H^\circ(\text{FeBr}_2, \text{cr}) = -96.372 \pm 0.24 \text{ kJ} \cdot \text{mol}^{-1}$, and using $\Delta_r H^\circ(1)$, $\Delta_f H^\circ(\text{FeCl}_2, \text{cr}) = -341.109 \pm 0.22 \text{ kJ} \cdot \text{mol}^{-1}$, in support of 59KOE/COU (Sec. 2.1.1.1). Similar measurements were made by 34HIE/WOE (No. 167) at 273.15 K for $\text{Fe}(\text{cr})$, $\text{Br}_2(\text{l})$ and $\text{FeBr}_2(\text{cr})$ to obtain (corrected to 298.15 K) $\Delta_f H^\circ(\text{FeBr}_2, \text{cr})$ or $\Delta_r H^\circ(1) = -251.44 \pm 5.0 \text{ kJ} \cdot \text{mol}^{-1}$. Since 34HIE/APP (No. 168) measured the enthalpies of solution of $\text{FeCl}_2(\text{cr})$ and $\text{FeBr}_2(\text{cr})$ in 2 mol-dm⁻³ HCl (see 8.2 for all details) we have, in place of the above reaction (2):

^bSelected from sources cited and used by 89COX/WAG in developing the key values for the thermodynamic property values of the ions.

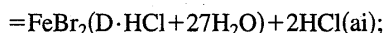
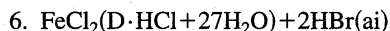
TABLE 1. The enthalpy of formation of $\text{FeCl}_2(\text{cr})$ from the reaction, $\text{FeCl}_2(\text{cr}) + \text{H}_2(\text{g}) = \text{Fe}(\text{cr}) + 2\text{HCl}(\text{g})$

	$\Delta_f H^\circ$, $\text{kJ}\cdot\text{mol}^{-1}$		$-\Delta_f H^\circ$, $\text{kJ}\cdot\text{mol}^{-1}$	
	II	III	II	III
27BAG (No. 82)	164.6 \pm 12	156.93 \pm 3.0	349.2 \pm 12	341.55 \pm 3.0
38SAN (No. 86)	158 \pm 4.0	154.84 \pm 1.7	342.7 \pm 4.0	339.46 \pm 1.7
43WAG/STE (No. 88)		157.10 \pm 1.0		341.72 \pm 1.0
50KAN/PET (No. 83)	155.8 \pm 5.2	159.87 \pm 1.5	340.4 \pm 5.2	344.49 \pm 1.5
52NOV/ORA (No. 84)	137 \pm 10	155.02 \pm 1.6	321.6 \pm 10	339.64 \pm 1.6
60NOV/MAK (No. 85)	134.6 \pm 4.3	158.01 \pm 1.8	319.2 \pm 4.3	342.63 \pm 1.8
This study		157.1 \pm 1.0		341.72 \pm 1.0



$$\Delta_f H^\circ = -4.99 \pm 1.6 \text{ kJ}\cdot\text{mol}^{-1}.$$

An estimate for



$$\Delta_f H^\circ = -1.96 \pm 0.4 \text{ kJ}\cdot\text{mol}^{-1}$$

based on the \bar{L}_2 values for HCl (in $27\text{H}_2\text{O}$) and HBr (in $27\text{H}_2\text{O}$) from 65PAR results in $\Delta_f H^\circ(4) = -3.03 \pm 1.6 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_f H^\circ(\text{FeCl}_2, \text{cr}) - \Delta_f H^\circ(\text{FeBr}_2, \text{cr}) = -94.37 \pm 1.6 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_f H^\circ(\text{FeCl}_2, \text{cr}) = -345.81 \pm 5.3 \text{ kJ}\cdot\text{mol}^{-1}$, in support of 1882THO. It should be pointed out that the $\Delta(\Delta_f H^\circ)$'s from 89EFI/EVD and 89EVD/EFI and the measurements of 34HIE/WOE and 34HIE/APP are in closer agreement than the enthalpies of formation indicate.

2.1.1.3. The high-temperature reduction of $\text{FeCl}_2(\text{cr})$ by $\text{H}_2(\text{g})$

For the reaction: $\text{FeCl}_2(\text{cr}) + \text{H}_2(\text{g}) = \text{Fe}(\text{cr}) + 2\text{HCl}(\text{g})$, 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.

2.1.1.4. Summary

The considered values for $\Delta_f H^\circ(\text{FeCl}_2, \text{cr})/\text{kJ}\cdot\text{mol}^{-1}$ are -341.66 ± 0.25 [59KOE/COU], -341.11 ± 0.22 [89EFI/EVD and 89EVD/EFI] and -341.72 ± 1.0 [see Sec. 2.1.1.3] (we reject from consideration the early 1882THO value of $-345.24 \pm 2.0 \text{ kJ}\cdot\text{mol}^{-1}$) from which we initially select $-341.66 \pm 0.25 \text{ kJ}\cdot\text{mol}^{-1}$ and which we will use in Sec. 2.1.2.

2.1.2. The Standard Enthalpy of Solution of $\text{FeCl}_2(\text{cr})$ in $\text{H}_2\text{O}(\text{l})$, and $\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao})$

For the process: $\text{FeCl}_2(\text{cr}) = \text{Fe}^{2+}(\text{ao}) + 2\text{Cl}^-(\text{ao})$, the measurements lead to the following:

	$\Delta_f H^\circ$, $\text{kJ}\cdot\text{mol}^{-1}$
52LI/GRE (No. 97)	-82.70 ± 0.84
77CER/HEP (No. 96)	-83.05 ± 0.42
82COB/MUR (No. 93)	-82.906 ± 0.32
90EFI/FUR (No. 94)	-83.11 ± 0.42

These values were obtained using ϕ_L obtained from the 82COB/MUR measurements of $\Delta_{\text{sol}} H^\circ$ of $\text{FeCl}_2(\text{cr})$ as a function of molality in the range 0.0002 to $0.011 \text{ mol}\cdot\text{kg}^{-1}$ (total ionic strength 0.01155 to $0.03713 \text{ mol}\cdot\text{kg}^{-1}$) and the direct enthalpies of dilution of a FeCl_2 solution by 79BER/MOR (No. 116) ($m = 4.43 \text{ mol}\cdot\text{kg}^{-1}$) to final solutions in the range 0.0016 to $0.0052 \text{ mol}\cdot\text{kg}^{-1}$ (total ionic strength 0.0049 to $0.0157 \text{ mol}\cdot\text{kg}^{-1}$).

We accept for a "tentative" or working value, $\Delta_{\text{sol}} H^\circ = -83.00 \pm 0.10 \text{ kJ}\cdot\text{mol}^{-1}$. With the initial value $\Delta_f H^\circ(\text{FeCl}_2, \text{cr}) = -341.66 \pm 0.25 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_{\text{sol}} H^\circ = -83.00 \pm 0.10 \text{ kJ}\cdot\text{mol}^{-1}$ we obtain $\Delta_f H^\circ(\text{FeCl}_2, \text{ai}) = -424.66 \pm 0.15 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao}) = -90.50 \pm 0.25 \text{ kJ}\cdot\text{mol}^{-1}$. It is obvious, however, from the spread in values for $\Delta_f H^\circ(\text{FeCl}_2, \text{cr})$: -340.4 ± 2.0 to $-345.24 \pm 2.0 \text{ kJ}\cdot\text{mol}^{-1}$, that the range of values for $\Delta_f H^\circ(\text{Fe}^{2+}, \text{aq})$ is -89.4 to $-94.08 \text{ kJ}\cdot\text{mol}^{-1}$.

In addition, the combination of 89EFI/EVD and 89EVD/EFI for $\Delta_f H^\circ(\text{FeCl}_2, \text{cr})$ ($-341.11 \pm 0.22 \text{ kJ}\cdot\text{mol}^{-1}$) and $\Delta_{\text{sol}} H^\circ$ ($-83.11 \pm 0.10 \text{ kJ}\cdot\text{mol}^{-1}$) from 90EFI/FUR results in a direct path to $\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao}) = -90.06 \pm 0.25 \text{ kJ}\cdot\text{mol}^{-1}$.

2.2. The Bromide System

2.2.1. $\Delta_f H^\circ(\text{FeBr}_2, \text{cr})$

2.2.1.1. Calorimetric measurements of the enthalpies of reaction of $\text{Fe}(\text{cr})$ and $\text{FeBr}_2(\text{cr})$ in aqueous (KBr , Br_2) solutions

In Sec. 2.1.1.2 we obtain two values for $\Delta_f H^\circ(\text{FeBr}_2, \text{cr})$, $-244.74 \pm 0.22 \text{ kJ}\cdot\text{mol}^{-1}$ [89EFI/EVD] and $-251.44 \pm 5.2 \text{ kJ}\cdot\text{mol}^{-1}$ [34HIE/WOE], although the $\Delta_f H^\circ(\text{FeCl}_2, \text{cr}) - \Delta_f H^\circ(\text{FeBr}_2, \text{cr})$'s are in closer agreement, -96.37 ± 0.24 [89EVD/EFI] and $-94.37 \pm 1.6 \text{ kJ}\cdot\text{mol}^{-1}$, respectively.^c We initially select $\Delta_f H^\circ(\text{FeBr}_2, \text{cr}) = -245.00 \pm 0.25 \text{ kJ}\cdot\text{mol}^{-1}$.

2.2.2. The Standard Enthalpy of Solution of $\text{FeBr}_2(\text{cr})$ in $\text{H}_2\text{O}(\text{l})$ and $\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao})$

From AI.b, we have $\Delta_{\text{sol}} H^\circ(\text{FeBr}_2, \text{cr})/\text{kJ}\cdot\text{mol}^{-1} = -86.85 \pm 0.12$ [90EFI/FUR (No. 178)], -86.53 ± 2.0 [52GRE/LI (No. 186)], -85.75 ± 0.6 [65PAO (No. 174)]^d, and -88.3 ± 4.0 [34HIE/APP (No. 170)]^d.

We take for our initial selection $\Delta_{\text{sol}} H^\circ = -86.85 \pm 0.12 \text{ kJ}\cdot\text{mol}^{-1}$, resulting in $\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao}) = -89.03 \pm 0.28 \text{ kJ}\cdot\text{mol}^{-1}$. However, com-

^cOne can also obtain $\Delta_f H^\circ(\text{FeCl}_2, \text{cr}) - \Delta_f H^\circ(\text{FeBr}_2, \text{cr}) = -95.08 \pm 0.5 \text{ kJ}\cdot\text{mol}^{-1}$ from the difference in the standard enthalpies of solution of both salts in H_2O (-83.11 and $-86.85 \text{ kJ}\cdot\text{mol}^{-1}$, respectively) [90EFI/FUR (Nos. 94 and 178)] and the difference in the $\Delta_f H^\circ$'s of the $\text{Cl}^-(\text{ao})$ and $\text{Br}^-(\text{ao})$.

^dUsing estimated ϕ_L values based on $\phi_{L(\text{D-H})}$ and the behavior of other bivalent-univalent halides [82WAG/EVA].

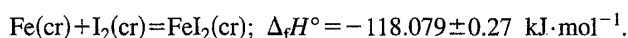
plete consistency with the 89EFI/EVD and 90EFI/FUR values for $\Delta_f H^\circ(\text{FeBr}_2, \text{cr})$ and $\Delta_{\text{sol}} H^\circ$ [90EFI/FUR] results in $-88.77 \pm 0.30 \text{ kJ} \cdot \text{mol}^{-1}$ for $\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao})$.

2.3. The Iodide System

2.3.1. $\Delta_f H^\circ(\text{FeI}_2, \text{cr})$

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

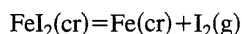
The measurements of 90EFI/EVD and 89EFI/EVD (No. 194) on the $\Delta_{\text{sol}} H$ of all three components in aqueous KBr, Br₂ solutions lead to:



From the results of 34HIE/WOE (No. 198), we obtain $\Delta_f H^\circ = -125.9 \pm 5.0 \text{ kJ} \cdot \text{mol}^{-1}$.

2.3.1.2. *Decomposition of FeI₂(cr)*

The measurements of 66ZAI/GRE (No. 196) on the decomposition pressure of FeI₂(cr) lead to a third law $\Delta H^\circ = 166.1 \pm 5.0 \text{ kJ} \cdot \text{mol}^{-1}$ for



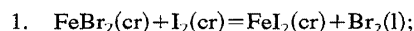
and $\Delta_f H^\circ = -103.7 \pm 5.1 \text{ kJ} \cdot \text{mol}^{-1}$.

The measurements of 56SCH/ORR (No. 197) on the decomposition of FeI₂(l) yield widely different values, a second law $\Delta H^\circ = 193.9 \pm 20 \text{ kJ} \cdot \text{mol}^{-1}$ and a third law $\Delta H^\circ = 149.4 \text{ kJ} \cdot \text{mol}^{-1}$ which result in $\Delta_f H^\circ = -131$ and $-87 \text{ kJ} \cdot \text{mol}^{-1}$, respectively.

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

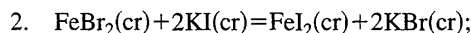
2.3.1.3. $\Delta_f H^\circ(\text{FeI}_2, \text{cr}) - \Delta_f H^\circ(\text{FeBr}_2, \text{cr})$ and $\Delta_f H^\circ(\text{FeI}_2, \text{cr})$

The measurements of 89EFI/EVD (Nos. 165 and 194) and 90EFI/EVD (No. 195) on the $\Delta_{\text{sol}} H$ of all components in aqueous KBr, Br₂, lead to:



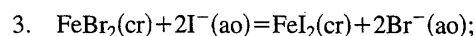
$$\Delta_f H^\circ = 126.658 \pm 0.24 \text{ kJ} \cdot \text{mol}^{-1},$$

and



$$\Delta_f H^\circ = -1.677 \pm 0.19 \text{ kJ} \cdot \text{mol}^{-1}.$$

Reaction (1) yields $\Delta_f H^\circ(\text{FeI}_2, \text{cr}) - \Delta_f H^\circ(\text{FeBr}_2, \text{cr}) = 126.658 \pm 0.24 \text{ kJ} \cdot \text{mol}^{-1}$. Since $\Delta_{\text{sol}} H^\circ(\text{KBr}, \text{cr}) = 19.75 \pm 0.05 \text{ kJ} \cdot \text{mol}^{-1}$ ^e and $\Delta_{\text{sol}} H^\circ(\text{KI}, \text{cr}) = 20.28 \pm 0.10 \text{ kJ} \cdot \text{mol}^{-1}$ ^e, we can obtain from reaction (2)



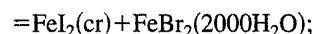
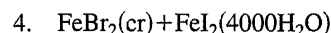
$$\Delta H^\circ = -2.74 \pm 0.30 \text{ kJ} \cdot \text{mol}^{-1} \text{ and } \Delta(\Delta_f H^\circ)$$

$$= 126.52 \pm 0.30 \text{ kJ} \cdot \text{mol}^{-1}.$$

Earlier, we obtained from 34HIE/WOE's similar measurements in (KBr, Br₂) solutions $\Delta_f H^\circ(\text{FeBr}_2, \text{cr}) = -251.44 \text{ kJ} \cdot \text{mol}^{-1}$ so that $\Delta(\Delta_f H^\circ) = 125.54 \text{ kJ} \cdot \text{mol}^{-1}$.

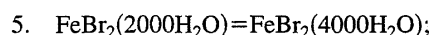
We can also obtain from the results of 34HIE/APP on the $\Delta_{\text{sol}} H^\circ(\text{FeBr}_2, \text{cr})$ and $\Delta_{\text{sol}} H^\circ(\text{FeI}_2, \text{cr})$ in 2 mol·dm⁻³ HCl (see AI.b, Nos. 168 and 199 for details) $\Delta H^\circ = 1.49 \text{ kJ} \cdot \text{mol}^{-1}$ for reaction (3) leading to $\Delta(\Delta_f H^\circ) = 130.75 \text{ kJ} \cdot \text{mol}^{-1}$.

The measurements on the $\Delta_{\text{sol}} H$ of FeBr₂(cr) in 2000H₂O(l) [65PAO (No. 174)] and on FeI₂(cr) in 4000H₂O(l) [65PAO/SAB (No. 201)] may be combined such that:



$$\Delta H = -2.93 \pm 0.56 \text{ kJ} \cdot \text{mol}^{-1}.$$

Estimating (AI.b, No. 176)



$$\Delta H = -0.20 \pm 0.20 \text{ kJ} \cdot \text{mol}^{-1},$$

and assuming correction to standard conditions is essentially the same for FeBr₂(4000H₂O) and FeI₂, we obtain $\Delta H^\circ(3) = -3.13 \pm 0.6 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta(\Delta_f H^\circ) = 126.13 \pm 0.6 \text{ kJ} \cdot \text{mol}^{-1}$.

The $\Delta(\Delta_f H^\circ)$'s are in good agreement, and using $\Delta(\Delta_f H^\circ) = 126.5 \pm 0.3 \text{ kJ} \cdot \text{mol}^{-1}$ and our tentative $\Delta_f H^\circ(\text{FeBr}_2, \text{cr}) = -245.00 \pm 0.25 \text{ kJ} \cdot \text{mol}^{-1}$, we obtain $-118.5 \pm 0.4 \text{ kJ} \cdot \text{mol}^{-1}$ for $\Delta_f H^\circ(\text{FeI}_2, \text{cr})$, in agreement with the direct determination $-118.08 \pm 0.27 \text{ kJ} \cdot \text{mol}^{-1}$ from 90EFI/EVD and 89EFI/EVD. We tentatively select $-118.5 \pm 0.4 \text{ kJ} \cdot \text{mol}^{-1}$.

2.3.2. The Standard Enthalpy of Solution of FeI₂(cr) in H₂O(l) and $\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao})$

The enthalpy of solution has been measured by 65PAO/SAB (No. 201) (in 4000H₂O) as $-81.42 \pm 0.25 \text{ kJ} \cdot \text{mol}^{-1}$. With an estimate for $\phi_L = 1.2 \pm 0.5 \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_{\text{sol}} H^\circ$ becomes $-82.62 \pm 0.6 \text{ kJ} \cdot \text{mol}^{-1}$ and with our "tentative" $\Delta_f H^\circ(\text{FeI}_2, \text{cr}) = -118.5 \pm 0.40 \text{ kJ} \cdot \text{mol}^{-1}$, we obtain $\Delta_f H^\circ(\text{FeI}_2, \text{ai}) = -201.12 \pm 0.72 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao}) = -87.56 \pm 0.8 \text{ kJ} \cdot \text{mol}^{-1}$. (If we use $\Delta_f H^\circ(\text{FeI}_2, \text{cr}) = -118.08 \pm 0.27$ with the above $\Delta_{\text{sol}} H^\circ$, $\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao}) = -87.14 \pm 0.7 \text{ kJ} \cdot \text{mol}^{-1}$.)

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

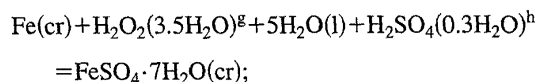
^eFrom their $\Delta_f H^\circ(\text{FeBr}_2, \text{cr}) - \Delta_f H^\circ(\text{FeCl}_2, \text{cr}) = 96.37 \pm 0.24 \text{ kJ} \cdot \text{mol}^{-1}$ one can obtain $\Delta_f H^\circ(\text{FeI}_2, \text{cr}) - \Delta_f H^\circ(\text{FeCl}_2, \text{cr}) = 222.97 \pm 0.31 \text{ kJ} \cdot \text{mol}^{-1}$. This relationship is equally important in the final smoothing process.

^eSelected 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

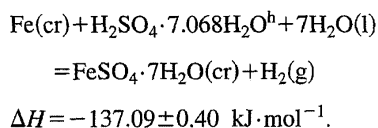
2.4.1. $\Delta_f H^\circ(\text{FeSO}_4 \cdot 7\text{H}_2\text{O}, \text{cr})$

The catalog entry in AI.b from 85VAS/DMI2 (No. 221) lists the following composite reaction from oxidation by H_2O_2 in HClO_4 solutions:



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

The resultant $\Delta_f H^\circ$ is $-3013.66 \pm 0.5 \text{ kJ} \cdot \text{mol}^{-1}$. 63ADA/KEL (No. 211) measured the enthalpy of reaction of $\text{Fe}(\text{cr})$ and the $\Delta_{\text{sol}} H^\circ$ of the heptahydrate in $\text{H}_2\text{SO}_4 \cdot 7.068\text{H}_2\text{O}$ such that

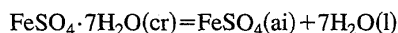


The resultant $\Delta_f H^\circ$ is $-3014.47 \pm 0.45 \text{ kJ} \cdot \text{mol}^{-1}$. The measurements are in excellent agreement with one another; an average value of $-3014.06 \pm 0.40 \text{ kJ} \cdot \text{mol}^{-1}$ shall be used for $\Delta_f H^\circ(\text{FeSO}_4 \cdot 7\text{H}_2\text{O}, \text{cr})$ in the following section.

2.4.1.1. Enthalpy of solution of the heptahydrate and $\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao})$

2.4.1.1.1. Enthalpy of solution in H_2O

The process of interest is:



The early measurements of 68LAR/CER (No. 229) and 68LAR are given as $\Delta_f H^\circ = 11.80 \pm 0.42 \text{ kJ} \cdot \text{mol}^{-1}$ (see catalog entry for details). This value includes estimates for ϕ_L , based on $\phi_L(\text{NiSO}_4)$. The recent measurements of 83DMI (No. 227) on $\Delta_{\text{sol}} H^\circ$, as a function of m enable one to obtain ϕ_L in $\text{FeSO}_4(\text{aq})$ and to recorrect; although the $\phi_L(\text{FeSO}_4)$ values differ from those contained in 68LAR/CER, the average value for $\Delta_{\text{sol}} H^\circ$ remains essentially the same. The resultant value for $\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao}) = -92.11 \pm 0.50 \text{ kJ} \cdot \text{mol}^{-1}$.

The more recent measurements of 83DMI (No. 227) have been extrapolated by us to obtain at $I=0$ $\Delta H^\circ = 12.90 \pm 0.10 \text{ kJ} \cdot \text{mol}^{-1}$ for the solution process. Dependence on ionic strength is described by the equation: $(\Delta_f H^\circ - \Delta H^\circ_{(D-H)})/\text{kJ} \cdot \text{mol}^{-1} = (12.90 \pm 0.10) + (35.57 \pm 2.37)(I/\text{mol} \cdot \text{kg}^{-1})$.

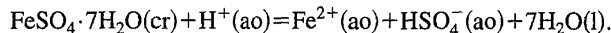
The calculated $\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao}) = -91.01 \pm 0.20 \text{ kJ} \cdot \text{mol}^{-1}$ using our working value for $\Delta_f H^\circ(\text{FeSO}_4 \cdot 7\text{H}_2\text{O}, \text{cr}) = -3014.06 \pm 0.40 \text{ kJ} \cdot \text{mol}^{-1}$. However the measurements by 83DMI are meant to be part of a cycle; hence, they may be used directly to obtain $\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao}) = -90.61 \pm 0.20 \text{ kJ} \cdot \text{mol}^{-1}$ from $\Delta_f H^\circ(\text{FeSO}_4 \cdot 7\text{H}_2\text{O}, \text{cr}) = -3013.66 \pm 0.5$ and $\Delta_{\text{sol}} H^\circ = 12.90 \pm 0.10 \text{ kJ} \cdot \text{mol}^{-1}$.

^g $\Delta_f H^\circ(\text{H}_2\text{O}_2 \cdot 3.5\text{H}_2\text{O})$ from 82WAG/EVA.

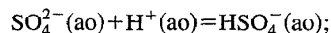
^h89PAR calculations provide $\Delta_f H^\circ(\text{H}_2\text{SO}_4 \cdot 0.3 \text{H}_2\text{O})$ and $\Delta_f H^\circ(\text{H}_2\text{SO}_4 \cdot 7.068 \text{H}_2\text{O}) = -823.752$ and $-876.568 \text{ kJ} \cdot \text{mol}^{-1}$, respectively, as values compatible with CODATA Key Values.

2.4.1.1.2. Measurements in HClO_4

Measurements were also made of the solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{cr})$ in 2, 3, and 4 $\text{mol} \cdot \text{dm}^{-3}$ HClO_4 solutions [83DMI (No. 223), 85VAS/DMI (No. 222)]. In these acidic solutions the reaction is predominantly:



Correction for residual $\text{SO}_4^{2-}(\text{ao})$ at each concentration has been made using 89COX/WAG:



$$\Delta H^\circ = -22.44 \pm 1.0 \text{ kJ} \cdot \text{mol}^{-1}.$$

The data contained in 83DMI are sufficiently detailed, in giving the varying concentrations of $\text{FeSO}_4(\text{aq})$ at each concentration of HClO_4 , 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 $m^{1/2}$ at fixed concentrations of HClO_4 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:

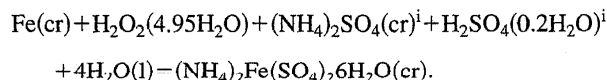
$$(\Delta_f H^\circ - \Delta H^\circ_{(D-H)})/\text{kJ} \cdot \text{mol}^{-1} \\ = (35.50 \pm 0.10) + (2.29 \pm 0.02)(I/\text{mol} \cdot \text{kg}^{-1}),$$

$$(\Delta_f H^\circ - \Delta H^\circ_{(D-H)})/\text{kJ} \cdot \text{mol}^{-1} \\ = (35.30 \pm 0.55) + (2.42 \pm 0.15)(I/\text{mol} \cdot \text{kg}^{-1}).$$

We accept the first equation. We then obtain with $\Delta_f H^\circ(\text{FeSO}_4 \cdot 7\text{H}_2\text{O}, \text{cr}) = -3014.06 \pm 0.40 \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao}) = -90.85 \pm 0.41 \text{ kJ} \cdot \text{mol}^{-1}$. Alternatively, using only 83DMI's value for consistency with his cycle, $\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao}) = -90.45 \pm 0.30 \text{ kJ} \cdot \text{mol}^{-1}$. (From the second equation, $\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao}) = -91.05 \pm 0.68$ and $-90.65 \pm 0.62 \text{ kJ} \cdot \text{mol}^{-1}$, respectively.)

2.4.2. $\Delta_f H^\circ((\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}, \text{cr})$ —Mohr's Salt

The value for $\Delta_f H^\circ$ is obtained from a series of measurements by 83DMI (No. 228), 78VAS/VAS (No. 225) of all components in 1, 2, 3, 4 $\text{mol} \cdot \text{dm}^{-3}$ HClO_4 solutions containing 1% or 1.5% H_2O_2 . The composite reaction is:



The individual values are:

ⁱ89PAR calculations provide $\Delta_f H^\circ(\text{H}_2\text{SO}_4, 0.20\text{H}_2\text{O}) = -820.668 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_f H^\circ((\text{NH}_4)_2\text{SO}_4, \text{cr}) = -1182.30 \text{ kJ} \cdot \text{mol}^{-1}$ as values compatible with the CODATA Key Values [89COX/WAG].

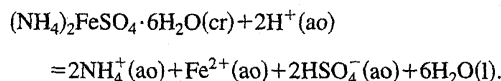
HClO_4 $\text{mol} \cdot \text{dm}^{-3}$	$\frac{\Delta H}{\text{kJ} \cdot \text{mol}^{-1}}$	
	1% H_2O_2	1.5 H_2O_2
1	-574.20 ± 1.15	-576.06 ± 0.73
2	-578.75 ± 0.65	-579.49 ± 0.56
3	-579.96 ± 0.89	-579.72 ± 0.78
4	-580.58 ± 0.92	-580.72 ± 0.96

The average value, $\Delta H = -579.68 \pm 0.44 \text{ kJ} \cdot \text{mol}^{-1}$, excludes the values in $1 \text{ mol} \cdot \text{dm}^{-3} \text{ HClO}_4$. The calculated $\Delta_f H^\circ = -3920.00 \pm 1.0 \text{ kJ} \cdot \text{mol}^{-1}$.

2.4.2.1. The standard enthalpy of solution of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}(\text{cr})$ and $\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao})$

2.4.2.1.1. Measurements in HClO_4

Measurements were also made by 83DMI (No. 226) on the enthalpy of solution of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}(\text{cr})$ in 2, 3 and $4 \text{ mol} \cdot \text{dm}^{-3} \text{ HClO}_4$. As for the measurements on $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{cr})$ the process is primarily:



Correction for the residual $\text{SO}_4^{2-}(\text{ao})$ 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 $m^{1/2}$ at fixed concentrations of HClO_4 and after that the calculation of the enthalpy of solution at $I=0$ of the solution.

Calculations using the first method give:

$$\begin{aligned} &(\Delta_f H_{(I)} - \Delta_f H_{(I-H)}^\circ) / (\text{kJ} \cdot \text{mol}^{-1}) \\ &= (69.47 \pm 0.18) + (0.31 \pm 0.05)(I / \text{mol} \cdot \text{kg}^{-1}). \end{aligned}$$

The second method gives

$$\begin{aligned} &(\Delta_f H_{(I)} - \Delta_f H_{(I-H)}^\circ) / (\text{kJ} \cdot \text{mol}^{-1}) \\ &= (68.4 \pm 1.1) + (0.2 \pm 0.3)(I / \text{mol} \cdot \text{kg}^{-1}). \end{aligned}$$

Adopting $69.40 \pm 0.20 \text{ kJ} \cdot \text{mol}^{-1}$ for the solution of Mohr's salt results in $\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao}) = -95.30 \pm 1.0 \text{ kJ} \cdot \text{mol}^{-1}$.

2.5. The Tentative Selected Parameters

Table 2. Summarizes the values for $\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao})$.

TABLE 2. The values for $\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao})$

	$\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao})$ $\text{kJ} \cdot \text{mol}^{-1}$
Section 2.1.2	
$\Delta_f H^\circ(\text{FeCl}_2, \text{cr}) = -341.66 \pm 0.25 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_{\text{sol}} H^\circ = -83.00 \pm 0.10 \text{ kJ} \cdot \text{mol}^{-1}$	-90.50 ± 0.25
Consistent Cycle,	
$\Delta_f H^\circ(\text{FeCl}_2, \text{cr}) = -341.11 \pm 0.22 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_{\text{sol}} H^\circ = -83.11 \pm 0.10 \text{ kJ} \cdot \text{mol}^{-1}$	-90.06 ± 0.25
Section 2.2.2	
$\Delta_f H^\circ(\text{FeBr}_2, \text{cr}) = -245.00 \pm 0.25 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_{\text{sol}} H^\circ = -86.85 \pm 0.12 \text{ kJ} \cdot \text{mol}^{-1}$	-89.03 ± 0.32
Consistent cycle,	
$\Delta_f H^\circ(\text{FeBr}_2, \text{cr}) = -244.74 \pm 0.22 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_{\text{sol}} H^\circ = -86.85 \pm 0.12 \text{ kJ} \cdot \text{mol}^{-1}$	-88.77 ± 0.30
Section 2.3.2	
From $\Delta_f H^\circ(\text{FeI}_2, \text{cr}) - \Delta_f H^\circ(\text{FeBr}_2, \text{cr})$ $= 126.5 \pm 0.30 \text{ kJ} \cdot \text{mol}^{-1}$, the "tentative" $\Delta_f H^\circ(\text{FeBr}_2, \text{cr}) = -245.00 \pm 0.25 \text{ kJ} \cdot \text{mol}^{-1}$, and $\Delta_{\text{sol}} H^\circ = -82.62 \pm 0.6 \text{ kJ} \cdot \text{mol}^{-1}$	-87.56 ± 0.72
$\Delta_f H^\circ(\text{FeI}_2, \text{cr}) = -118.08 \pm 0.27 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_{\text{sol}} H^\circ = -82.62 \pm 0.6 \text{ kJ} \cdot \text{mol}^{-1}$	-87.14 ± 0.66
Sections 2.4.1.1.1 and 2.4.1.1.2	
$\Delta_f H^\circ(\text{FeSO}_4 \cdot 7\text{H}_2\text{O}, \text{cr}) = -3014.06 \pm 0.40 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_{\text{sol}} H^\circ = +12.90 \pm 0.10 \text{ kJ} \cdot \text{mol}^{-1}$ (to $\text{SO}_4^{2-}(\text{ao})$) or $\Delta_{\text{sol}} H^\circ = 35.50 \pm 0.10 \text{ kJ} \cdot \text{mol}^{-1}$ (to $\text{HSO}_4^-(\text{ao})$)	-91.01 ± 0.20 -90.85 ± 0.41
$\Delta_f H^\circ(\text{FeSO}_4 \cdot 7\text{H}_2\text{O}, \text{cr}) = -3013.66 \pm 0.50 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_{\text{sol}} H^\circ = +12.90 \pm 0.10 \text{ kJ} \cdot \text{mol}^{-1}$ (to $\text{SO}_4^{2-}(\text{ao})$) or $35.50 \pm 0.10 \text{ kJ} \cdot \text{mol}^{-1}$ (to $\text{HSO}_4^-(\text{ao})$)	-90.61 ± 0.20 -90.45 ± 0.30
Section 2.4.2.1	
$\Delta_f H^\circ((\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}, \text{cr})$ $= 3920.0 \pm 1.0 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_{\text{sol}} H^\circ$ $= 69.40 \pm 0.20 \text{ kJ} \cdot \text{mol}^{-1}$ (to $\text{HSO}_4^-(\text{ao})$)	-95.30 ± 1.0
Tentative Selected Value	-90.00 ± 0.5

The tabulated values indicate good agreement from the $\text{FeCl}_2(\text{cr})$, $\text{FeBr}_2(\text{cr})$, and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{cr})$ systems for $\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao})$. We select $\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao}) = -90.00 \pm 0.5 \text{ kJ} \cdot \text{mol}^{-1}$ as our "tentative" value. As a result of this, some modifications must be made in the previous selections for $\Delta_f H^\circ(\text{FeCl}_2, \text{cr})$, $\Delta_f H^\circ(\text{FeBr}_2, \text{cr})$, $\Delta_f H^\circ(\text{FeI}_2, \text{cr})$, and $\Delta_f H^\circ(\text{FeSO}_4 \cdot 7\text{H}_2\text{O}, \text{cr})$. These changes from the initial se-

lections are given below. With the exception of the $\Delta_f H^\circ(\text{FeSO}_4 \cdot 7\text{H}_2\text{O}, \text{cr})$ and its $\Delta_{\text{sol}} H^\circ$, these adjusted values will become our final recommended values.

	Initial Selections $\Delta_f H^\circ$ $\text{kJ} \cdot \text{mol}^{-1}$	Adjusted Tentative Values $\Delta_f H^\circ$ $\text{kJ} \cdot \text{mol}^{-1}$
$\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao})$	-90.00 ± 0.5	
$\Delta_{\text{sol}} H^\circ(\text{FeCl}_2, \text{cr})$	-83.00 ± 0.14 (Sec. 2.1.2)	
$\Delta_f H^\circ(\text{FeCl}_2, \text{cr})$	-341.66 ± 0.60 (Sec. 2.1.1.4)	-341.16 ± 0.60
$\Delta_{\text{sol}} H^\circ(\text{FeSO}_4 \cdot 7\text{H}_2\text{O}, \text{cr})$	$+12.90 \pm 0.10$ (Sec. 2.4.1.1.1)	$+12.90 \pm 0.10$
$\Delta_f H^\circ(\text{FeSO}_4 \cdot 7\text{H}_2\text{O}, \text{cr})$	-3014.06 ± 0.40 (Sec. 2.4.1)	-3013.05 ± 0.65
$\Delta_f H^\circ(\text{FeBr}_2, \text{cr})$	-245.0 ± 0.25 (Sec. 2.2.1)	-245.7 ± 0.7
$\Delta_f H^\circ(\text{FeI}_2, \text{cr})$	-118.5 ± 0.4 (Sec. 2.3.1.3)	-118.7 ± 0.8

3. The Evaluation of the Enthalpy of Formation of the Aqueous Ion Fe^{3+} , $\Delta_f H^\circ(\text{Fe}^{3+}, \text{ao})$

The $\Delta_f H^\circ(\text{Fe}^{3+}, \text{ao})$ is evaluated. We begin with:

- (1) the determinations for $\Delta_f H^\circ(\text{FeCl}_3, \text{cr})$, those independent of other Fe compounds as well as those linked to $\text{FeCl}_2(\text{cr})$, combined with a selection for $\Delta_{\text{sol}} H^\circ(\text{FeCl}_3, \text{cr})$ which in itself requires a working value.
- (2) the direct determination of $\Delta_f H^\circ(\text{Fe}^{3+}, \text{ao})$ through oxidation of $\text{Fe}(\text{cr})$.
- (3) the enthalpy of formation relationship between $\text{Fe}^{3+}(\text{ao})$ and $\text{Fe}^{2+}(\text{ao})$.

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

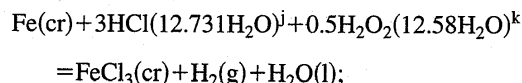
3.1. The Chloride System

3.1.1. $\Delta_f H^\circ(\text{FeCl}_3, \text{cr})$

3.1.1.1. Solution calorimetry with aqueous H_2O_2

59KOE/COU (No. 124) have also measured the enthalpy of oxidation of the FeCl_2 solution formed from the reaction of $\text{Fe}(\text{cr})$ with $4.36 \text{ mol} \cdot \text{kg}^{-1}$ HCl by H_2O_2 (see reaction No. 90 and Sec. 2.1.1) and also the enthalpy of solution of $\text{FeCl}_3(\text{cr})$ in the same molality of HCl (see catalog entry).

The composite reaction and its $\Delta_r H$ are:

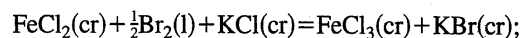


$$\Delta_r H = -102.59 \pm 0.30 \text{ kJ} \cdot \text{mol}^{-1}$$

from which $\Delta_f H^\circ(\text{FeCl}_3, \text{cr}) = -399.24 \pm 0.35 \text{ kJ} \cdot \text{mol}^{-1}$.

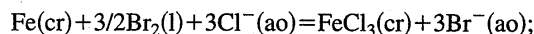
3.1.1.2. Solution calorimetry with aqueous (KBr , Br_2)

89EVD/EFI (No. 127) have measured the enthalpy of reaction of $\text{FeCl}_3(\text{cr})$ with aqueous (KBr , Br_2) solutions. Rearranging the reaction listed in A.I.b:



$$\Delta H^\circ = -11.386 \pm 0.18 \text{ kJ} \cdot \text{mol}^{-1}$$

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

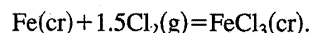


$$\Delta H^\circ = -258.65 \pm 0.40 \text{ kJ} \cdot \text{mol}^{-1}$$

and $\Delta_f H^\circ(\text{FeCl}_3, \text{cr}) = -395.66 \pm 0.40 \text{ kJ} \cdot \text{mol}^{-1}$.

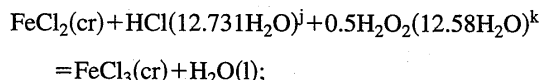
3.1.1.3 Bomb combustion

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



3.1.2. The Relationship Between $\Delta_f H^\circ(\text{FeCl}_3, \text{cr})$ and $\Delta_f H^\circ(\text{FeCl}_2, \text{cr})$

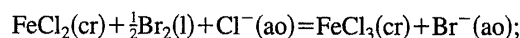
The measurements of 59KOE/COU leading to $\Delta_f H^\circ(\text{FeCl}_2, \text{cr})$ (No. 90) and $\Delta_f H^\circ(\text{FeCl}_3, \text{cr})$ (No. 124) may also be rearranged so that:



$$\Delta H = -85.55 \pm 0.21 \text{ kJ} \cdot \text{mol}^{-1}$$

resulting in $\Delta_f H^\circ(\text{FeCl}_3, \text{cr}) - \Delta_f H^\circ(\text{FeCl}_2, \text{cr}) = -57.58 \pm 0.25 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_f H^\circ(\text{FeCl}_3, \text{cr}) = -399.30 \pm 0.35 \text{ kJ} \cdot \text{mol}^{-1}$.

For the reaction given in 3.1.1.2 [89EVD/EFI] and the $\Delta_{\text{sol}} H^\circ$'s for $\text{KCl}(\text{cr})$ and $\text{KBr}(\text{cr})$, cited in 2.1.1.2, we have:



$$\Delta H^\circ = -8.881 \pm 0.19 \text{ kJ} \cdot \text{mol}^{-1}$$

from which we obtain $\Delta_f H^\circ(\text{FeCl}_3, \text{cr}) - \Delta_f H^\circ(\text{FeCl}_2, \text{cr}) = -54.55 \pm 0.20 \text{ kJ} \cdot \text{mol}^{-1}$

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

	$\Delta H^\circ, \text{kJ} \cdot \text{mol}^{-1}$
25MAI (No. 129)	53.51 ± 1.8
50KAN/PET (No. 130)	52.49 ± 1.2
53SCH/OEN (No. 131)	54.27 ± 0.75
58WIL/GRE (No. 132)	54.38 ± 0.75

It is obvious that the mean enthalpy of decomposition, $\sim 53.9 \pm 0.70 \text{ kJ} \cdot \text{mol}^{-1}$ from the vapor pressure measure-

^j ϕL from 65PAR.

^k $\Delta_f H^\circ$ from 82WAG/EVA.

ments (all in good agreement with one another) disagrees with the calorimetrically determined $\Delta(\Delta_f H^\circ) = 57.58 \pm 0.25 \text{ kJ} \cdot \text{mol}^{-1}$ from 59KOE/COU but agrees with that derived from 89EVD/EFI, $54.55 \pm 0.20 \text{ kJ} \cdot \text{mol}^{-1}$. From the $\Delta(\Delta_f H^\circ) = 53.9 \text{ kJ} \cdot \text{mol}^{-1}$ we obtain $\Delta_f H^\circ(\text{FeCl}_3, \text{cr}) = -395.16 \pm 0.75 \text{ kJ} \cdot \text{mol}^{-1}$; from the 89EVD/EFI $\Delta(\Delta_f H^\circ) = 54.55 \pm 0.20 \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_f H^\circ(\text{FeCl}_3, \text{cr}) = -395.71 \pm 0.54 \text{ kJ} \cdot \text{mol}^{-1}$ ($-395.66 \pm 0.40 \text{ kJ} \cdot \text{mol}^{-1}$ from 89EVD/EFI's consistent cycle) which supports the direct chlorination enthalpy measured by 82LAV/TIM, 84LAV/TIM, as $-396.02 \pm 0.14 \text{ kJ} \cdot \text{mol}^{-1}$ which is our initial working value that we shall use in the following section.

3.1.3. The Standard Enthalpy of Solution of $\text{FeCl}_3(\text{cr})$ and the Derived $\Delta_f H^\circ(\text{Fe}^{3+}, \text{ao})$

There are some measurements of the enthalpy of solution of $\text{FeCl}_3(\text{cr})$ 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 $I=0$.

In addition, 52LI/GRE and 85SOL/MON have measured the enthalpy of solution in H_2O (No. 133). The values have been corrected for the formation of complexes, $\text{FeOH}^{2+}(\text{ao})$ and $\text{FeCl}^{2+}(\text{ao})$.

The two approaches lead to:

$$\text{FeCl}_3(\text{cr}) = \text{FeCl}_3(\text{ai}), \Delta H^\circ = -146.5 \pm 3.0 \text{ kJ} \cdot \text{mol}^{-1}$$

from the measurements in HCl and

$$\text{FeCl}_3(\text{cr}) = \text{FeCl}_3(\text{ai}), \Delta H^\circ = -158.99 \pm 0.84 \text{ kJ} \cdot \text{mol}^{-1}$$

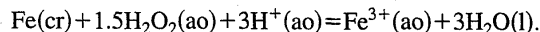
from the measurements in H_2O . The resultant $\Delta_f H^\circ(\text{FeCl}_3, \text{ai})$ values are -542.52 ± 3.1 and $-555.01 \pm 0.85 \text{ kJ} \cdot \text{mol}^{-1}$, respectively and $\Delta_f H^\circ(\text{Fe}^{3+}, \text{ao}) = -41.3 \pm 3.1 \text{ kJ} \cdot \text{mol}^{-1}$ and $-53.79 \pm 0.85 \text{ kJ} \cdot \text{mol}^{-1}$, respectively. (A different selection for $\Delta_f H^\circ(\text{FeCl}_3, \text{cr})$, e.g. -399.24 kJ from 59KOE/COU would result in $\Delta_f H^\circ(\text{Fe}^{3+}, \text{ao}) = -44.55$ and $-56.01 \text{ kJ} \cdot \text{mol}^{-1}$).

The measurements of 90EFI/FUR (Nos. 142–144) on the enthalpy of solution of $\text{FeCl}_3(\text{cr})$ in $\text{HClO}_4(\text{aq})$ as a function of concentration of HClO_4 , extrapolated to $I=0$ result in $\Delta_{\text{sol}} H^\circ = -156.58 \pm 1.2 \text{ kJ} \cdot \text{mol}^{-1}$ (No. 141) and this results in $\Delta_f H^\circ(\text{Fe}^{3+}, \text{ao}) = 51.36 \pm 1.2 \text{ kJ} \cdot \text{mol}^{-1}$, using our initial tentative selection of $-396.02 \pm 0.14 \text{ kJ} \cdot \text{mol}^{-1}$ for $\Delta_f H^\circ(\text{FeCl}_3, \text{cr})$.

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

3.2. The Direct Determination of $\Delta_f H^\circ(\text{Fe}^{3+}, \text{ao})$

The measurements of 76VAS/RAS (No. 8) on the oxidation of $\text{Fe}(\text{cr})$ by aqueous solutions of H_2O_2 in varying concentrations of HClO_4 are applicable



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 two stage approach: extrapolation to infinite dilution against $m(\text{Fe}^{3+}, \text{aq})^{1/2}$, and then extrapolation to $I=0$ of solution.

According to the first method

$$\begin{aligned} &(\Delta_f H^\circ(I) - \Delta_f H^\circ(D-H)) / \text{kJ} \cdot \text{mol}^{-1} \\ &= (-617.21 \pm 0.31) - (1.84 \pm 0.10)(I / \text{mol} \cdot \text{kg}^{-1}) \end{aligned}$$

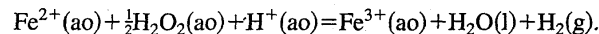
and to the second method

$$\begin{aligned} &(\Delta_f H^\circ(I) - \Delta_f H^\circ(D-H)) / \text{kJ} \cdot \text{mol}^{-1} \\ &= (-617.33 \pm 0.35) - (1.83 \pm 0.11)(I / \text{mol} \cdot \text{kg}^{-1}). \end{aligned}$$

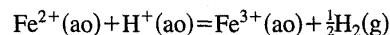
Both methods of extrapolation gave the same results and adopting the first mentioned equation $\Delta H^\circ = -617.21 \pm 0.31 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_f H^\circ(\text{Fe}^{3+}, \text{ao}) = -46.48 \pm 0.32 \text{ kJ} \cdot \text{mol}^{-1}$.

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

Appendix AI.b contains three calorimetric measurements of the oxidation of $\text{Fe}^{2+}(\text{aq})$ by H_2O_2 . The skeleton reaction is

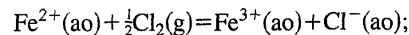


The measurements are all in dilute solutions. The measurements, the $\Delta_f H^\circ$'s and the calculated $\Delta_f H^\circ(\text{Fe}^{3+}, \text{ao}) - \Delta_f H^\circ(\text{Fe}^{2+}, \text{ao})$ are tabulated (Table 3). Also tabulated are the $\Delta(\Delta_f H^\circ)$'s derived from the c.m.f.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



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

From Sec. 3.1.2 we have $\Delta_f H^\circ(\text{FeCl}_3, \text{cr}) - \Delta_f H^\circ(\text{FeCl}_2, \text{cr}) = -54.55 \pm 0.20 \text{ kJ} \cdot \text{mol}^{-1}$ from 89EVD/EFI. With the 90EFI/FUR (Nos. 94, 141) measurements of $\Delta_{\text{sol}} H^\circ$ for $\text{FeCl}_3(\text{cr})$ and $\text{FeCl}_2(\text{cr})$ in HClO_4 (-156.58 ± 1.2 and $-83.11 \pm 0.42 \text{ kJ} \cdot \text{mol}^{-1}$, respectively) we obtain



$$\Delta H^\circ = -128.02 \pm 1.3 \text{ kJ} \cdot \text{mol}^{-1}$$

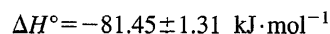
and

$$\Delta_f H^\circ(\text{Fe}^{3+}, \text{ao}) - \Delta_f H^\circ(\text{Fe}^{2+}, \text{ao}) = 39.06 \pm 1.3 \text{ kJ} \cdot \text{mol}^{-1}.$$

Similarly from the reaction catalog from the measurements by 89EFI/EDV (No. 184) we have $\Delta_f H^\circ(\text{FeBr}_3, \text{cr}) - \Delta_f H^\circ(\text{FeBr}_2, \text{cr}) = -17.90 \pm 0.14 \text{ kJ} \cdot \text{mol}^{-1}$, which we may combine with the $\Delta_{\text{sol}} H^\circ$'s for $\text{FeBr}_3(\text{cr})$ and $\text{FeBr}_2(\text{cr})$ (-150.4 ± 1.3 (No. 178) and $-86.85 \pm 0.12 \text{ kJ} \cdot \text{mol}^{-1}$ (No. 190), respectively) to obtain

	$\Delta_f H^\circ$ kJ·mol ⁻¹	$\Delta_f H^\circ(\text{Fe}^{3+}, \text{ao}) - \Delta_f H^\circ(\text{Fe}^{2+}, \text{ao})$ kJ·mol ⁻¹
68SOU/CHA (No. 9)	-146.13 ± 1.0	44.12 ± 1.0
71BER/TUM (No. 10)	-148.76 ± 0.10	41.48 ± 0.10
47FON (Nos. 11, 12)	-150.16 ± 0.50	40.08 ± 0.5
72WHI/LAN (No. 14)		38.41 ± 1.5 ^l
73NIK/ANT (No. 17)		42.75 ± 1.5 ^m
53MAG/HUI (No. 22)		46.7 ± 2.0 ^m
51CON/McV (No. 24)		40.58 ± 0.84
89EVD/EFI and 90EFI/FUR (chloride system) (Nos. 94, 127, 141)		41.61 ± 1.0
89EFI/EVD and 90EFI/FUR (bromide system) (Nos. 178, 184, 190)		39.06 ± 1.3
		39.96 ± 1.32

^mOur calculations using C_p measurements of $\text{Fe}^{2+}(\text{ao})$ and $\text{Fe}^{3+}(\text{ao})$ by 88HOV.



3.4. The Tentative Selected Parameters

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 ± 0.5 kJ·mol⁻¹ for $\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao})$ and the $\Delta(\Delta_f H^\circ)$ s from E° vs T , the oxidation by the O₂ and from the chloride and bromide systems; 2) the initial selection of $\Delta_f H^\circ(\text{FeCl}_3, \text{cr}) = -396.02 \pm 0.14$ kJ·mol⁻¹ and $\Delta_{\text{so}} H^\circ = -156.38 \pm 0.28$ kJ·mol⁻¹; and 3) the direct determination of $\Delta_f H^\circ(\text{Fe}^{3+}, \text{ao}) = -51.00 \pm 1.3$ kJ·mol⁻¹. This 'consistent' path narrows the range of values to between -51 and -47 kJ·mol⁻¹.

We select $\Delta(\Delta_f H^\circ) = 41.0 \pm 1.5 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_f H^\circ(\text{Fe}^{3+}, \text{ao}) = -49.0 \pm 1.5 \text{ kJ} \cdot \text{mol}^{-1}$ and modify our selection of $\Delta_f H^\circ(\text{FeCl}_3, \text{cr})$ from $-396.02 \pm 0.14 \text{ kJ} \cdot \text{mol}^{-1}$ to $-395.66 \pm 0.50 \text{ kJ} \cdot \text{mol}^{-1}$. The selected values are given below and become our final recommendations.

	$\frac{\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao})}{\text{kJ} \cdot \text{mol}^{-1}}$	$\frac{\Delta(\Delta_f H^\circ)}{\text{kJ} \cdot \text{mol}^{-1}}$	$\frac{\Delta_f H^\circ(\text{Fe}^{3+}, \text{ao})}{\text{kJ} \cdot \text{mol}^{-1}}$	
Tentative Selection (Rejected Value)	-90.0 ± 0.5 (-95.5)			
E° vs T		38.41 ± 1.5^n 42.75 ± 1.5^p 46.7 ± 2.0^p 40.58 ± 0.84 41.61 ± 1.0	-51.59 -47.25 -43.3 -49.42 -48.39	(-57.09) (-52.75) (-48.8) (-54.42) (-53.89)
Calorimetric				
Oxidation with H_2O_2		44.11 ± 1.0 41.48 ± 0.10 40.08 ± 0.5	-45.89 -48.52 -49.42	(-51.39) (-54.02) (-55.42)
Chloride system		39.06 ± 1.3	-50.94	(-56.44)
Bromide system		39.96 ± 1.32	-50.04	(-55.54)
Initial (Rejected) Selection for $\Delta_f H^\circ(\text{FeCl}_3, \text{cr}) = -396.02 \pm 0.14 \text{ kJ} \cdot \text{mol}^{-1}$ ($-399.24 \text{ kJ} \cdot \text{mol}^{-1}$) and $\Delta_{\text{sol}} H^\circ(\text{FeCl}_3, \text{cr}) = -146.5 \pm 3.0 \text{ kJ} \cdot \text{mol}^{-1}$ (from measurements in HCl) or $\Delta_{\text{sol}} H^\circ(\text{FeCl}_3, \text{cr}) = -158.99 \pm 0.84 \text{ kJ} \cdot \text{mol}^{-1}$ (from measurements in H_2O) or $\Delta_{\text{sol}} H^\circ(\text{FeCl}_3, \text{cr}) = -156.58 \pm 1.2 \text{ kJ} \cdot \text{mol}^{-1}$ (from measurements in HClO_4)			-41.3 ± 3.1 (-44.55)	
Direct determination (76VAS/RAS)			-46.48 ± 0.32	
(89EVD/EFI and 90EFI/FUR)			-51.00 ± 1.3	

^{P72}WHI/LAN and ⁷³NIK/ANT results corrected for ΔC_p 's using 88HOV.

Compound	$\Delta_f H^\circ$, kJ·mol ⁻¹
Fe ²⁺ (ao)	-90.0 ± 0.5
Fe ³⁺ (ao)	-49.0 ± 1.5
FeCl ₂ (ai)	-550.24 ± 1.5
FeCl ₂ (cr)	-395.66 ± 0.50
FeBr ₃ (ai)	-413.23 ± 1.5
FeBr ₃ (cr)	-263.8 ± 0.7

4. The Evaluation of the Gibbs Energy of Formation of the Aqueous Ion, Fe²⁺, $\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao})$

Some controversy was generated as a result of the selection, made independently by two evaluation groups [69WAG/EVA and 82WAG/EVA, 72MED/BER], for $\Delta_f G^\circ(\text{Fe}^{2+}, \text{aq}) = -78.9$ 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 $\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao})$ is evaluated from:

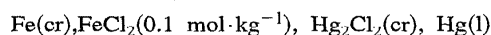
- 1) e.m.f. (Sec. 4.1) and some equilibrium constant measurements (section 4.2.1) that result in values for $\Delta_f G^\circ$ independent of other Fe species.
- 2) equilibrium measurements involving solubilities of Fe₃O₄(cr, magnetite) (Sec. 4.2.2) and FeSO₄·7H₂O(cr) (Sec. 4.2.3) and FeCl₂·4H₂O(cr) (Sec. 4.2.4) which also involves its vapor pressure.

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

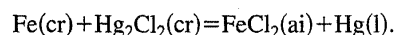
4.1. The e.m.f. Measurements

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:



obtaining $E = 0.7996 \pm 0.0010$ V. Then, using γ_{\pm} from 79GOL/NUT, $E^\circ = 0.7027 \pm 0.0010$ V and $\Delta G^\circ = -135.60 \pm 0.20$ kJ·mol⁻¹ for

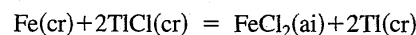


Two different samples of Fe(cr) were used, one electrolytically prepared and deposited on Pt electrodes at 1373 K and the second by the reduction of pure Fe₂O₃(cr) with H₂ at temperatures of 1073 to 1123 K. Oxygen was carefully excluded from both as described by 32RAN/FRA. The cell measurements for E 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 26HAM (No. 73) on the same cell. These measurements were made in various concentrations of FeCl₂ ($m > 0.1$ mol·kg⁻¹) and, corrected to the standard state, result in $E^\circ = 0.710 \pm 0.0014(2s)$ V ($\Delta G^\circ = -137.01 \pm 0.30$ kJ·mol⁻¹), 0.0073 V greater than their measurements. They ex-

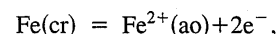
plained the differences by asserting that electrodes prepared from finely divided iron, used by 26HAM, give too high a value since treatment of the finely divided iron by acid or by prolonged exposure to solutions of FeCl₂ reduces the activity of the iron and the measured E approaches their value of $E^\circ = 0.70217$ V.

The 26HAM (No. 72) measurements on



yield $E^\circ = -0.1225$ 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 TlCl(aq) removes the finer particles of iron.

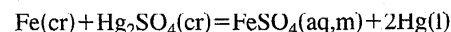
For the half cell,



the values from the Hg₂Cl₂(cr) cell are $E^\circ = 0.4346 \pm 0.0010$ V ($\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao}) = -83.86 \pm 0.20$ kJ·mol⁻¹) from 32RAN/FRA2, and $E^\circ = 0.4418 \pm 0.0015$ V ($\Delta_f G^\circ = -85.26 \pm 0.30$ kJ·mol⁻¹) from 26HAM. From the TlCl(cr) cell, $E^\circ = 0.4340 \pm 0.005$ V ($\Delta_f G^\circ = -83.75 \pm 1.0$ kJ·mol⁻¹).⁹

Much earlier, 06RIC/BEH conducted measurements on the system Fe[FeSO₄(0.5 mol·dm⁻³)]KCl(0.1 mol·dm⁻³) Hg₂Cl₂-Hg. Although it is not possible to obtain an E° for this cell because of the unknown liquid potential and the high concentration of FeSO₄, 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), Fe²⁺(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 fusion 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), Hg₂SO₄(cr) half cell (No. 206):



cell	m mol·kg ⁻¹	E V	γ_{\pm}^r	E° V	γ_{\pm} (72PIT)	E° V
1	.0718	1.1335	.193	1.02361	.186	1.0226
7	.029(aii)	1.1485	.281	1.0249	.275	1.0244
4	.0274	1.1488	.290	1.02463	.283	1.02394
5	.0220	1.1522	.330	1.0257	.305	1.0236
			avg.	1.0247		1.0236

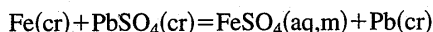
⁹ $\Delta_f G^\circ(\text{TlCl}, \text{cr}) = -184.93$ kJ·mol⁻¹ [82WAG/EVA] and $\Delta_f G^\circ = -184.97 \pm 3.0$ kJ·mol⁻¹ [71MED/BER].

^r γ_{\pm} s listed by 53PAT/THO from measurements by 41DEM/IED.

Thus, E° for the cell is 1.0247 ± 0.0003 V ($\Delta G^\circ = -197.74 \pm 0.06$ kJ·mol⁻¹) using γ_{\pm} s given by 53PAT/THO and $E^\circ = 1.0236 \pm 0.0003$ V using Pitzer's (72PIT) γ_{\pm} s for MgSO₄.

The resultant values for E° for the Fe(cr)–Fe²⁺(ao) half cell are 0.4119 ± 0.0003 V ($\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao}) = -79.483 \pm 0.60$ kJ·mol⁻¹) and 0.4180 ± 0.0003 V ($\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao}) = -79.263 \pm 0.60$ kJ·mol⁻¹), respectively.

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

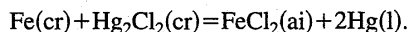


$E = 0.1654$ V when $m = 0.0677$ mol·kg⁻¹ using massive iron. If $\gamma_{\pm} = 0.198$ as given by 53PAT/THO, $E^\circ = 0.05461$ V. If $\gamma_{\pm} = 0.192$ from 72PIT is used, then $E^\circ = 0.0538$ V.

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

It follows (with 53PAT/THO γ_{\pm} s) that $E^\circ = 0.05461$ V (massive iron) and 0.05439 V (iron powder) or (with 72PIT's γ_{\pm}) $E^\circ = 0.05380$ and 0.05374 V, respectively. The two different iron electrodes give essentially the same result $E^\circ = 0.05450 \pm 0.0001$ or 0.05377 ± 0.0001 V ($\Delta G^\circ = -10.517 \pm 0.020$ kJ·mol⁻¹ or -10.376 ± 0.020 kJ·mol⁻¹). The resultant Fe(cr)–Fe²⁺(ao) standard half cell potential is 0.4121 or 0.4113 V ($\Delta_f G^\circ = -79.516$ or -79.375 kJ·mol⁻¹).

The third reference electrode used was the Hg₂Cl₂–Hg half cell (No. 74) in conjunction with a massive iron electrode and also with an iron powder electrode.



The measured E 's [$m(\text{FeCl}_2, \text{aq}) = 0.0760$ and 0.0160 mol·kg⁻¹] are 0.7770 (massive iron) and 0.8298 V (iron powder) which lead to $E^\circ = 0.6712$ V ($\Delta G^\circ = -129.522$ kJ·mol⁻¹) and $E^\circ = 0.6735$ V ($\Delta G^\circ = -129.966$ kJ·mol⁻¹) and for the standard potential of the Fe(cr)–Fe²⁺(ao) half cell $E^\circ = 0.4031$ and 0.4055 V ($\Delta_f G^\circ = -77.777$ and -78.221 kJ·mol⁻¹, respectively). The E° values are as follows:

	half cell	E° (V)
32RAN/FRA2	(No. 75) Hg ₂ Cl ₂ , Hg	0.4346 ± 0.0010
26HAM	(No. 73) Hg ₂ Cl ₂ , Hg	0.4418
	TiCl ₃ (cr)	0.4340
53PAT/THO	(No. 74) Hg ₂ Cl ₂ , Hg	0.4043
	(No. 206) Hg ₂ SO ₄ , Hg	0.4108
		using Pitzer's coefficients
	(No. 207) PbSO ₄ , Pb	0.4113
		using Pitzer's coefficients

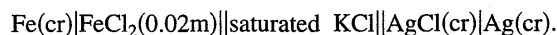
53PAT/THO also made their measurements as a function of time. For all deoxygenated cells using massive iron or iron powder there was a sharp initial rise in potential followed by a general approach to a steady value within a period of 12 to

30 d. The authors note, however, that the presence of small amounts of oxygen in the cells from the carbonyl iron powder effected 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:

$E = 0.8065$ V at $m(\text{FeCl}_2, \text{aq}) = 0.0864$ mol·kg⁻¹ with $\gamma_{\pm} = 0.511$ [79GOL/NUT] for the cell containing air, leading to $E^\circ = 0.7041$ V and E° for the Fe(cr)–Fe²⁺(ao) half cell $= 0.4361$ V ($\Delta_f G^\circ = -84.15$ kJ·mol⁻¹), in excellent agreement with the 32RAN/FRA2 measurements, indicating the possibility of air being present in the cells used by 32RAN/FRA2.

The second cell (completely deoxygenated) gave $E = 0.8520$ V with $m = 0.0675$ mol·kg⁻¹ ($\gamma_{\pm} = 0.511$) so that E° for the cell is 0.7423 and for the half cell 0.4742 V ($\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao}) = -91.51$ kJ·mol⁻¹), significantly higher than the E° s they obtained from the carbonyl reduced iron half cells that were deoxygenated. The above data appeared to establish $E^\circ = 0.4088$ 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/HEP in Sec. 4.2.3 on $\Delta_{\text{sol}} G^\circ$ of FeSO₄·7H₂O(cr) and FeCl₂·4H₂O(cr)). The 60HUR (No. 6) measurements as well as those of 78JOH/BAU (No. 5) on the half cell indicate even greater discrepancies. The e.m.f. measurements of 60HUR at 293 K are indicative of this. He obtained $E^\circ = 0.467$ V from extrapolation of forward and reverse kinetic data (in acidic FeCl₂ 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 ($\sim 0.3\%$) and the method of preparation is unknown. The solutions of FeCl₂(aq), though, were presaturated with hydrogen in the presence of platinized platinum to reduce any Fe³⁺ 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° values. 78JOH/BAU considered the earlier discordant measurements and measured the cell



The Fe–Fe²⁺ half cell was prepared from coulometrically generated Fe²⁺(aq) from spectroscopic grade rod Fe (containing less than 10 ppm total spectroscopically detectable impurities under N₂ or Ar). About 10 ppm H was also contained in the Fe. Cleaned electrodes were annealed at 993 K for several hours in evacuated and sealed Vycor tubes. One electrode was further treated to remove H more completely by cycling between room temperature and 1073 K under an active vacuum of 4×10^{-7} mm Hg. Their measurements on

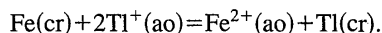
the vacuum annealed Fe(cr) cells indicate that the apparent standard potential for the Fe(cr)/Fe²⁺(aq) is strongly dependent on pH in the acidic region but becomes independent at pH ≥ 5.8 and is 0.415 ± 0.001 V ($\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao}) = -80.08 \pm 0.20 \text{ kJ} \cdot \text{mol}^{-1}$). If the Fe was not particularly degassed, the potential increased to ~0.435 V ($\Delta_f G^\circ = -83.94 \text{ kJ} \cdot \text{mol}^{-1}$) 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 $\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao})$ and E° of the half cell.

4.2. The Equilibrium Constants

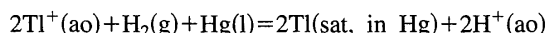
4.2.1. The Reaction of Fe(cr) With Aqueous TiClO₄ and NaClO₄

The measurements of 82GAM/REI (No. 4) are considered. Neutral aqueous solutions of TiClO₄ 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

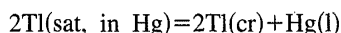


A plot of log [Fe²⁺] vs log [Ti⁺] gives a straight line with a slope of 2.0 and $\Delta G^\circ = -6.93 \pm 0.4 \text{ kJ} \cdot \text{mol}^{-1}$. Correction (see catalog entry) to 298.15 K and I=0 results in $\Delta G^\circ = -13.51 \pm 1.5 \text{ kJ} \cdot \text{mol}^{-1}$ ($E^\circ = 0.0700 \text{ V}$) and $\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao}) = -78.28 \pm 1.5 \text{ kJ} \cdot \text{mol}^{-1}$ (E° for the Fe(cr)-Fe²⁺(ao) half cell = 0.4057 V), if $\Delta_f G^\circ(\text{Ti}^+, \text{ao}) = -32.38 \text{ kJ} \cdot \text{mol}^{-1}$ [82WAG/EVA and 71MED/BER].

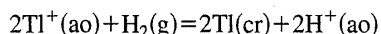
However, 79HEI (a coauthor of the above work) has also measured the e.m.f. of



at 323 K under the same conditions and obtained $E^\circ = -0.3865 \text{ V}$ (I=1.0). Using $E^\circ = -0.0031 \text{ V}$ from 19RIC/DAN and 22GER for



$E^\circ = -0.3896 \text{ V}$ (I=1.0) at 323.15 K is obtained for

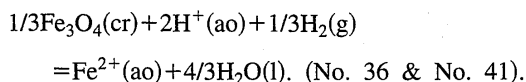


and $E^\circ = -0.3567 \text{ V}$ (I=0) at 298.15 K. Then for the Fe(cr)/Fe²⁺(ao) half cell $E^\circ = 0.4267 \text{ V}$ and $\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao}) = -82.34 \text{ kJ} \cdot \text{mol}^{-1}$.

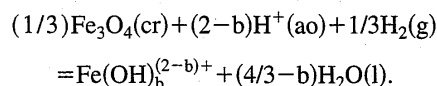
Obviously these measurements could support either the 53PAT/THO or the 32RAN/FRA2 values.

4.2.2. Solubility Measurements of Fe₃O₄(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 K_s values at 298 K for the following process:



Both sets of solubility measurements were conducted in flow systems with varying pH, redox conditions, and temperature (70SWE/BAE temperature range 323 to 573 K, 80TRE/LEB 373 to 573 K). 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)₃⁻ species, Fe²⁺(ao), FeOH⁺(ao), Fe(OH)₂(ao), and Fe(OH)₃(ao). (80TRE/LEB also include ferric species Fe(OH)₃(ao) and Fe(OH)₄⁻(ao)). The reactions for Fe(II) take the following form:



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 ($p^\circ = 1 \text{ atm}$). With the selected value for $\Delta_f G^\circ(\text{Fe}_3\text{O}_4, \text{cr})$ from 88HAA = -1013.30 ± 2.15 kJ·mol⁻¹, $\Delta_f G^\circ = -90.18 \pm 3.1$ and -85.82 ± 2.12 kJ·mol⁻¹ respectively. In Table 6 of the 80TRE/LEB paper is given their calculated value for $\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao})$, obtained from $\Delta_f G^\circ(298.15 \text{ K}) = -66.7 \text{ kJ} \cdot \text{mol}^{-1}$ using $\Delta C_p = 120 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. This $\Delta_f G^\circ$ results in $\Delta_f G^\circ = -88.26 \text{ kJ} \cdot \text{mol}^{-1}$. Comparison of their measured values with the 70SWE/BAE measurements shows the following:

T/K	lg K		
	70SWE/BAE (No. 36)	80TRE/LEB (No. 41)	Δ
373	8.55	8.23 ± 0.08	0.32
473	5.73	5.92 ± 0.05	-0.19
573	3.98	4.42 ± 0.05	-0.44

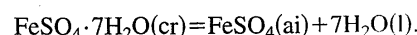
The disagreement is disturbing. However, both sets of measurements indicate a more negative value for $\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao})$ than that of 53PAT/THO or 32RAN/FRA.

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, $\gamma_{\pm} = 0.0344$ and ϕ , the osmotic coefficient, = 0.578 from 59ROB/STO were used (reaction No. 209 in 8.2), resulting in $\Delta_{\text{sol}} G^\circ = 14.12 \pm 0.50 \text{ kJ} \cdot \text{mol}^{-1}$ for the process



Values from the 72PIT tabulation are in agreement.

The experimental results of 74OYK/BAL require an estimate at $m=0.10 \text{ mol}\cdot\text{kg}^{-1}$ for γ_{\pm} . With $\gamma_{\pm} = 0.15$ from 59ROB/STO, γ_{\pm} and a_w at saturation are 0.0423 and 0.925 respectively, leading to $\Delta G^\circ = 13.24 \text{ kJ}\cdot\text{mol}^{-1}$ for the above process. (74OYK/BAL use $m=1.964 \text{ mol}\cdot\text{kg}^{-1}$ and give $\gamma_{\pm} = 0.0425$ and $a_w = 0.951$ resulting in $\Delta G^\circ = 13.18 \text{ kJ}\cdot\text{mol}^{-1}$). However 86REA/BEC point out that reanalysis of the data on the 2:2 type electrolytes by 72PIT indicates that a better value for γ_{\pm} for FeSO_4 at $m=0.10 \text{ mol}\cdot\text{kg}^{-1}$, based on 72PIT's value for MgSO_4 (0.161) is 0.161 ± 0.01 , resulting in $\gamma_{\pm} = 0.048$ and $a_w = 0.952$ so that $\lg K_s = -2.205$ and $\Delta_{\text{sol}}G^\circ = 12.58 \pm 0.30 \text{ kJ}\cdot\text{mol}^{-1}$ (reaction No. 210).

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

The C_p measurements of 49LYO/GIA (No. 208) lead to $S^\circ = 409.2 \pm 1.2 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for $\text{FeSO}_4\cdot 7\text{H}_2\text{O}(\text{cr})$ at 298.15 K.

We have, in Sec. 2.3, accepted, for our first iteration, $\Delta_{\text{sol}}H^\circ = 12.90 \pm 0.10 \text{ kJ}\cdot\text{mol}^{-1}$. With $\Delta_{\text{sol}}G^\circ = 12.58 \pm 0.30 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_{\text{sol}}S^\circ = 1.07 \pm 1.1 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. The calculated $S^\circ(\text{Fe}^{2+}, \text{ao}) = -97.88 \pm 1.4 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ and $\Delta_f S^\circ = 5.37 \pm 1.55 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ($S^\circ(\text{Fe}, \text{cr}) = 27.319 \pm 0.002 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$). With our tentative $\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao}) = -90.0 \pm 0.50 \text{ kJ}\cdot\text{mol}^{-1}$ we obtain $\Delta_f G^\circ = -91.60 \pm 0.85 \text{ kJ}\cdot\text{mol}^{-1}$, ($E^\circ = 0.4747 \pm 0.004 \text{ V}$), surprisingly more negative than all other values.⁸ Using 74OYK/BAL's original values for $\gamma_{\text{sol}}G^\circ = 13.24 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_{\text{sol}}S^\circ = -1.14 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, so that $S^\circ(\text{Fe}^{2+}, \text{ao}) = -100.09 \pm 1.14 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ and $\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao}) = -90.94 \pm 0.85 \text{ kJ}\cdot\text{mol}^{-1}$.

The earlier $\Delta_{\text{sol}}G^\circ = 14.12 \pm 0.50 \text{ kJ}\cdot\text{mol}^{-1}$ used in the 69WAG/EVA evaluation (based on an estimated γ_{\pm}) with $\Delta_f G^\circ(\text{FeSO}_4\cdot 7\text{H}_2\text{O}, \text{cr}) = -2509.87 \text{ kJ}\cdot\text{mol}^{-1}$ had led to $\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao}) = -91.3 \text{ kJ}\cdot\text{mol}^{-1}$ which was rejected because it appeared to be too negative, possibly because the properties of $\text{FeSO}_4(\text{aq})$ 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

$$\log K_s = 1.447 - 0.004153(T/K) - 21494(K/T)^2.$$

The calculated $\Delta_{\text{sol}}H^\circ = 20.54 \text{ kJ}\cdot\text{mol}^{-1}$ and with $\Delta_{\text{sol}}G^\circ = 12.58 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_{\text{sol}}S^\circ = 27.70 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, and $S^\circ(\text{Fe}^{2+}, \text{ao}) = -71.3 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ and $\Delta_f G^\circ = -100.0 \text{ kJ}\cdot\text{mol}^{-1}$.

4.2.4. Measurements on $\text{FeCl}_2\cdot 4\text{H}_2\text{O}(\text{cr})$

4.2.4.1. Vapor pressure measurements

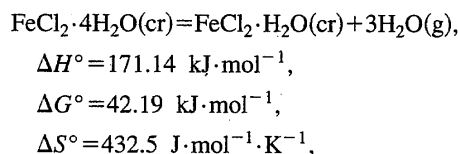
The catalog lists the various measurements on the hydrates $\text{FeCl}_2\cdot 4\text{H}_2\text{O}(\text{cr})$, $\text{FeCl}_2\cdot 2\text{H}_2\text{O}(\text{cr})$, and $\text{FeCl}_2\cdot \text{H}_2\text{O}(\text{cr})$. ($\text{FeCl}_2\cdot 6\text{H}_2\text{O}(\text{cr})$ exists below 283 K). The vapor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

⁸Alternatively, since we have tentatively selected $\Delta_f H^\circ(\text{FeSO}_4\cdot 7\text{H}_2\text{O}, \text{cr}) = -3013.05 \pm 0.65 \text{ kJ}\cdot\text{mol}^{-1}$ and $S^\circ = 409.2 \pm 1.2 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, $\Delta_f G^\circ = -2508.61 \pm 0.74 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao}) = -91.10 \pm 0.8 \text{ kJ}\cdot\text{mol}^{-1}$

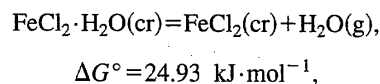
1. $\text{FeCl}_2\cdot 4\text{H}_2\text{O}(\text{cr}) = \text{FeCl}_2\cdot 2\text{H}_2\text{O}(\text{cr}) + 2\text{H}_2\text{O}(\text{g})$ (No.119),
 $\Delta H^\circ = 108.04 \pm 4.0 \text{ kJ}\cdot\text{mol}^{-1}$,
 $\Delta G^\circ = 23.62 \pm 1.0 \text{ kJ}\cdot\text{mol}^{-1}$,
 $\Delta S^\circ = 283.1 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$,
2. $\text{FeCl}_2\cdot 2\text{H}_2\text{O}(\text{cr}) = \text{FeCl}_2\cdot \text{H}_2\text{O}(\text{cr}) + \text{H}_2\text{O}(\text{g})$ (No.120),
 $\Delta H^\circ = 63.1 \pm 5.0 \text{ kJ}\cdot\text{mol}^{-1}$,
 $\Delta G^\circ = 18.57 \pm 2.0 \text{ kJ}\cdot\text{mol}^{-1}$,
 $\Delta S^\circ = 149.4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$,
3. $\text{FeCl}_2\cdot \text{H}_2\text{O}(\text{cr}) = \text{FeCl}_2(\text{cr}) + \text{H}_2\text{O}(\text{g})$ (No.121),
 $\Delta H^\circ = 63.1 \pm 5.0 \text{ kJ}\cdot\text{mol}^{-1}$,
 $\Delta G^\circ = 24.93 \pm 2.0 \text{ kJ}\cdot\text{mol}^{-1}$,
 $\Delta S^\circ = 128.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

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

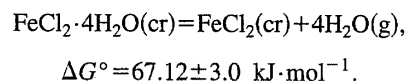
We now have



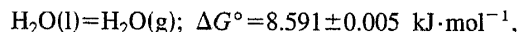
and



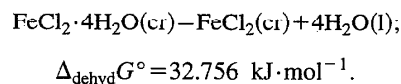
so that



Using 89COX/WAG for



we obtain



This will be combined with $\Delta_{\text{sol}}G^\circ(\text{FeCl}_2\cdot 4\text{H}_2\text{O}, \text{cr})$.

4.2.4.2. The Gibbs energy of solution of $\text{FeCl}_2\cdot 4\text{H}_2\text{O}(\text{cr})$

The solubility of $\text{FeCl}_2\cdot 4\text{H}_2\text{O}(\text{cr})$, the stable phase at 298.15 K, has recently been measured by 85CHO/PHO. The 79GÖL/NUT evaluation of a_w , ϕ , and γ_{\pm} of $\text{FeCl}_2(\text{aq})$ lists recommended values up to $m=2.05 \text{ mol}\cdot\text{kg}^{-1}$. However, they also present the osmotic coefficients, ϕ , obtained from the vapor pressure measurements of 62KAN/GRO which were measured in the range 1 to 5 $\text{mol}\cdot\text{kg}^{-1}$ but were given no weight in the evaluation. A comparison of the values reveals a 3% difference in ϕ at $m=2.0 \text{ mol}\cdot\text{kg}^{-1}$. Increasing

TABLE 5. The enthalpy of formation of FeOOH(cr, Goethite) from Fe₂O₃(cr) and H₂O(l)

Investigator	$\Delta H/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_f H^\circ(\text{FeOOH, cr})/\text{kJ}\cdot\text{mol}^{-1}$	
		$\Delta_f H^\circ(\text{Fe}_2\text{O}_3, \text{cr}) = -824.9 \pm 3.2$	$\Delta_f H^\circ(\text{Fe}_2\text{O}_3, \text{cr}) = -823 \pm 6$
59SCH (No. 63)	15 \pm 10	-562.9 \pm 5.2	-561.9
75KOR/FAD (No. 65)	13.70 \pm 4.0	-562.2 \pm 2.6	-561.3
65BAR (No. 51)	7.87 \pm 0.84	-559.3 \pm 1.7	-558.4
64FER (No. 64)	4.9 \pm 1.2	-557.8 \pm 1.8	-556.9

the uncertainty of 62KAN/GRO's tabulated γ_{\pm} s and ϕ s to 5% at the saturation point ($m=4.951 \text{ mol}\cdot\text{kg}^{-1}$) we obtain, as indicated in the catalog (reaction No. 118).

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

for $\text{FeCl}_2\cdot 4\text{H}_2\text{O}(\text{cr}) = \text{FeCl}_2(\text{ai}) + 4\text{H}_2\text{O}(\text{l})$.

Combining the $\Delta_{\text{sol}} G^\circ$ with the $\Delta_{\text{dehyd}} G^\circ$ for the tetrahydrate, we obtain

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

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

In Sec. 2.3 we selected $\Delta_{\text{sol}} H^\circ$ for the above process to be $-83.00 \pm 0.14 \text{ kJ}\cdot\text{mol}^{-1}$. The $\Delta_{\text{sol}} S^\circ$ then is $-112.02 \pm 10 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ and $S^\circ(\text{Fe}^{2+}, \text{ao}) = -107.2 \pm 10 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, resulting in $\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao}) = -89.4 \pm 3.1 \text{ kJ}\cdot\text{mol}^{-1}$ 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 $\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao})$

The range of values for $\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao})$ 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/THO and 78JOH/BAU. The equilibrium measurements of 82GAM/REI confirm this; however, the values from three other paths (the solubility of Fe₃O₄(cr), and from the entropies of the Fe²⁺(ao) from the FeSO₄·7H₂O(cr) and the FeCl₂·4H₂O(cr)–FeCl₂(cr) systems), indicate a much more negative value. It is particularly difficult to ascribe a major error in the $\Delta_{\text{sol}} G^\circ$ for FeSO₄·7H₂O(cr). See 87REA/BEC for further discussion. The e.m.f. measurements of 60HUR agree with the very negative values. He hypothesized 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⁺(ao)). We therefore base our initial selection for $\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao})$ on the values from the Fe₃O₄(cr), FeSO₄·7H₂O(cr), and FeCl₂·4H₂O(cr)–FeCl₂(cr) paths, accepting $\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao}) = -90.5 \pm 1.0 \text{ kJ}\cdot\text{mol}^{-1}$ ($p^\circ=1 \text{ atm}$). Table 6 in Sec. 5.2 shows the measurements. (This initial selection for $\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao})$ will become our final recommended value.)

5. The Evaluation of the Gibbs Energy of Formation of the Aqueous Ion Fe³⁺, $\Delta_f G^\circ(\text{Fe}^{3+}, \text{ao})$

The $\Delta_f G^\circ(\text{Fe}^{3+}, \text{ao})$ is evaluated by:

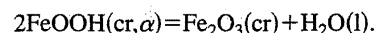
- (1) establishing the thermochemical property values of FeOOH(cr, Goethite) and its $\Delta_{\text{sol}} G^\circ$ (section 5.1.3) to obtain a value for $\Delta_f G^\circ$ and
- (2) obtaining values for $\Delta_f G^\circ(\text{Fe}^{3+}, \text{ao}) - \Delta_f G^\circ(\text{Fe}^{2+}, \text{ao})$ (Sec. 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 $\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao})$ to obtain other values for $\Delta_f G^\circ(\text{Fe}^{3+}, \text{ao})$.

In Secs. 5.1 and 5.2 we finalize the selections for the $\Delta(\Delta_f G^\circ)$ s and for $\Delta_f G^\circ(\text{Fe}^{3+}, \text{ao})$ ($p^\circ=1 \text{ atm}$), rationalizing our selections by reviewing the effect on values for $\Delta_f H^\circ$ and $\Delta_{\text{sol}} H^\circ$ of substances in the key network.

5.1. The Properties of Goethite, FeOOH(cr, α)

5.1.1. $\Delta_f H^\circ(\text{FeOOH, cr, } \alpha)$

One path to the $\Delta_f G^\circ(\text{Fe}^{3+}, \text{ao})$ is from $\Delta_{\text{sol}} G^\circ(\text{FeOOH, cr, } \alpha)$ and $\Delta_f G^\circ(\text{FeOOH, cr, } \alpha)$. This involves the $\Delta_f H^\circ(\text{FeOOH, cr, } \alpha)$. There are four measurements leading to $\Delta_f H^\circ(\text{FeOOH, cr})$ from reactions involving Fe₂O₃(cr) and Goethite. The reaction is



The 59SCH (No. 63) results on the stability regions of Fe₂O₃–FeOOH through pressure and temperature measurements (800, 900, and 970 bar and 411 to 453 K) lead to $\Delta H = 15 \pm 10 \text{ kJ}\cdot\text{mol}^{-1}$ (3rd law). The 75KOR/FAD (No. 65) differential scanning calorimetric measurements (corrected for $\Delta_{\text{vap}} H^\circ(\text{H}_2\text{O}, \text{l}) = 44.004 \text{ kJ}\cdot\text{mol}^{-1}$) lead to $13.70 \pm 4.0 \text{ kJ}\cdot\text{mol}^{-1}$ for ΔH .

Calorimetric measurements of the $\Delta_{\text{sol}} H$ of FeOOH(cr, α) and Fe₂O₃(cr) in 20.1 wt% aqueous HF at 298.15 K by 65BAR (No. 51) and in 20.1% aqueous HCl (HCl+7.60H₂O) containing 0.18% FeCl₃ at 344 K by 64FER (No. 64) give $\Delta H = 7.87 \pm 0.84$ and $4.9 \pm 1.2 \text{ kJ}\cdot\text{mol}^{-1}$, respectively. A summary, Table 5, with $\Delta_f H^\circ(\text{Fe}_2\text{O}_3, \text{cr}) = -824.9 \pm 3.2 \text{ kJ}\cdot\text{mol}^{-1}$ [88HAA] and $-823 \pm 6 \text{ kJ}\cdot\text{mol}^{-1}$ [86ARI/BER] follows.

In our initial assessment, we select $\Delta_f H^\circ(\text{FeOOH, cr}, \alpha) = -559.3 \pm 1.7 \text{ kJ}\cdot\text{mol}^{-1}$ based on 65BAR and $\Delta_f H^\circ(\text{Fe}_2\text{O}_3, \text{cr}) = -824.9 \pm 3.2 \text{ kJ}\cdot\text{mol}^{-1}$.

5.1.2. $\Delta_f G^\circ(\text{FeOOH}, \text{cr}, \alpha)$

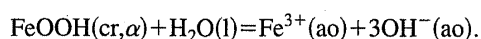
From the C_p measurements on FeOOH of 70KIN/WEL (51 K to 298 K), $S^\circ(298.15 \text{ K})$ is tabulated as $60.40 \pm 0.60 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ (Nos. 48, 49 in A.I.b), resulting in $\Delta_f S^\circ = -237.250 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ and $\Delta_f G^\circ = -488.6 \pm 1.7 \text{ kJ}\cdot\text{mol}^{-1}$.

5.1.3. Gibbs Energy of Solution of FeOOH(cr, α) and $\Delta_f G^\circ(\text{Fe}^{3+}, \text{ao})$

The equilibrium between the solid ferric oxyhydrates and their aqueous solutions is complex. There are various reviews of the stability of the various ferric oxyhydroxides precipitated from $\text{Fe}^{3+}(\text{aq})$, e.g. 69LAN, 71LAN, 71LAN/WHI, and 85HSU/MAR.

The various naturally occurring ferric oxyhydroxides are amorphous, designated as $\text{Fe}(\text{OH})_3(\text{am})$, and the crystalline forms which we write as $\text{FeOOH}(\text{cr})$ [α for the Goethite form, β for the Akageneite form, and γ for the Lepidocrocite form], as well as $\text{Fe}_2\text{O}_3(\text{cr})$ [α for hematite and γ for maghemite].

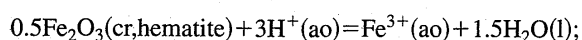
The precipitate in contact with solutions containing $\text{Fe}^{3+}(\text{ao})$ depends upon the pH of the solution, temperature, time, the presence of $\text{Fe}^{2+}(\text{ao})$, an oxidizing medium, and various foreign ions. The amorphous (freshly precipitated, after about 2 h, called active) ages to a form considered inactive (after about 2 a) and eventually to Goethite and/or hematite or other crystalline forms with different solubilities. The $K_s = a(\text{Fe}^{3+})a(\text{OH}^-)^3$ is thus difficult to ascribe accurately to a single, well-defined phase. 85HSU/MAR (No. 28) obtained the activity products, $a(\text{Fe}^{3+})a(\text{OH}^-)^3$, of $\text{Fe}(\text{ClO}_4)_3$ solutions hydrolyzed and aged at room temperature ($298.15 \pm 3 \text{ K}$) 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/WHI, 71LAN, 74WHI/LAN). The $\text{p}K_s$ were 39.80, 40.32, and 40.83 for ionic strengths of about 0.005, 0.04 and $0.2 \text{ mol}\cdot\text{dm}^{-3}$ and correspond to the reaction,



Extrapolation to $I=0$ results in $\text{p}K_s = 39.5$ and $\Delta_f G^\circ = 225.46 \pm 2.0 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_f G^\circ(\text{Fe}^{3+}, \text{ao}) = -28.52 \pm 2.6 \text{ kJ}\cdot\text{mol}^{-1}$.

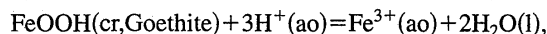
Earlier 71LAN/WHI had indicated that the "pK" from precipitation, initially at concentration of $\text{Fe}^{2+}(\text{ao})$ or $\text{Fe}^{3+}(\text{ao})$ of $10^{-2} \text{ mol}\cdot\text{dm}^{-3}$ varied from 37.3 to 43.3, beginning as amorphous material and that the $\text{p}K_s$ of the aged, macroscopic 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 $10^{-3.33}$ to $10^{5.40} \text{ mol}\cdot\text{dm}^{-3}$ $\text{Fe}^{2+}(\text{ao})$ and suspended oxyhydroxides, "pK" was 37.1 to 43.5. If we adopt 43.4 ± 0.5 as the $\text{p}K_s$ from 71LAN/WHI (No. 27) we obtain $\Delta_f G^\circ = 247.7 \pm 3.0 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_f G^\circ = -6.3 \pm 3.5 \text{ kJ}\cdot\text{mol}^{-1}$.

More recently 89KHO reviewed the oxyhydroxy- H_2O system and in a preliminary communiqué indicated that for



$$\Delta_f G^\circ = 3.0 \pm 2.5 \text{ kJ}\cdot\text{mol}^{-1}.$$

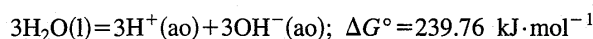
Since we have accepted $\Delta H = 3.94 \pm 0.42 \text{ kJ}\cdot\text{mol}^{-1}$ for the dehydration of Goethite to hematite and $\Delta S^\circ = 18.27 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for this process (from A.I.b, Nos. 47 and 49), $\Delta_f G^\circ = -1.51 \pm 0.5 \text{ kJ}\cdot\text{mol}^{-1}$, and for



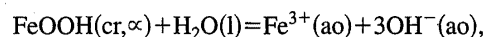
$$\Delta_f G^\circ = 1.49 \pm 2.6 \text{ kJ}\cdot\text{mol}^{-1}.$$

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

Converting these to the $K_s = a(\text{Fe}^{3+})a(\text{OH}^-)^3$ for Goethite, using



we obtain $\Delta_f G^\circ = 241.25 \pm 2.6$ and $240.90 \pm 2.8 \text{ kJ}\cdot\text{mol}^{-1}$ for the process



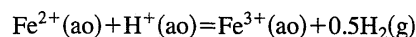
and $\Delta_f G^\circ = -12.75 \pm 2.6$ and $-12.45 \pm 2.8 \text{ kJ}\cdot\text{mol}^{-1}$, respectively.

These values are tabulated.

5.1.4. The Direct Relationship Between $\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao})$ and $\Delta_f G^\circ(\text{Fe}^{3+}, \text{ao})$

5.1.4.1. The cell measurements

72WHI/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, $E^\circ = -0.7698 \pm 0.002 \text{ V}$ for

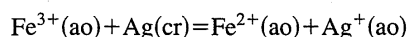


resulting in $\Delta_f G^\circ = 74.274 \pm 0.20 \text{ kJ}\cdot\text{mol}^{-1}$. 73NIK/ANT (No. 16) also measured the E° 's (using $\text{Ti}(\text{Hg})$, $\text{TiCl}(\text{cr})$ reference electrode with saturated KCl solution). At 298.15 K, $E^\circ = -0.770 \pm 0.005 \text{ V}$ and $\Delta_f G^\circ = 74.30 \pm 0.50 \text{ kJ}\cdot\text{mol}^{-1}$, in excellent agreement with 72WHI/LAN although the values diverge above 298 K resulting in $\Delta H^\circ(298 \text{ K})$ values that differ by $4 \text{ kJ}\cdot\text{mol}^{-1}$. (See Nos. 17 and 15.)

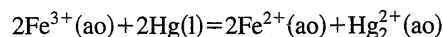
The earlier measurements of 37SCH/SHE (No. 19) ($E^\circ = -0.770 \pm 0.010 \text{ V}$) and 51CON/MCV (No. 25) ($E^\circ = -0.771 \pm 0.005 \text{ V}$) are in agreement. Other measurements are listed in the reaction catalog.

5.1.4.2. The equilibrium constants

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



to be $K = 0.363 \pm 0.015$ (measurements of 12NOY/BRA) or $\Delta_f G^\circ = 2.512 \pm 0.25 \text{ kJ}\cdot\text{mol}^{-1}$ and $K = 0.137 \pm 0.010$ for



(measurements of 31POP/FLE) or $\Delta_f G^\circ = 4.927 \pm 0.50 \text{ kJ}\cdot\text{mol}^{-1}$ (No. 21).

The resultant $\Delta_f G^\circ$ s for

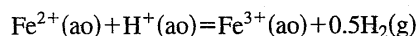


TABLE 6. The Gibbs energies of formation of $\text{Fe}^{2+}(\text{ao})$ and $\text{Fe}^{3+}(\text{ao})$ and $\Delta(\Delta_f G^\circ) = \Delta_f G^\circ(\text{Fe}^{3+}, \text{ao}) - \Delta_f G^\circ(\text{Fe}^{2+}, \text{ao})(p^\circ = 1 \text{ atm})$

Source	$\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao})/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta(\Delta_f G^\circ)/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_f G^\circ(\text{Fe}^{3+}, \text{ao})/\text{kJ}\cdot\text{mol}^{-1}$
e.m.f. measurements			
26HAM	-85.26 ± 0.30		
	-83.75 ± 1.0		
32RAN/FRA and 32FRA2	-83.86 ± 0.20		
53PAT/THO	-78.95 ± 0.5		
60HUR	-90.11 ± 0.8		
78JOH/BAU	-80.08 ± 0.20		
72WHI/LAN (Selected Value)		74.27 ± 0.20	
73NIK/ANT		74.30 ± 0.50	
Equilibrium Constants			
82GAM/REI	-78.28 ± 1.5		
(Fe(cr) and $\text{Ti}^+(\text{ao})$)	or		
	-82.34 ± 1.5		
34BRA/HER		74.47 ± 0.50	
(Hg, ag reduction)			
$\text{Fe}_3\text{O}_4(\text{cr})$ solubility ¹			
70SWE/BAE	-90.18 ± 3.1		
80TRE/LEB	-88.26 ± 2.1		
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{cr})$, solubility			
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}(\text{cr})$	-91.60 ± 0.85		
vapor pressure and solubility			
$\text{FeOOH}(\text{cr}, \text{Goethite})$, solubility			
84HSU/MAR ($pK=39.5$)			-28.5 ± 2.6
71LAN/WHI ($pK=43.4$)			-6.3 ± 4.4
$\text{Fe}_2\text{O}_3(\text{cr}, \text{hermatite})$, solubility			
89KHO re-analysis of data			-12.6 ± 2.8
(calculated $pK_{sp}(\text{Goethite})=42.3$)			

¹ $\Delta_f H^\circ$, $\Delta_f G^\circ(p^\circ = 1 \text{ atm})$, S° for $\text{Fe}_3\text{O}_4(\text{cr}, \text{magnetite}) = -1116.72 \pm 2.2 \text{ kJ}\cdot\text{mol}^{-1}$, $-1010.30 \pm 2.15 \text{ kJ}\cdot\text{mol}^{-1}$, and $145.438 \pm 0.32 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, respectively.

are 74.60 ± 0.50 and $74.34 \pm 0.5 \text{ kJ}\cdot\text{mol}^{-1}$, respectively ($E^\circ = -0.773 \pm 0.005$ and $-0.7705 \pm 0.005 \text{ V}$).

Similarly the measurements of 35SCH/SWE (No. 13) on the reduction of $\text{Fe}^{3+}(\text{ao})$ to $\text{Fe}^{2+}(\text{ao})$ by $\text{Ag}(\text{cr})$ yield $K=0.499$ and $\Delta G^\circ = 1.724 \pm 0.20 \text{ kJ}\cdot\text{mol}^{-1}$, so that ΔG° for the $\text{Fe}^{2+}\text{-Fe}^{3+}$ couple is $75.39 \pm 0.2 \text{ kJ}\cdot\text{mol}^{-1}$ ($E^\circ = -0.781 \text{ V}$).

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

The e.m.f. measurements and the equilibrium measurements are in good agreement and it would appear that the $\Delta_f G^\circ(\text{Fe}^{3+}, \text{ao}) - \Delta_f G^\circ(\text{Fe}^{2+}, \text{ao}) = 74.27 \pm 0.20 \text{ kJ}\cdot\text{mol}^{-1}$ and $E^\circ = -0.7698 \pm 0.002 \text{ V}$.

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

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

It is quite obvious that if we accept $\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao}) = -90.5 \pm 1.0 \text{ kJ}\cdot\text{mol}^{-1}$ and we maintain $\Delta(\Delta_f G^\circ) = 74.27 \pm 0.20 \text{ kJ}\cdot\text{mol}^{-1}$ our value for $\Delta_f G^\circ(\text{Fe}^{3+}, \text{ao})$ must be $-16.2 \pm 1.1 \text{ kJ}\cdot\text{mol}^{-1}$, in marginal agreement with the 89KHO value obtained from the solubility of $\text{Fe}_2\text{O}_3(\text{cr}, \text{hematite})$. It is also obvious that the more positive

value of $-6.3 \text{ kJ}\cdot\text{mol}^{-1}$ for $\Delta_f G^\circ(\text{Fe}^{3+}, \text{ao})$ would support the more positive values for $\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao})$ 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 $\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao})$, from the solubility of $\text{Fe}_3\text{O}_4(\text{cr}, \text{hematite})$, the solubility of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{cr})$, and the solubility of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}(\text{cr})$ and the decomposition of the tetrahydrate. Although the uncertainties on the values from Fe_3O_4 and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ are large and some adjustments could be made in the interpretations of the Gibbs energies of reaction, a 6 to $10 \text{ kJ}\cdot\text{mol}^{-1}$ adjustment is not possible. If we attempt to go the other way, that is, to select a value of $-81 \text{ kJ}\cdot\text{mol}^{-1}$ (or even $-84 \text{ kJ}\cdot\text{mol}^{-1}$) for $\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao})$ and use the Gibbs energies of reaction of the three above mentioned paths we would obtain calculated values for the enthalpies of formation of $\text{Fe}_3\text{O}_4(\text{cr})$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{cr})$, and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}(\text{cr})$ and $\text{FeCl}_2(\text{cr})$ that are incompatible with the selected values for these substances and their $\Delta_{\text{sol}} H^\circ$'s. (See sections on $\Delta_f H^\circ(\text{FeSO}_4 \cdot 7\text{H}_2\text{O}, \text{cr})$, $\Delta_f H^\circ(\text{FeCl}_2, \text{cr})$, and $\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao})$). We therefore accept:

$$\Delta_f G^\circ(\text{Fe}^{3+}, \text{ao}) = -16.23 \pm 1.1 \text{ kJ}\cdot\text{mol}^{-1}$$

and our previous "tentative" value for $\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao}) = -90.5 \pm 1.0 \text{ kJ}\cdot\text{mol}^{-1}$.

TABLE 7. Recommended thermodynamic property values ($p^\circ=1$ atm)

Substance	$\Delta_f H^\circ$ kJ·mol ⁻¹	$\Delta_f G^\circ$ kJ·mol ⁻¹	S° J·mol ⁻¹ ·K ⁻¹
Fe(cr)	0	0	27.319±0.002
Fe ²⁺ (ao)	-90.0±0.5	-90.5±1.0	-101.6±3.7
Fe ³⁺ (ao)	-49.0±1.5	-16.23±1.1	278.4±7.7
FeOOH(cr, Goethite)	-559.3±1.7	-488.56±1.7	60.4±0.6
FeCl ₂ (cr)	-341.16±0.6	-301.74±0.6	118.06±0.20
FeCl ₂ (ai)	-424.16±0.6	-353.00±1.1	+11.60±3.7
FeCl ₃ (cr)	-395.66±0.5	-331.86±0.6	147±0.30
F ₃ (ai)	-550.24±1.5	-409.98±1.2	-108.60±7.7
FeBr ₂ (cr)	-245.7±0.7	-234.11±0.7	140.67±0.20
FeBr ₂ (ai)	-332.82±0.6	-298.23±1.1	63.50±3.7
FeBr ₃ (cr)	-263.8±0.7		
FeBr ₃ (ai)	-413.23±1.5	-327.83±1.2	-30.75±7.7
FeI ₂ (cr)	-118.7±0.8		
FeI ₂ (ai)	-203.56±0.6	-193.98±1.1	111.30±3.7
FeSO ₄ (ai)	999.34±0.7	834.60±1.2	83.10±3.8
FeSO ₄ ·7H ₂ O(cr)	-3012.6±0.9	-2508.16±1.0	409.2±1.2
FeSO ₄ ·7H ₂ O(ai)	-3000.15±0.7	-2494.92±1.2	406.6±3.8

TABLE 8. Recommended thermodynamic property values ($p^\circ=1$ bar)

Substance	$\Delta_f H^\circ$ kJ·mol ⁻¹	$\Delta_f G^\circ$ kJ·mol ⁻¹	S° J·mol ⁻¹
Fe(cr)	0	0	27.319±0.002
Fe ²⁺ (ao)	-90.0±0.5	-90.53±1.0	-101.6±3.7
Fe ³⁺ (ao)	-49.0±1.5	-16.28±1.1	-278.4±7.7
FeOOH(cr, Goethite)	-559.3±1.7	-488.51±1.7	60.4±10.6
FeCl ₂ (cr)	-341.16±0.6	-301.70±0.6	118.06±0.20
FeCl ₂ (ai)	-424.16±0.6	-352.96±1.1	+11.60±3.7
FeCl ₃ (cr)	-395.66±0.5	-331.81±0.6	147.80±0.30
FeCl ₃ (ai)	-550.24±1.5	-409.93±1.2	-108.60±7.7
FeBr ₂ (cr)	-245.7±0.7	-234.11±0.7	140.67±0.20
FeBr ₂ (ai)	-332.82±0.6	-298.23±1.1	63.50±3.7
FeBr ₃ (cr)	-263.8±0.7		
FeBr ₃ (ai)	-413.23±1.5	-327.83±1.2	-30.75±7.7
FeI ₂ (cr)	-118.7±0.8		
FeI ₂ (ai)	-203.56±0.6	-193.98±1.1	111.30±3.7
FeSO ₄ (ai)	999.34±0.7	834.53±1.2	-83.10±3.8
FeSO ₄ ·7H ₂ O(cr)	-3012.6±0.9	-2507.75±1.0	409.2±1.2
FeSO ₄ ·7H ₂ O(ai)	-3000.15±0.7	-2494.51±1.2	406.6±3.8

6. Summary

All final recommended property values and uncertainties are tabulated ($p^\circ=1$ atm and $p^\circ=1$ bar). Predicted (calculated) process values and uncertainties for many of the reactions used in this evaluation are also tabulated ($p^\circ=1$ bar). In addition, a list of reactions (contained in the reaction catalogs) 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 Fe²⁺(ao) $\Delta_f H^\circ = -90.0 \pm 0.5$ kJ·mol⁻¹
 $\Delta_f G^\circ = -90.5 \pm 1.0$ kJ·mol⁻¹ ($p^\circ=1$ atm)
 $\Delta_f G^\circ = -90.53 \pm 1.0$ kJ·mol⁻¹ ($p^\circ=1$ bar),
 $S^\circ = -101.6 \pm 3.7$ J·mol⁻¹·K⁻¹
 For Fe³⁺(ao) $\Delta_f H^\circ = -49.0 \pm 1.5$ kJ·mol⁻¹,
 $\Delta_f G^\circ = -16.23 \pm 1.1$ kJ·mol⁻¹ ($p^\circ=1$ atm),
 $= -16.28 \pm 1.1$ kJ·mol⁻¹ ($p^\circ=1$ bar)
 $S^\circ = -278.44 \pm 7.7$ J·mol⁻¹·K⁻¹.

This requires a small modification in the values for $\Delta_f H^\circ$ and/or $\Delta_f G^\circ$ for FeSO₄·7H₂O(cr). We have chosen to adjust $\Delta_{\text{sol}} G^\circ = 13.2$ kJ·mol⁻¹ by returning to the 74OYK/BAL γ_\pm values with $\gamma_\pm = 0.15$ at $m=0.1$ mol·kg⁻¹. This results in an adjustment to $\Delta_f H^\circ$ (FeSO₄·7H₂O,cr) from the tentative value of -3013.05 ± 0.85 kJ·mol⁻¹ given in Sec. 2.5 to -3012.6 ± 0.9 kJ·mol⁻¹. The equation for the enthalpy of solution is adjusted for this so that

$$\Delta_r H_{(I)} - \Delta H_{(D-H)} / \text{kJ} \cdot \text{mol}^{-1} = (12.45 \pm 0.12) \\ + (64.16 \pm 2.83)I - (382.5 \pm 57.07)I^2.$$

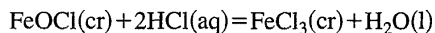
Recommended values for the thermodynamic property values for all substances considered are given in Tables 7 and 8. In addition "reconstituted" process values are given in Table 9.

TABLE 9. The standard thermodynamic properties of reaction ($p^\circ=1$ bar)

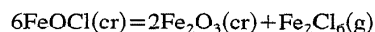
Substance	$\Delta_r H^\circ$ kJ·mol ⁻¹	$\Delta_r G^\circ$ kJ·mol ⁻¹	$\Delta_r S^\circ$ J·mol ⁻¹ ·K ⁻¹
Fe(cr)+2H ⁺ (ao)+Fe ²⁺ (ao)+H ₂ (g)	-90.0 ±0.5	-90.53 ±1.0	1.76 ±3.7
Fe ²⁺ (ao)+H ⁺ (ao) =Fe ³⁺ (ao)+0.5H ₂ (g)	41.0 ±1.5	74.25 ±0.20	-111.46 ±5.1
FeOOH(cr, Goethite)+H ₂ O(l) =Fe ³⁺ (ao)+3OH ⁻ (ao)	106.08 ±2.3	237.71 ±2.0	-441.4 ±7.7
Fe(cr)+2HCl(g) =FeCl ₂ (cr)+H ₂ (g)	156.54 ±0.5	-111.11 ±0.6	-152.38 ±0.25
FeCl ₂ (cr)=FeCl ₂ (ai)	-83.00 ±0.14	-51.26 ±1.1	-106.46 ±3.7
FeCl ₂ (cr)+HCl(g) =FeCl ₃ (cr)+0.5H ₂ (g)	37.81 ±0.25	65.19 ±0.27	-91.82 ±0.36
FeCl ₃ (cr)=FeCl ₂ (cr)+0.5Cl ₂ (g)	54.50 ±0.25	30.11 ±0.27	81.80 ±0.36
FeCl ₃ (cr)=FeCl ₃ (ai)	-154.6 ±1.5	-78.12 ±1.2	-256.4 ±7.7
FeCl ₂ (cr)+2HBr(ai) =FeBr ₂ (cr)+2HCl(ai)	4.12 ±0.30	12.86 ±0.32	-29.29 ±0.40
FeCl ₂ (cr)+2HBr(g) =FeBr ₂ (cr)+2HCl(g)	-16.58 ±0.30	-16.27 ±0.31	-0.99 ±0.28
FeBr ₂ (cr)=FeBr ₂ (ai)	-87.12 ±0.25	-64.12 ±1.1	-77.17 ±3.17
FeBr ₃ (cr)=FeBr ₃ (ai)	-149.4 ±1.5		
FeI ₂ (cr)=Fe(cr)+I ₂ (g)	181.12 ±0.80		
FeI ₂ (cr)+2HBr(ai) =FeBr ₂ (cr)+2HI(ai)	2.26 ±0.5		
FeI ₂ (cr)=FeI ₂ (ai)	-84.86 ±0.5		
FeSO ₄ ·7H ₂ O(cr) =FeSO ₄ (ai)+7H ₂ O(l)	12.45 ±0.5	13.24 ±0.5	-2.6 ±3.8

6.2. Other Cycles in the Fe Network

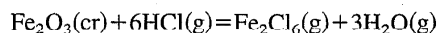
In addition to the cycles used here, there are others which we initially considered and rejected from further consideration because they are too indirect and the values we would obtain for the thermodynamic properties of $\text{FeCl}_3(\text{cr})$ and $\text{FeCl}_2(\text{cr})$ would not be weighted 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 AI.b and AI.c. Those involving $\text{FeCl}_3(\text{g})$ are contained in 89EFI. The reactions are as follows:



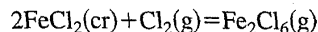
(Appendix AI.b, Nos. 159 and 160),



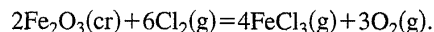
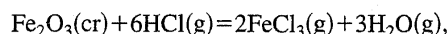
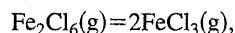
(Appendix AI.b, No. 161)



(Appendix AI.b, No. 162),



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



6.3. Effect of values on other networks

The values given here for some iron compounds, particularly for $\Delta_f G^\circ(\text{Fe}^{2+}, \text{ao})$ and for $\Delta_f H^\circ(\text{FeCl}_3, \text{cr}) - \Delta_f H^\circ(\text{FeCl}_2, \text{cr})$ 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 the $\Delta_f H^\circ(\text{FeCl}_3, \text{cr}) - \Delta_f H^\circ(\text{FeCl}_2, \text{cr})$ from 82WAG/EVA in the analysis of the $\text{UCl}_4(\text{cr}) - \text{UO}_2\text{Cl}_2(\text{cr})$ relationship. The new selections indicate revisions may be necessary not only for $\Delta_f H^\circ(\text{UCl}_4, \text{cr})$, $\Delta_f H^\circ(\text{UF}_4, \text{cr})$, and $\Delta_f H^\circ(\text{UF}_3, \text{cr})$ (see 85O'H and 92FUG), but also for $\Delta_f H^\circ(\text{UO}_3, \text{cr}, \gamma)$, $\Delta_f H^\circ(\text{UO}_2\text{F}_2, \text{cr})$, $\Delta_f H^\circ(\text{UO}_2\text{Cl}_2, \text{cr})$, $\Delta_f H^\circ(\text{U}^{4+}, \text{ao})$, and $\Delta_f H^\circ(\text{UO}_2^{2+}, \text{ao})$. The latter two have also been defined by CODATA (see 89COX/WAG) from 83FUG/PAR.

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* Computer Readable Reaction Catalog

* For Selected Fe Compounds 3/91

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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 "=").

Appendix I: Reaction Catalogs for Selected Fe Compounds

* Chemical Thermodynamics Data Center

* National Institute of Standards and Technology

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 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 " \pm ".

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

$\text{kJ}=\text{kJ}\cdot\text{mol}^{-1}$ for H, G, and $\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for S, C_p ,

$\text{kC}=\text{kcal}\cdot\text{mol}^{-1}$ for H, G, and $\text{kcal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for S, C_p ,

$\text{J}=\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for S, C_p ,

$\text{C}=\text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for S, C_p ,

K, $^\circ\text{C}$ =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 [82IUP] 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:

- ai =hypothetical standard state, $m=1\text{ mol kg}^{-1}$
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,
- 250H₂O, etc. =solution of specified composition,
- D =differential (partial molar property).

A1.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 subscripts, and Greek and math characters are not used. As mentioned in A1.a, for example, the "\$" character in the computer file is actually the " \pm " mathematical symbol; " C_p " is actually " C_p "; " dH " is " ΔH ."

1. Z: 90CTT
R: =Fe(cr)
DV: S, 27.319 \$ 0.002 J
C: bcc phase; $C_p=25.154\text{ } \$ 0.065\text{ J/mol.K}$. At 200 K $\text{H-H}(298)=-2.317\text{ kJ}$, $S=17.9417\text{ J/(mol.K)}$ and $C_p=21.6054\text{ J/(mol.K)}$. From 90HAA/CHA. Using $\text{H-H}(0)=2.192\text{ kJ/mol}$ at 200 K from 85CHA/DAV, $\text{H-H}(0)=4.509\text{ kJ/mol}$ at 298 K.
S: 8/89 VBP, 8/90 VBP
2. Z: 89CTT
R: =Fe(g)
DV: S, 180.489 \$ 0.030 J
C: 1 bar, $C_p=25.675\text{ } \$ 0.010\text{ J/(mol.K)}$, $\text{H-H}(0)=6.850\text{ } \$ 0.005\text{ kJ/mol}$.
S: 8/89 VBP, 4/90 VBP
3. Z: 89CTT
R: Fe(cr)=Fe(g)
DV: H, 415.144 \$ 3.0 kJ
W: -1
C: Separate evaluation by IVTAN.
S: 11/89 VBP
4. Z: 82GAM/REI
R: $\text{Fe}+2(\text{ao})+2\text{Ti}(\text{cr})=\text{Fe}(\text{cr})+2\text{Ti}+(\text{ao})$
DV: G, +13.51 \$ 1.5 kJ
C: K' at 323K and concentration $\text{NaClO}_4=1.0\text{ mol/(kg H}_2\text{O)}$ is $0.07592\text{ } \$ 0.06$. Correction of dG to 298.15 K= $(+6.9\text{ kJ})$ and to $I=0$ (-0.33 kJ). Note: Authors use co-author's half cell value for $2\text{Ti}+(\text{ao})+\text{H}_2(\text{g})=2\text{Ti}(\text{cr})+2\text{H}+(\text{ao})$, $dG_0=68.826\text{ kJ/mol}$ at 298.15 K. NIST and IVTAN evaluations give 64.852 kJ/mol .
S: VBP Aug. 85, 11-87
Z: 78JOH/BAU
5. R: $\text{Fe}(\text{cr})+2\text{H}+(\text{ao})=\text{Fe}+2(\text{ao})+\text{H}_2(\text{g})$
DV: G, -80.08 \$0.20 kJ
C: From cell $\text{Fe}(\text{cr})|\text{FeCl}_2(0.02\text{m})||\text{sat'd KCl}||\text{AgCl}|\text{Ag}(\text{cr})$ E0 constant when ph is over 5.8. Fe(cr) used was 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 $\sim 0.435\text{ V}$. $p=1\text{ atm}$.
S: 5/86 VBP
Z: 60HUR
6. R: $\text{Fe}(\text{cr})+2\text{H}+(\text{ao})=\text{Fe}+2(\text{ao})+\text{H}_2(\text{g})$
DV: G, -90.11\$0.80 kJ
C: From $E_0=+0.467\text{ V}$ at 293 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 $2\text{Fe}(\text{cr})+\text{OH}-(\text{ao})=2\text{Fe}+2(\text{ao})+\text{OH}-(\text{ao})-4\text{e}$. Correction to 298 K is negligible. $p=1\text{ atm}$.
S: 5/86 VBP
Z: 76VAS/RAS
7. R: $\text{Fe}(\text{cr})+3/2\text{ H}_2\text{O}_2(\text{ao})+3\text{HClO}_4(\text{ai})=\text{Fe}(\text{ClO}_4)_3(\text{ai})+3\text{H}_2\text{O}(1)$
DV: H, -617.349\$0.84 kJ
W: 99
C: Linear extrapolation to $I=0$ from measurements in 1, 2, 3 and 4 mol dm⁻³ HClO₄ aqueous solutions containing 1% and 1.5% H₂O₂ using thermal corrections given by 78VAS/YAS. From 1% H₂O₂, $d\text{solnH}_0=-616.89\text{ kJ/mol}$. From 1.5% H₂O, $d\text{solnH}_0=-617.81\text{ kJ/mol}$. Using 67VAS 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: $\text{Fe}(\text{cr}) + 3/2 \text{H}_2\text{O}_2(\text{ao}) + 3\text{HClO}_4(\text{ai}) = \text{Fe}(\text{ClO}_4)_3(\text{ai}) + 3\text{H}_2\text{O}(\text{l})$
DV: H, -617.21\$0.3 kJ
C: Reextrapolation to $I=0$ using Khodakovskii's '86 equation and constants. Individual experimental values are: For $m \text{Fe} + 3(\text{ao}) = 0.012 \text{ mol}/(\text{kg H}_2\text{O})$ in 1.058, 2.220, 3.501, 4.920 molal HClO_4 solns containing 1.0% H_2O_2 , $dH = -616.43, -618.27, -621.24$ and -623.08 kJ/mol , respectively, in solns containing 1.5% H_2O_2 , $dH = -616.51, -618.65, -620.61$ and -622.45 kJ/mol respectively. $dH-D-H$ corrections for extrapolation are 2.67, 3.08, 3.326, and 3.50 kJ/mol.
9. S: O.D., I.Kh. with VBP 5/87
Z: 68SOU/CIHA
R: $\text{Fe} + 2(\text{ao}) + 1/2 \text{H}_2\text{O}_2(\text{ao}) + \text{H} + (\text{ao}) = \text{Fe} + 3(\text{ao}) + \text{H}_2\text{O}(\text{l})$
DV: H, -146.13\$1.0 kJ
C: Oxidation of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ soln (0.1 molal) in .05m H_2SO_4 ; final concentration $\text{Fe} + 3(\text{ao})$ is $5\text{E}-04$ molal with $dH = -146.65$ \$0.84 kJ/mol, and oxidation of $\text{Fe}(\text{ClO}_4)_2$ soln (0.2 molal) in 0.1 HClO_4 soln; final concentration $\text{Fe} + 3$ is $5\text{E}-04$ molal with $dH = -145.60$ \$1.3 kJ/mol
10. S: 6/86 VBP
Z: 71BER/TUM
R: $\text{Fe} + 2(\text{ao}) + 1/2 \text{H}_2\text{O}_2(\text{ao}) + \text{H} + (\text{ao}) = \text{Fe} + 3(\text{ao}) + \text{H}_2\text{O}(\text{l})$
DV: H, -148.76\$0.10 kJ
C: Used FeSO_4 solutions, $m = .003$ to $.009 \text{ mol}/(\text{kg H}_2\text{O})$ with about 0.01 m H_2SO_4 .
11. S: 6/86 VBP
Z: 47FON
R: $\text{Fe} + 2(\text{ao}) + 1/2 \text{H}_2\text{O}_2(\text{ao}) + \text{H} + (\text{ao}) = \text{Fe} + 3(\text{ao}) + \text{H}_2\text{O}(\text{l})$
DV: H, -150.16\$0.50 kJ
F: TN
C: In 0.5 mol $\text{dm}^{-3} \text{HClO}_4$
12. S: 6/86 VBP
Z: 47FON
R: $\text{Fe} + 3(\text{ao}) + 1/2 \text{H}_2(\text{g}) = \text{Fe} + 2(\text{ao}) + \text{H} + (\text{ao})$
DV: H, -40.08\$0.50 kJ
F: TN
C: in 0.5 mol $\text{dm}^{-3} \text{HClO}_4$ solutions
13. S: 6/86 VBP
Z: 35SCH/SWE
R: $\text{Fe} + 2(\text{ao}) + \text{Ag} + (\text{ao}) = \text{Fe} + 3(\text{ao}) + \text{Ag}(\text{cr})$
DV: G, -1.72\$0.2 kJ
C: K meas. from $\text{Fe} + 3(\text{ao})$ reduction in HClO_4 aqueous solutions, $m = 0.9255$ to $0.07404 = \text{mol}/(\text{kg H}_2\text{O})$. Ionic strength solution 1.4 to 0.10. Extrapolation to zero using Davies equation for activity coefficients.
14. S: 6/86, 10/90 VBP
Z: 72WHI/LAN
R: $\text{Fe} + 2(\text{ao}) + \text{H} + (\text{ao}) = \text{Fe} + 3(\text{ao}) + 1/2 \text{H}_2(\text{g})$
DV: G, +74.274\$0.20 kJ
- DV: G, 278.15 K, 71.959\$0.20 kJ
DV: G, 283.15 K, 72.576\$0.20 kJ
DV: G, 288.15 K, 73.165\$0.20 kJ
DV: G, 293.15 K, 73.734\$0.20 kJ
DV: G, 303.15 K, 74.795\$0.20 kJ
DV: G, 308.15 K, 75.287\$0.20 kJ
C: E measured in perchlorate solns at ph 1.48 and ionic strengths of 0.0824 to 0.0840 from 278–308.15 K. Used PT electrode + Ag-AgCl reference electrode with sat'd KCl internal solution. E_0 values were corrected for $\text{FeOH} + 2(\text{ao})$ and $\text{Fe}_2(\text{OH})_2 + 4(\text{ao})$ complexes. $p = 1 \text{ atm}$.
15. S: 6/86 VBP
Z: 72WHI/LAN
R: $\text{Fe} + 2(\text{ao}) + \text{H} + (\text{ao}) = \text{Fe} + 3(\text{ao}) + 1/2 \text{H}_2(\text{g})$
DV: H, 42.75 \$ 1.5 kJ
C: See G reaction. E's measured 278.15 to 308.15 K. 2nd law; authors give 42.67 \$ 1.7 kJ/mol. Calculated $dS = -105.9 \text{ J}/(\text{mol.K})$; See 73NIK/ANT for use of this dS and 88HOV Cp data.
16. S: 8/88 VBP, 3/90 VBP
Z: 73NIK/ANT
R: $\text{Fe} + 2(\text{ao}) + \text{H} + (\text{ao}) = \text{Fe} + 3(\text{ao}) + 1/2 \text{H}_2(\text{g})$
DV: G, +74.30 \$ 0.50 kJ
DV: G, 323.15 K, 76.61 \$ 0.50 kJ
DV: G, 343.15 K, 78.25 \$ 0.8 kJ
DV: G, 363.15 K, 81.77 \$ 0.8 kJ
DV: G, 373.15 K, 83.17 \$ 1.0 kJ
DV: G, 398.15 K, 85.58 \$ 1.0 kJ
DV: G, 423.15 K, 86.93 \$ 1.0 kJ
C: E measured in 0.125 to 1.913 mol $\text{dm}^{-3} \text{HClO}_4$ (10 concentrations). $\text{Fe} + 2(\text{ao})$, $\text{Fe} + 3(\text{ao})$ concentrations are less than 0.01 M. Corrected for ionic strength of solution. Used $\text{Ti}(\text{Hg})$, $\text{TiCl}(\text{cr})$ sat'd KCl solution half cell. $p = 1 \text{ atm}$.
17. S: 3/90 VBP
Z: 73NIK/ANT
R: $\text{Fe} + 2(\text{ao}) + \text{H} + (\text{ao}) = \text{Fe} + 3(\text{ao}) + 1/2 \text{H}_2(\text{g})$
DV: H, 46.7 \$ 2.0 kJ
C: E measured in 0.125 to 1.913 mol $\text{dm}^{-3} \text{HClO}_4$ (10 concentrations). $\text{Fe} + 2(\text{ao})$, $\text{Fe} + 3(\text{ao})$ concentrations are less than 0.01 M. Corrected for ionic strength of solution. Used $\text{Ti}(\text{Hg})$, $\text{TiCl}(\text{cr})$ 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. $d(H-H_{298.15})$ at mean $T(319 \text{ K}) = 1.2 \text{ kJ/mol}$, taken from Cp measurements $\text{Fe} + 2(\text{ao})$ and $\text{Fe} + 3(\text{ao})$ by 88HOV. Third Law value, using $dS = -105.9 \text{ J}/(\text{mol.K})$ is 42.27 \$ 1.4 kJ/mol. dS over range 298 to 323 K is $-57.9 \text{ J}/(\text{mol.K})$. Over entire range $dS = -72.2 \text{ J}/(\text{mol.K})$.
18. S: 3/90 VBP
Z: 58LAP
R: $\text{Fe} + 2(\text{ao}) + \text{H} + (\text{ao}) = \text{Fe} + 3(\text{ao}) + 1/2 \text{H}_2(\text{g})$
DV: G, 71.206\$2.0 kJ
W: 99
C: Effect of ph in the range from 1.5 to 11.0 on oxid-red'n potential of $\text{Fe} + 3(\text{ao}) - \text{Fe} + 2(\text{ao}) - \text{SO}_4^{2-}(\text{ao})$ aqueous system. Obtains E_0

- Fe+2(ao) Fe+3(ao)=0.738 V and log saturated calomel half cell. Concentration of SO₄-2(ao)=0.04 mol dm⁻³. Corrects for aFe+3/aFe+2 using Debye-Huckel eqn; no extrapolation to I=0. See recalculations by 60MAT. p=1 atm.
19. S: 6/86 VBP
Z: 37SCH/SHE
R: Fe+2(ao)+H+(ao)=Fe+3(ao)+1/2 H₂(g)
DV: G, +74.303\$0.010 kJ
C: From cell measurements(H₂ electrode) in HClO₄, m=0.273 to 0.0259 mol/(kg H₂O)-1. Ratio of [Fe+3] to [Fe+2] maintained at 1.0. Corrects for activity coef. and extrap. to m=0. Corrects for hydrolysis of Fe+3(ao) to Fe(OH)+2(ao). p=1 atm.
20. S: 6/86 VBP
Z: 34BRA/HER
R: Fe+2(ao)+Ag+(ao)=Fe+3(ao)+Ag(cr)
DV: G, -2.512 \$ 0.25 kJ
C: Corrected data of 12NOY/BRA. Measurements in acidified nitrate salt solutions at high ionic strength
21. S: 6/86, 10/90 VBP
Z: 34BRA/HER
R: Fe+2(ao)+1/2 Hg₂+2(ao)=Fe+3(ao)+Hg(l)
DV: G, -2.46 \$ 0.25 kJ
C: Corrected data of 31POP/FLE. Measurements in acidified perchlorate salt solutions at low ionic strength.
22. S: 6/86, 10/90 VBP
Z: 53MAG/HUI
R: Fe(ClO₄)₂(HClO₄+55.5H₂O:au)
+HClO₄(D:HClO₄+55.5H₂O)
=Fe(ClO₄)₃(HClO₄+55.5H₂O:au)+1/2 H₂(g)
DV: H, +40.58\$0.84 kJ
C: From e.m.f. meas. at 288, 298 and 623 K. p=1 atm.
23. S: 6/86 VBP
Z: 53MAG/HUI
R: Fe+2(ao)+H+(ao)=Fe+3(ao)+1/2 H₂(g)
DV: G, 73.44\$1.0 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.
24. S: 6/86 VBP
Z: 51CON/MCV
R: Fe(ClO₄)₂(HClO₄+110H₂O:au)
+HClO₄(D:HClO₄+110H₂O)
=Fe(ClO₄)₃(HClO₄+110H₂O:au)+1/2 H₂(g)
DV: H, +41.61\$1.0 kJ
C: From e.m.f. meas. 283-308 K. Initial concentration Fe+2(ao)~0.025 moles (kg H₂O)-1.
25. S: 6/86 VBP
Z: 51CON/MCV
R: Fe+2(ao)+H+(ao)=Fe+3(ao)+1/2 H₂(g)
DV: G, +74.37\$0.50 kJ
C: E=0.7394 V in 0.504 mol 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
26. Z: 60MAT
R: Fe+2(ao)+H+(ao)=Fe+3(ao)+1/2 H₂(g)
DV: G, +74.35\$0.20 kJ
C: E₀=-0.771 V. Recalculation of results of 58LAP; corrects for Fe+3-SO₄-2 complexing. Uses Davies equation. p=1 atm.
- S: 6/86 VBP
27. Z: 71LAN/WHI
R: FeOOH(cr, a)+H₂O(l)=Fe+3(ao)+3OH-(ao)
DV: G, +247.7 \$ 3.0 kJ
C: From laboratory solution containing crystalline Goethite and ground waters for beds containing iron minerals.
- S: 8/87, 10/90 VBP
28. Z: 85HSU/MAR
R: FeOOH(cr, al)+H₂O(l)=Fe+3(ao)+3 OH-(ao)
DV: G, 225.46 \$ 2.0 kJ
C: Aged Fe(ClO₄)₃ solutions, nine to sixteen a, at 298 \$ 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 ionic strength solutions of 0.005, 0.04 and 0.2 M. Corrections for hydrolysis were made.
- S: 10/90 VBP
29. Z: 60MAT
R: Fe(OH)₃(cr)=Fe+3(ao)+3 OH-(ao)
DV: G, +223.47\$1.0 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
30. Z: 89CTT
R: Fe(OH)₂(g)
DV: S, 286.94 \$ 8.0 J
C: One Bar value. H-H₀=17.816 \$ 2.00 KJ/mol, Cp=84.444 \$ 6.0 J/(mol.K) Sent 9/87
- S: 8/89 VBP
31. Z: 1882THO
R: FeCl₃(300H₂O)+3NaOH(100H₂O)
=Fe(OH)₃(am)+3NaCl(600H₂O)
DV: H, -104.43\$2.0 kJ
F: TN
C: dH=-102.51 kJ/mol at 293 K; estimated dCp=+380 J/(mol.K)
- S: 6/87 VBP
32. Z: 1873BER
R: Fe₂(SO₄)₃(au)+6KOH(200H₂O)
=Fe(OH)₃(am)+3K₂SO₄(400H₂O)
DV: H, -246.9\$6.0 kJ
F: TN
C: dH=-251.0 kJ/mol at 291 K; estimated dCp=-600 J/(mol.K).
- S: 6/87 VBP
33. Z: 60MAT
R: 3Fe+2(ao)+4H₂O(l)=Fe₃O₄(cr)+8H+(ao)+2e
DV: G, 237.23\$1.0 kJ

- 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: $\text{Fe}+2(\text{ao})+3\text{H}_2\text{O}(\text{l})=\text{Fe}(\text{OH})_3(\text{cr})+3\text{H}+(\text{ao})+\text{e}$
 DV: G, 87.61\$2.0 kJ
 W: 99
 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 Fe+2(ao)-Fe+3(ao)=0.738 V and lg Ks0 Fe(OH)3(cr)=-39.43. Reference electrode was a saturated calomel half cell. Concentration of SO4-2(ao)=0.04 mol dm-3. Corrects for aFe+3/aFe+2 using Debye-Huckel equation; no extrapolation to I=0. See recalculations by 60MAT. $p=1$ atm.
- S: 6/86 VBP
 Z: 58LAP
 R: $3\text{Fe}+2(\text{ao})+4\text{H}_2\text{O}(\text{l})=\text{Fe}_3\text{O}_4(\text{cr})+8\text{H}+(\text{ao})+2\text{e}$
 DV: G, 232.72\$2.0
 W: 99
 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 Fe+2(ao)-Fe+3(ao)=0.738 V and lg Ks0 Fe(OH)3(cr)=-39.43. Reference electrode was a saturated calomel half cell. Concentration of SO4-2(ao)=0.04 mol dm-3. Corrects for aFe+3/aFe+2 using Debye-Huckel equation; no extrapolation to I=0. See recalculations by 60MAT. $p=1$ atm.
- S: 6/86 VBP
 Z: 70SWE/BAE
 R: $1/3\text{Fe}_3\text{O}_4(\text{cr})+2\text{H}+(\text{ao})+1/3\text{H}_2(\text{g})=\text{Fe}+2(\text{ao})+4/3\text{H}_2\text{O}(\text{l})$
 DV: G, -68.6\$3.0 kJ
 C: Solubility Fe3O4(cr) in dilute aqueous solns satd 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(ao), FeOH+(ao), Fe(OH)2(ao), and Fe(OH)3-1(ao). dS(298) for reaction forming Fe+2(ao) 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, 7/88 VBP
 Z: 70SWE/BAE
 R: $1/3\text{Fe}_3\text{O}_4(\text{cr})+\text{H}+(\text{ao})+1/3\text{H}_2(\text{g})=\text{FeOH}+(\text{ao})+1/3\text{H}_2\text{O}(\text{l})$
 DV: G, -15.43 \$ 5.0 kJ
 DV: S, -99\$17 J
- C: Solubility Fe3O4(cr) in dilute aqueous solns satd 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(ao), FeOH+(ao), Fe(OH)2(ao), and Fe(OH)3-1(ao). dS(298) for reaction forming Fe+2(ao) was restricted to -25.3 cal/(mol.K) using S0(Fe+2, ao) from 68LAR/CER. Used dCp=14 J/(mol.K). $p=1$ atm.
- S: 5/86 VBP, 7/88 VBP
 Z: 70SWE/BAE
 R: $1/3\text{Fe}_3\text{O}_4(\text{cr})+1/3\text{H}_2(\text{g})+2/3\text{H}_2\text{O}(\text{l})=\text{Fe}(\text{OH})_2(\text{ao})+\text{H}+(\text{ao})$
 DV: G, +48.71\$10 kJ
 DV: S, -99 \$ 25 J
 C: Solubility Fe3O4(cr) in dilute aqueous solns satd 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(ao), FeOH+(ao), Fe(OH)2(ao), and Fe(OH)3-1(ao). dS(298) for reaction forming Fe+2(ao) was restricted to -25.3 cal/(mol.K) using S0(Fe+2, ao) from 68LAR/CER. $p=1$ atm.
- S: 5/86 VBP
 Z: 70SWE/BAE
 R: $1/3\text{Fe}_3\text{O}_4(\text{cr})+5/3\text{H}_2(\text{g})+1/3\text{H}_2\text{O}(\text{l})=\text{Fe}(\text{OH})_3-1(\text{ao})+\text{H}+(\text{ao})$
 DV: G, +99.42\$10 kJ
 DV: S, -207\$30 J
 C: Solubility Fe3O4(cr) in dilute aqueous solns satd 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(ao), FeOH+(ao), Fe(OH)2(ao), and Fe(OH)3-1(ao) was restricted. dS(298) for reaction forming Fe+2(ao) was restricted to -25.3 cal/(mol.K) using S0(Fe+2, ao) from 68LAR/CER. $p=1$ atm.
- S: 5/86 VBP
 Z: 70SWE/BAE
 R: $\text{Fe}+2(\text{ao})+\text{H}_2\text{O}(\text{l})=\text{FeOH}+(\text{ao})+\text{H}+(\text{ao})$
 DV: G, +53.1\$2.9 kJ
 C: Difference in 2 extrapolated K's.
 S: 5/86 VBP
41. Z: 80TRE/LEB

- R: $1/3\text{Fe}_3\text{O}_4(\text{cr}) + 2\text{H} + (\text{ao}) + 1/3\text{H}_2(\text{g}) = \text{Fe} + 2(\text{ao}) + 4/3\text{H}_2\text{O}(\text{l})$
 DV: H, -85.44\$4.0 kJ
 DV: G, -64.26\$ 2.0 kJ
 C: $dH(473\text{ K}) = -78.09\text{ kJ/mol}$ and $dS(473\text{ K}) = -51.63\text{ J/(mol.K)}$. Evaluator used $dC_p = 42\text{ J/(mol.K)}$ from 70SWE/BAE
- C: Solubility of carefully characterized $\text{Fe}_3\text{O}_4(\text{cr})$ in dilute aqueous solutions satd with $\text{H}_2(\text{g})$ measured from 373 to 573 K in flow apparatus. Solution compositions included either HCl molalities of up to 1 mmole(kg H_2O)-1 or NaOH molalities of up to 40 mmole (kg H_2O)-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 $\text{Fe}+2(\text{ao})$, $\text{FeOH}+(\text{ao})$, $\text{Fe}(\text{OH})_2(\text{cr})$, $\text{Fe}(\text{OH})_3-(\text{ao})$, $\text{Fe}(\text{OH})_3(\text{cr})$ and $\text{Fe}(\text{OH})_4-(\text{ao})$. Values extrapolated by authors to 298.15 K. $S_0(\text{FeOH}+(\text{ao})-S_0(\text{Fe}+2, \text{ao}))$ was constrained to be 12.6 J/(K.mol) from 78JOH/BAU. $p=1\text{ atm}$.
- S: 5/86 VBP, 3/88 VBP
42. Z: 80TRE/LEB
 R: $1/3\text{Fe}_3\text{O}_4(\text{cr}) + \text{H} + (\text{ao}) + 1/3\text{H}_2(\text{g}) = \text{FeOH}+(\text{ao}) + 1/3\text{H}_2\text{O}(\text{l})$
 DV: H, -58.9\$6.0 kJ
 DV: G, -9.11\$ 2.5 kJ
 C: Authors established $dC_p = 125\text{ J/(mol.K)}$ used. $dH(473\text{ K}) = -36.78\text{ kJ/mol}$ with $dS(475\text{ K}) = -108.96\text{ J/(mol.K)}$. If use $dC_p = 14\text{ J/mol}$ from 70 SWE/BAE, dH and dG are -39.23 and -4.8 kJ/mol respectively.
- C: Solubility of carefully characterized $\text{Fe}_3\text{O}_4(\text{cr})$ in dilute aqueous solutions satd with $\text{H}_2(\text{g})$ measured from 373 to 573 K in flow apparatus. Solution compositions included either HCl molalities of up to 1 mmole(kg H_2O)-1 or NaOH molalities of up to 40 mmole (kg H_2O)-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 $\text{Fe}+2(\text{ao})$, $\text{FeOH}+(\text{ao})$, $\text{Fe}(\text{OH})_2(\text{cr})$, $\text{Fe}(\text{OH})_3-(\text{ao})$, $\text{Fe}(\text{OH})_3(\text{cr})$ and $\text{Fe}(\text{OH})_4-(\text{ao})$. Values extrapolated by authors to 298.15 K. $S_0(\text{FeOH}+(\text{ao})-S_0(\text{Fe}+2, \text{ao}))$ was constrained to be 12.6 J/(K.mol) from 78JOI/BAU. $p=1\text{ atm}$.
- S: 5/86 VBP, 3/88 VBP
43. Z: 80TRE/LEB
 R: $1/3\text{Fe}_3\text{O}_4(\text{cr}) + 5/3\text{H}_2\text{O}(\text{l}) + 1/3\text{H}_2(\text{g}) = \text{Fe}(\text{OH})_3-1(\text{ao}) + \text{H} + (\text{ao})$
 DV: H, 72.8\$8.0 kJ
 DV: G, 127.7\$3.0 kJ
 C: Authors est'd $dC_p = -10.6\text{ J/(mol.K)}$ used. $dH(473\text{ K}) = 71.58\text{ kJ/mol}$ and $dS(473\text{ K}) = -188.71\text{ J/(mol.K)}$.
- C: Solubility of carefully characterized $\text{Fe}_3\text{O}_4(\text{cr})$ in dilute aqueous solutions satd with $\text{H}_2(\text{g})$ measured from 373 to 573 K in flow apparatus. Solution compositions included either HCl molalities of up to 1 mmole(kg H_2O)-1 or NaOH molalities of up to 40 mmole (kg H_2O)-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 $\text{Fe}+2(\text{ao})$, $\text{FeOH}+(\text{ao})$, $\text{Fe}(\text{OH})_2(\text{cr})$, $\text{Fe}(\text{OH})_3-(\text{ao})$, $\text{Fe}(\text{OH})_3(\text{cr})$ and $\text{Fe}(\text{OH})_4-(\text{ao})$. Values extrapolated by authors to 298.15 K. $S_0(\text{FeOH}+(\text{ao})-S_0(\text{Fe}+2, \text{ao}))$ was constrained to be 12.6 J/(K.mol) from 78JOH/BAU. $p=1\text{ atm}$.
- S: 5/86 VBP, 3/88 VBP
44. Z: 80TRE/LEB
 R: $1/3\text{Fe}_3\text{O}_4(\text{cr}) + 1/3\text{H}_2(\text{g}) + 2/3\text{H}_2\text{O}(\text{l}) = \text{Fe}(\text{OH})_2(\text{ao})$
 DV: H, 20.8\$4.0 kJ
 DV: G, 55.7\$ 2.0 kJ
 C: Authors established $dC_p = 27\text{ J/(mol.K)}$ used. $dH(473\text{ K}) = 25.5\text{ kJ/mol}$ and $dS(473\text{ K}) = -102.35\text{ J/(mol.K)}$.
- C: Solubility of carefully characterized $\text{Fe}_3\text{O}_4(\text{cr})$ in dilute aqueous solutions satd with $\text{H}_2(\text{g})$ measured from 373 to 573 K in flow apparatus. Solution compositions included either HCl molalities of up to 1 mmole(kg H_2O)-1 or NaOH molalities of up to 40 mmole (kg H_2O)-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 $\text{Fe}+2(\text{ao})$, $\text{FeOH}+(\text{ao})$, $\text{Fe}(\text{OH})_2(\text{cr})$, $\text{Fe}(\text{OH})_3-(\text{ao})$, $\text{Fe}(\text{OH})_3(\text{cr})$ and $\text{Fe}(\text{OH})_4-(\text{ao})$. Values extrapolated by authors to 298.15 K. $S_0(\text{FeOH}+(\text{ao})-S_0(\text{Fe}+2, \text{ao}))$ was constrained to be 12.6 J/(K.mol) from 78JOH/BAU. $p=1\text{ atm}$.
- S: 5/86 VBP, 3/88 VBP
45. Z: 80TRE/LEB
 R: $1/3\text{Fe}_3\text{O}_4(\text{cr}) + 5/3\text{H}_2\text{O}(\text{l}) = \text{Fe}(\text{OH})_3(\text{ao}) + 1/6\text{H}_2(\text{g})$
 DV: S, -72\$8.0 J
 C: Authors $dC_p = -10.6\text{ J/(mol.K)}$ used. $dS(473\text{ K}) = 75.4\text{ J/(mol.K)}$.
- C: Solubility of carefully characterized $\text{Fe}_3\text{O}_4(\text{cr})$ in dilute aqueous solutions satd with $\text{H}_2(\text{g})$ measured from 373 to 573 K in flow apparatus. Solution compositions included either HCl molalities of up to 1 mmole(kg H_2O)-1 or NaOH molalities of up to 40 mmole (kg H_2O)-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 $\text{Fe}+2(\text{ao})$, $\text{FeOH}+(\text{ao})$, $\text{Fe}(\text{OH})_2(\text{cr})$, $\text{Fe}(\text{OH})_3-(\text{ao})$, $\text{Fe}(\text{OH})_3(\text{cr})$ and $\text{Fe}(\text{OH})_4-(\text{ao})$. Values extrapolated by authors to 298.15 K. $S_0(\text{FeOH}+(\text{ao})-S_0(\text{Fe}+2, \text{ao}))$ was constrained to be 12.6 J/(K.mol) from 78JOH/BAU. $p=1\text{ atm}$.

- FeOH+(ao), Fe(OH)2(cr), Fe(OH)3-(ao), Fe(OH)3(cr) and Fe(OH)4-(ao). Values extrapolated by authors to 298.15 K. S0(FeOH, +ao)-S0(Fe+2, ao) was constrained to be 12.6 J/(K.mol) from 78JOH/BAU. p=1 atm.
46. S: 5/86 VBP, 3/88 VBP
Z: 80TRE/LEB
R: $1/3\text{Fe}_3\text{O}_4(\text{cr}) + 8/3\text{H}_2\text{O}(\text{l}) = \text{Fe}(\text{OH})_4-1(\text{ao}) + 1/6\text{H}_2(\text{g}) + \text{H}+(\text{ao})$
DV: S, -192.6\$8.0
C: Authors dCp=10.5 J/(mol.K) used. dS (473 K) = 187.76 J/(mol.K).
C: Solubility of carefully characterized Fe3O4(cr) in dilute aqueous solutions satd with H2(g) measured from 373 to 573 K in flow apparatus. Solution compositions included either HCl molalities of up to 1 mmole(kg H2O)-1 or NaOH molalities of up to 40 mmole (kg H2O)-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 Fe+2(ao), FeOH+(ao), Fe(OH)2(cr), Fe(OH)3-(ao), Fe(OH)3(cr) and Fe(OH)4-(ao). Values extrapolated by authors to 298.15 K. S0(FeOH, +ao)-S0(Fe+2, ao) was constrained to be 12.6 J/(K.mol) from 78JOH/BAU. p=1 atm.
47. S: 5/86 VBP
Z: 89CTT
R: =Fe2O3 (cr)
DV: S, 87.483 \$ 0.06 J
C: Evaluation of J. Haas
48. S: 10/89 VBP
Z: 70KIN/WEL
R: =FeOOH(cr)
DV: S, 60.38\$0.63 J
C: low temp Cp measurements 51 to 298 K.
49. S: 6/86 VBP
Z: 90CTT
R: =FeOOH(cr)
DV: S, 60.40 \$ 0.6 J
C: Work of 70KIN/WEL. H-H0=10.820 \$ 0.08 kJ, Cp=74.480 \$ 0.07 J/(mol.K).
50. S: 5/90 VBP
Z: 90CTT
R: =Fe(OH)2 (cr)
DV: S, 93.00 \$ 6.0 J
C: Est'd by IVTAN
51. S: 3/90 VBP
Z: 65BAR
R: $2\text{FeOOH}(\text{cr}) = \text{Fe}_2\text{O}_3(\text{cr}) + \text{H}_2\text{O}(\text{l})$
F: TN
DV: H, 7.87\$0.84 kJ
C: Also IVTAN Equation 367, with additional decimal. dsolnH FeOOH(cr) in 20.1 wt% HF = -82.26\$0.60 kJ/mol combined with dsolnH Fe2O3(cr) = -175.90\$0.60 kJ/mol and ddilnH = +1.76 kJ/mol.
52. S: 5/86 VBP
Z: 53LEU/KOL
R: $\text{Fe}(\text{OH})_2(\text{cr}) = \text{Fe} + 2(\text{ao}) + 2\text{OH}-(\text{ao})$
DV: G, 86.17\$1.0 kJ
53. F: TN
C: K=8(\$3)E-16. Used activity coefficients from 37KIE
S: 5/86 VBP
Z: 53LEU/KOL
R: $\text{Fe}(\text{OH})_2(\text{cr}) = \text{FeOH}+(\text{ao}) + \text{OH}-(\text{ao})$
F: TN
DV: G, 53.7\$0.6 kJ
C: K=3.9 (\$1.0)E-10. Used activity coefficients from 37KIE
S: 5/86 VBP
Z: 80DIB/CHE
R: $\text{Fe}(\text{cr}) + \text{Cd}(\text{OH})_2(\text{cr}) = \text{Fe}(\text{OH})_2(\text{cr}) + \text{Cd}(\text{cr})$
DV: H, -10.61\$1.0kJ
C: Electrochem. measurements anodic enthalpy plateau.
54. S: 5/86 VBP
Z: 43FRI/RIH
R: $\text{Fe}(\text{OH})_2(\text{cr}) + 1/4\text{O}_2(\text{g}) = 0.5 \text{Fe}_2\text{O}_3(\text{cr}) + \text{H}_2\text{O}(\text{l})$
DV: H, -125.3\$2.5 kJ
C: dE(296 K) = -124.68 kJ/mol used as dH in IVTAN catalog equation 372
55. S: 5/86 VBP
Z: 78JOH/BAU
R: $\text{Fe} + 2(\text{ao}) + \text{H}_2\text{O}(\text{l}) = \text{FeOH} + 1(\text{ao}) + \text{H}+(\text{ao})$
DV: G, 52.69\$0.57 kJ
DV: H, 35.6\$5.0 kJ
C: From FeCl2 (aq) or Fe(ClO4)2 (aq), ionic strength less than 0.1. Activity coef. for all species from Debye-Huckel relationship.
56. S: 5/86 VBP
Z: 78JOH/BAU
R: $\text{Fe}(\text{OH})_2(\text{am}) = \text{Fe} + 2(\text{ao}) + 2\text{OH}-(\text{ao})$
DV: H, 19.66\$1.7 kJ
DV: G, 82.14\$0.21 kJ
C: Freshly pptd.
57. S: 5/86 VBP
Z: 32RAN/FRA
R: $\text{Fe}(\text{cr}) + \text{HgO}(\text{cr}) + \text{H}_2\text{O}(\text{l}) = \text{Hg}(\text{l}) + \text{Fe}(\text{OH})_2(\text{cr})$
DV: G, -187.76\$0.97 kJ
F: TN
W: 99
C: See combined reaction, linking Fe(OH)2(cr) to Fe+2(ao) or FeCl2(ai). E=0.973\$0.005 V. IVTAN equation 374 assigned value to dH0 incorrectly.
58. S: 5/86 VBP
Z: 33KRI/AWS
R: $\text{Fe}(\text{OH})_2(\text{cr}) = \text{Fe} + 2(\text{ao}) + 2\text{OH}-(\text{ao})$
DV: G, 82.7\$ kJ
C: Potentiometric
59. S: 7/86 VM
Z: 50ARD
R: $\text{Fe}(\text{OH})_2(\text{cr}) = \text{Fe} + 2(\text{ao}) + 2\text{OH}-(\text{ao})$
DV: G, 77.7\$ kJ
C: Potentiometric
60. S: 7/86 VM
Z: 51QUI
R: $\text{Fe}(\text{OH})_2(\text{cr}) = \text{Fe} + 2(\text{ao}) + 2\text{OH}-(\text{ao})$
DV: G, 84.4\$ kJ
C: Potentiometric
61. S: 7/86 VM
Z: 63BER/KOV
R: $3\text{Fe}(\text{OH})_2(\text{cr}) = \text{Fe}_3\text{O}_4(\text{cr}) + 2\text{H}_2\text{O}(\text{g}) + \text{H}_2(\text{g})$

- DV: H, 207.9\$11
C: Third law value. Second law value=308 kJ/mol. DTA, 422-465 K. Graph only.
63. S: 7/86 VM
Z: 59SCH
R: $2\text{FeOOH}(\text{cr})=\text{Fe}_2\text{O}_3(\text{cr})+\text{H}_2\text{O}(\text{l})$
DV: H, 14.7 \$ 10 kJ
F: TN
C: $dG(400\text{ K})=0$; 3rd law value. PVT, 411-453 K.
S: VM 7/86, 8/89 VBP
64. Z: 64FER
R: $2\text{FeOOH}(\text{cr})=\text{Fe}_2\text{O}_3(\text{cr})+\text{H}_2\text{O}(\text{l})$
DV: H, 4.9 \$ 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 ($dH=5.2\text{ kJ/mol}$); corrected to 298.15 K and $\text{H}_2\text{O}(\text{l})$ using $d(\text{H}-\text{H}298)=1.37\text{ kJ/(mol H}_2\text{O)}$
S: VM 7/86, 5/89 VBP
65. Z: 75KOR/FAD
R: $2\text{FeOOH}(\text{cr})=\text{Fe}_2\text{O}_3(\text{cr})+\text{H}_2\text{O}(\text{g})$
DV: H, 57.7\$4.0 kJ
C: IVTAN 3-85 eq. 368; corrected from 57.9 kJ/mol; differential scan. calorimetry
S: VM 7/86
66. Z: 1882THO
R: $\text{FeCl}_2(\text{cr})+\text{H}_2\text{SO}_4(200\text{H}_2\text{O})+2\text{KOH}(100\text{H}_2\text{O})=2\text{HCl}(100\text{H}_2\text{O})+\text{K}_2\text{SO}_4(200\text{H}_2\text{O})+\text{Fe}(\text{OH})_2(\text{cr})$
DV: H, -116.3\$3.0 kJ
C: IVTAN 3-85 eq. 369; summation of $d\text{solnH}(\text{FeCl}_2, \text{cr})=-74.89\text{ kJ/mol}$, $d\text{mixH}(\text{FeCl}_2(200\text{H}_2\text{O})\text{ with H}_2\text{SO}_4(200\text{H}_2\text{O}))=-15.06\text{ kJ/mol}$ and $d\text{neutH}=-26.53\text{ kJ/mol}$. $dH(292\text{ K})=-116.5\text{ kJ/mol}$ corrected by VBP using $dC_p=40\text{ J/(mol.K)}$
S: VM 7/86, 5/87 VBP
67. Z: 1882THO
R: $\text{FeSO}_4(200\text{H}_2\text{O})+\text{Ba}(\text{OH})_2(200\text{H}_2\text{O})=\text{BaSO}_4(\text{c})+\text{Fe}(\text{OH})_2(\text{cr})$
DV: H, -47.6\$5.0 kJ
C: dH meas at 292 K=-50.2 kJ/mol. $dC_p=440\text{ J/(mol.K)}$ used by VBP. IVTAN 3-85 eq. 370
S: VM 7/86, 6/87 VBP
68. Z: 1882THO
R: $\text{Fe}(\text{OH})_2(\text{cr})+0.25\text{O}_2(\text{g})=0.5\text{Fe}_2\text{O}_3(\text{cr})+\text{H}_2\text{O}(\text{l})$
DV: H, -114.2\$5.0 kJ
C: IVTAN 3-85 eq. 371. Combustion calorimetry.
S: VM 7/86
69. Z: 75KOR/FAD
R: $\text{FeOOH}(\text{cr})=\text{FeOOH}(\text{cr}_2)$
DV: H, 21\$10.0 kJ
C: $\text{FeOOH}(\text{cr})$ is alpha form (Goethite); cr_2 is gamma form (lepidocrite). From differences in dH dehydration.
S: 6/87 VBP
70. Z: 37FRI/ZER
R: $\text{FeOOH}(\text{cr})=\text{FeOOH}(\text{cr}_2)$
DV: H, 11.7\$5.0 kJ
C: Enthalpy meas. of alpha and gamma forms in 40% HF solutions at 293.6 K corrected for moisture content of samples.
71. S: 6/87 VBP
Z: 32RAN/FRA
R: $\text{Fe}(\text{OH})_2(\text{cr})+\text{Hg}_2\text{Cl}_2(\text{cr})=\text{Hg}(\text{l})+\text{HgO}(\text{cr})+\text{H}_2\text{O}(\text{l})+\text{FeCl}_2(\text{ai})$
DV: G, +52.16\$0.96 kJ
F: TN
C: Combined reaction. Measured $\text{Fe}(\text{cr})-\text{Fe}(\text{OH})_2(\text{cr})$ E0 combined with 32RAN/FRA2 $\text{Fe}(\text{cr})-\text{FeCl}_2(\text{ai})$. E0=-0.270\$0.005 V.
S: 5/86 VBP
72. Z: 26HAM
R: $\text{Fe}(\text{cr})+2\text{TlCl}(\text{cr})=\text{FeCl}_2(\text{ai})+2\text{Tl}(\text{cr})$
DV: G, +23.65\$1.0 kJ
C: From left side of equilibrium. Molality $\text{FeCl}_2=0.0453\text{ moles/(kg H}_2\text{O)}$ and $\text{TlCl}=0.0042\text{ moles/(kg H}_2\text{O)}$. gamma from 79GOL/NUT. 32RAN/FRA2 say better agreement with their results is because the 26HAM treatment with $\text{TlCl}(\text{aq})$ removes the finer particles of iron.
S: 5/86 VBP
73. Z: 26HAM
R: $\text{Fe}(\text{cr})+\text{Hg}_2\text{Cl}_2(\text{cr})=\text{FeCl}_2(\text{ai})+2\text{Hg}(\text{l})$
DV: G, -137.0\$2.0 kJ
C: Used electrodes prepared from finely divided $\text{Fe}(\text{cr})$. $\text{Fe}_2\text{O}_3(\text{cr})$ was reduced with H_2 which was O_2 and H_2O free. Mean of 4 meas. with $m=0.10, 0.0865, 0.050$, and 0.0095 . 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 that are too high, prolonged exposure to solutions of FeCl_2 makes activity of the finely divided iron approach those of 32RAN/FRA2.
S: 5/86 VBP
74. Z: 53PAT/THO
R: $\text{Fe}(\text{cr})+\text{Hg}_2\text{Cl}_2(\text{cr})=\text{FeCl}_2(\text{ai})+2\text{Hg}(\text{l})$
DV: G, -129.73\$0.50 kJ
F: TN
C: E0=0.6723\$0.0025 V; mean of measurements: $m\text{ FeCl}_2(\text{aq})=0.0760$ and 0.0160 ; gamma=0.5324 and 0.6857 from 79GOL/NUT. H_2 free Fe was prep'd. by thermal decomposition of $\text{Fe}(\text{CO})_5$ under vacuum (powder obtained used directly as electrode material.) Also massive iron electrodes were prep'd by vacuum fusion of Fe powder. Also special care to remove all traces of O_2 from cells. Authors indicate that variations from their values in E0 for $\text{Fe}|\text{Fe}+2(\text{ao})$ such as from 32RAN/FRA are due to presence of atomic H in metal. This dE was measured to be $\sim 0.054\text{ V}$.
S: 5/86 VBP
75. Z: 32RAN/FRA2
R: $\text{Fe}(\text{cr})+\text{Hg}_2\text{Cl}_2(\text{cr})=\text{FeCl}_2(\text{ai})+2\text{Hg}(\text{l})$
DV: G, -135.60\$0.20 kJ
F: TN
C: E=0.7996 V for 0.1 m FeCl_2 solution; gamma=0.5093 from 79GOL/NUT. E0=0.7027 V. Used two differently prep'd samples $\text{Fe}(\text{cr})$, electrolytic iron deposited on Pt electrodes and Fe produced by reduction of FeO with H_2 . O_2

- carefully excluded from both as described by
32RAN/FRA
76. S: 5/86 VBP
Z: 89CTT
R: =FeF(g)
DV: S, 241.536 \$ 0.6 J
C: H-HO=10.574 \$ 0.10 kJ/mol, Cp=38.868 \$ 0.50 J/(mol.K) One Bar Value. Sent 9/87
77. S: 8/89 VBP
Z: 89CTT
R: =FeF2(cr)
DV: S, 87.00 \$ 0. J
C: H-HO=12.760 kJ/mol, Cp=68.120 J/(mol.K)
** Cp to S above differs widely from 85CHA/DAV. Earlier IVTAN thermal functions give Cp=59.138 J/(mol.K) at 298.15 K.
78. S: 10/89 VBP
Z: 89CTT
R: =FeF2(g)
DV: S, 268.305 \$ 3.0 J
C: H-HO=14.103 \$ 0.400 kJ/mol, Cp=58.527 \$ 2.0 J/(mol.K)
One Bar value
** 9/87 IVTAN and 3/90 Tables list S=268.307 and Cp=58.528 J/(mol.K)
S: 11/89 and 3/91 VBP
79. Z: 89CTT
R: =FeF3(cr)
DV: S, 112.00 \$ 8.0 J
C: H-HO=17.80 \$ 0.50 kJ/mol, Cp=91.40 \$ 1.0 J/(mol.K)
S: 10/89 VBP
80. Z: 90CTT
R: =FeF3(g)
DV: S, 308.211 \$ 7.0 J
C: One Bar, H-HO=15.512 \$ 0.90 kJ/mol, Cp=67.833 \$ 3.0 J/(mol.K). Value from IVTAN 9/87=307.725 J/(mol.K)
S: 10/89 and 4/90 VBP
81. Z: 1882THO
R: Fe(cr)+2HCL(200H2O)=FeCl2(cr)+H2(g)
DV: H, -12.85\$2.0kJ
F: TN
C: Measurements at 292K of Fe(cr), dH=-89.16, and FeCl2(cr), 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(200H2O).
S: 3/86 VBP
82. Z: 27BAG
R: FeCl2(cr)+H2(g)=2HCl(g)+Fe(cr)
DV: H, 156.93\$3.0 kJ
F: TN
C: IVTAN 3-85 EQ. 230, values readjusted (vbp) using S(298.15 K)=118.0 J/(mol.K) from JANAF and 86ARI/BER text calculations. Transpiration; Temp. range 975-1278 K, 7 pts, 3rd law. 2nd law 164.6\$12 kJ/mol. 29JEL/KOO tabulated 4 of these points
S: VM 5/87 and 10/87, 7/88 VBP
83. Z: 50KAN/PET
R: FeCl2(cr)+H2(g)=2HCl(g)+Fe(cr)
- DV: H, 159.87\$1.5kJ
F: TN
C: IVTAN 3-85 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 155.8\$5.2 kJ/mol
S: VM 5/87 and 10/87, 7/88 VBP
84. Z: 52NOV/ORA
R: FeCl2(cr)+H2(g)=2HCl(g)+Fe(cr)
DV: H, 155.02\$1.6kJ
C: IVTAN 3-85 EQ. 232, values readjusted (vbp) using S(298.15 K)=118.0 J/(mol.K) from JANAF and 86ARI/BER text calculations. Circulation; Temp. range 696-796 K, 18pts, third law, second law 137\$10 kJ/mol.
S: VM 5/87 and 10/87, 7/88 VBP
85. Z: 60NOV/MAK
R: FeCl2(cr)+H2(g)=2HCl(g)+Fe(cr)
DV: H, 158.01 \$1.8 kJ
F: TN
C: IVTAN 3-85 EQ. 233, values readjusted (vbp) using S(298.15 K)=118.0 J/(mol.K) from JANAF and 86ARI/BER text calculations. Circulation; Temp. range 673-823 K, 4 pts, third law. second law 134.6 \$4.3 kJ/mol.
S: VM 5/87 and 10/87, 7/88 VBP
86. Z: 38SAN
R: FeCl2(cr)+H2(g)=2HCl(g)+Fe(cr)
DV: H, 154.8 \$1.7 kJ
C: Circulation; Temp. range 769-868 K, 9 pts, 3rd law. 2nd law 158.1 \$4.0 kJ/mol. Values readjusted (vbp) using S(298.15 K)=118.0 J/(mol.K) from JANAF and 86ARI/BER text calculations.
S: VM 5/87 and 10/87, 7/88 VBP
87. Z: 76BUR/GER
R: FeCl2(cr)+H2(g)=2HCl(g)+Fe(cr)
DV: H, 146.2 \$5.1 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 5/87 and 10/87, 7/88 VBP
88. Z: 43WAG/STE
R: FeCl2(cr)+H2(g)=Fe(cr)+2HCl(g)
DV: H, 157.66 \$2.0 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. estimated dCp ~ -300 J/(mol.K)
S: 3/86 VBP; 4/87 VBP
90. Z: 59KOE/COU
R: Fe(cr)+2HCL(12.731H2O)=FeCl2(cr)+H2(g)
DV: H -17.04 \$0.21 kJ
F: TN

- C: Summation of 4 reactions at 303 K, corrected using $dC_p = 236 \text{ J}/(\text{mol}\cdot\text{K})$. $d\text{solnH Fe}(\text{cr})$ and $\text{FeCl}_2(\text{cr})$ at 303 K = $-87.11 \text{ } \$0.17$ and $-62.76 \text{ } \$0.09 \text{ kJ/mol}$ respectively. Same reaction as IVTAN Eq. 389.
- S: 3/86 VBP
91. Z: 88CTT
R: $=\text{FeCl}_2(\text{cr})$
DV: S, 118.0 $\$0.40 \text{ J}$
C: $\text{H}-\text{H}(0) = 16.27 \text{ kJ/mol}$, $C_p = 76.66 \text{ J/mol}\cdot\text{K}$
** See updated 89CTT value below.
** Change in values for S and $\text{H}-\text{H}(0)$ at 298 K results in small differences in third law and second law dH values for all entries for $\text{FeCl}_2(\text{cr})$; dependent upon T correction. Comments spell out values used.
- S: 8/88 VBP
92. Z: 89CTT
R: $=\text{FeCl}_2(\text{cr})$
DV: S, 118.060 $\$0.20 \text{ J}$
C: $\text{H}-\text{H}(0) = 16.10 \text{ kJ/mol}$, $C_p = 76.60 \text{ J/mol}\cdot\text{K}$
S: 11/89 VBP
93. Z: 82COB/MUR
R: $\text{FeCl}_2(\text{cr}) = \text{FeCl}_2(\text{ai})$
DV: H, $-82.906 \text{ } \$0.32 \text{ kJ}$
C: Debye Huckel extrap. from measurements in 0.005 molal HClO_4 . Molality salt from 2E-03 to 0.01; nine points. AH adjusted from 688 to 710 cal/mol.
- S: VBP Aug. 85
94. Z: 90EFI/FUR
R: $\text{FeCl}_2(\text{cr}) = \text{Fe} + 2(\text{ao}) + 2\text{Cl}-(\text{ao})$
DV: H, $-83.11 \text{ } \$0.42 \text{ kJ}$
C: Authors' extrapolation after correction for phi_L D-H from measurements in 0.001 m HClO_4 . Measured values are -82.680 , -82.639 , -82.502 and -81.925 kJ/mol for m $\text{FeCl}_2(\text{aq}) = 0.00459$, 0.00422 , 0.00550 and 0.00849 . Phi L 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: 90EFI/FUR
R: $\text{FeCl}_2(\text{cr}) = \text{FeCl}_2(0.1315(\text{HClO}_4 + 55500\text{H}_2\text{O}))$
DV: H, $-82.437 \text{ } \$0.45 \text{ kJ}$
C: Average of 4 experimental measurements in 0.001 m HClO_4 . See above for individual measurements.
- S: 5/89 VBP
96. Z: 77CER/HEP
R: $\text{FeCl}_2(\text{cr}) = \text{FeCl}_2(\text{ai})$
DV: H, $-83.05 \text{ } \$0.42 \text{ kJ}$
C: Measurements on $\text{FeCl}_2 \cdot 0.0082 \text{ H}_2\text{O}(\text{cr})$, $dH = -82.97 \text{ kJ/mol}$ and $\text{FeCl}_2 \cdot 0.0228(\text{cr})$, $dH = -82.38 \text{ kJ/mol}$, at infinite dilution. These measurements were corrected to anhydrous $\text{FeCl}_2(\text{cr})$ assuming presence of $\text{FeCl}_2 \cdot \text{H}_2\text{O}(\text{cr})$ or $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}(\text{cr})$ in samples with $dH = -62.8 \text{ kJ/mol}$ and -41.8 kJ/mol respectively. This reaction is also in IVTAN catalog, reaction 390.
- S: 3/86, 6/87 VBP
97. Z: 52LI/GRE
R: $\text{FeCl}_2(\text{cr}) = \text{FeCl}_2(8000\text{H}_2\text{O})$
DV: H, $-81.84 \text{ } \$0.84 \text{ kJ}$
F: TN
C: Mean of 5 measurements. Molality range 0.00139 to 0.0117 mols/kg H_2O . In IVTAN catalog, reaction 386 as $dH = -81.5 \text{ } \$0.2 \text{ kJ/mol}$ at infinite dilute. If $\text{phi}(L) = 860 \text{ J/mol}$, $dH_0 = -82.70 \text{ kJ/mol}$.
- S: 3/86 VBP
98. Z: 10RIC/BUR
R: $\text{Fe}(\text{cr}) + 2\text{HCl}(\text{D}:6.31\text{H}_2\text{O}) = \text{FeCl}_2(\text{HCl} + 6.31\text{H}_2\text{O}:\text{au}) + \text{H}_2(\text{g})$
DV: H, -85.78 kJ
C: dH meas at 293 K; Estimated $dC_p = +40 \text{ J/mol}\cdot\text{K}$
- S: 4/87 VBP
99. Z: 47FON2
R: $\text{FeCl}_2(\text{cr}) = \text{FeCl}_2(72.7\text{HClO}_4 + 8000\text{H}_2\text{O})$
DV: H, $-79.50 \text{ } \$0.42 \text{ kJ}$
S: 4/87 VBP
100. Z: 62AKH/KOP
R: $\text{Fe}(\text{cr}) + 2\text{HCl}(\text{D}:55.51\text{H}_2\text{O}) = \text{FeCl}_2(10.6\text{HCl} + 700\text{H}_2\text{O}) + \text{H}_2(\text{g})$
DV: H, $-84.94 \text{ } \$0.10 \text{ kJ}$
F: TN
S: 4/87 VBP
101. Z: 10RIC/ROW
R: $\text{Fe}(\text{cr}) + 2\text{HCl}(200\text{H}_2\text{O}) = \text{FeCl}_2(400\text{H}_2\text{O}) + \text{H}_2(\text{g})$
DV: H, $-86.28 \text{ } \$2.0 \text{ kJ}$
F: TN
C: Measurement at 293.2 K, in concentrated HCl corrected by authors for HCl diln. to obtain value, $dH = -87.03 \text{ kJ/mol}$ for product free of excess acid. Estimated $dC_p = +40 \text{ J/mol}\cdot\text{K}$
- S: 5/87 VBP
102. Z: 87NBS
R: $\text{FeCl}_2(12.54\text{H}_2\text{O}) = \text{FeCl}_2(1100\text{H}_2\text{O})$
DV: H, -15.55 kJ
C: Extrapolated from 41PER measurements at 285.7 K of $d\text{solnH FeCl}_2:4\text{H}_2\text{O}(\text{cr})$ in $n\text{H}_2\text{O}$ from $n=12.8$ to 1100; dC_p corrections using phi Cp from 79BER/MOR.
- S: 4/87 VBP
103. Z: 87NBS
R: $\text{FeCl}_2(13\text{H}_2\text{O}) = \text{FeCl}_2(1100\text{H}_2\text{O})$
DV: H, -15.65 kJ
C: From measurements by 41PER on $d\text{solnH FeCl}_2:4\text{H}_2\text{O}(\text{cr})$ in $n\text{H}_2\text{O}$ from $n=12.8$ to 1100; dC_p corrections using phi Cp from 79BER/MOR
- S: 4/87 VBP
104. Z: 87NBS
R: $\text{FeCl}_2(15\text{H}_2\text{O}) = \text{FeCl}_2(1100\text{H}_2\text{O})$
DV: H, -14.20 kJ
C: From measurements by 41PER on $d\text{solnH FeCl}_2:4\text{H}_2\text{O}(\text{cr})$ in $n\text{H}_2\text{O}$ from $n=12.8$ to 1100; dC_p corrections using phi Cp from 79BER/MOR
- S: 4/87 VBP

105. Z: 87NBS
R: $\text{FeCl}_2(20\text{H}_2\text{O}) = \text{FeCl}_2(1100\text{H}_2\text{O})$
DV: H, -11.00 kJ
C: From measurements by 41PER on dsolnH $\text{FeCl}_2:4\text{H}_2\text{O}(\text{cr})$ in nH_2O from $n=12.8$ to 1100; dCp corrections using ϕ Cp from 79BER/MOR
S: 4/87 VBP
106. Z: 87NBS
R: $\text{FeCl}_2(30\text{H}_2\text{O}) = \text{FeCl}_2(1100\text{H}_2\text{O})$
DV: H, -7.90 kJ
C: From measurements by 41PER on dsolnH $\text{FeCl}_2:4\text{H}_2\text{O}(\text{cr})$ in nH_2O from $n=12.8$ to 1100; dCp corrections using ϕ Cp from 79BER/MOR
S: 4/87 VBP
107. Z: 87NBS
R: $\text{FeCl}_2(40\text{H}_2\text{O}) = \text{FeCl}_2(1100\text{H}_2\text{O})$
DV: H, -6.20 kJ
C: From measurements by 41PER on dsolnH $\text{FeCl}_2:4\text{H}_2\text{O}(\text{cr})$ in nH_2O from $n=12.8$ to 1100; dCp corrections using ϕ Cp from 79BER/MOR
S: 4/87 VBP
108. Z: 87NBS
R: $\text{FeCl}_2(50\text{H}_2\text{O}) = \text{FeCl}_2(1100\text{H}_2\text{O})$
DV: H, -5.10 kJ
C: From measurements by 41PER on dsolnH $\text{FeCl}_2:4\text{H}_2\text{O}(\text{cr})$ in nH_2O from $n=12.8$ to 1100; dCp corrections using ϕ Cp from 79BER/MOR
S: 4/87 VBP
109. Z: 87NBS
R: $\text{FeCl}_2(75\text{H}_2\text{O}) = \text{FeCl}_2(1100\text{H}_2\text{O})$
DV: H, -3.60 kJ
C: From measurements by 41PER on dsolnH $\text{FeCl}_2:4\text{H}_2\text{O}(\text{cr})$ in nH_2O from $n=12.8$ to 1100; dCp corrections using ϕ Cp from 79BER/MOR
S: 4/87 VBP
110. Z: 87NBS
R: $\text{FeCl}_2(100\text{H}_2\text{O}) = \text{FeCl}_2(1100\text{H}_2\text{O})$
DV: H, -2.80 kJ
C: From measurements by 41PER on dsolnH $\text{FeCl}_2:4\text{H}_2\text{O}(\text{cr})$ in nH_2O from $n=12.8$ to 1100; dCp corrections using ϕ Cp from 79BER/MOR
S: 4/87 VBP
111. Z: 87NBS
R: $\text{FeCl}_2(200\text{H}_2\text{O}) = \text{FeCl}_2(1100\text{H}_2\text{O})$
DV: H, -1.33 kJ
C: From measurements by 41PER on dsolnH $\text{FeCl}_2:4\text{H}_2\text{O}(\text{cr})$ in nH_2O from $n=12.8$ to 1100; dCp corrections using ϕ Cp from 79BER/MOR
S: 4/87 VBP
112. Z: 87NBS
R: $\text{FeCl}_2(500\text{H}_2\text{O}) = \text{FeCl}_2(1100\text{H}_2\text{O})$
DV: H, -0.40 kJ
C: From measurements by 41PER on dsolnH $\text{FeCl}_2:4\text{H}_2\text{O}(\text{cr})$ in nH_2O from $n=12.8$ to 1100; dCp corrections using ϕ Cp from 79BER/MOR
S: 4/87 VBP
113. Z: 87NBS
R: $\text{FeCl}_2(1000\text{H}_2\text{O}) = \text{FeCl}_2(1100\text{H}_2\text{O})$
DV: H, -0.10 kJ
C: From measurements by 41PER on dsolnH $\text{FeCl}_2:4\text{H}_2\text{O}(\text{cr})$ in nH_2O from $n=12.8$ to 1100; dCp corrections using ϕ Cp from 79BER/MOR
S: 4/87 VBP
114. Z: 1882THO
R: $\text{FeCl}_2:4\text{H}_2\text{O}(\text{cr}) = \text{FeCl}_2(\text{cr}) + 4\text{H}_2\text{O}(\text{l})$
DV: H, +64.31 \pm 2.0 kJ
F: TN
C: dsolnH tetrahydrate = -11.51 \pm 1.0 kJ/mol at 292 K combined with dsolnH anhydrous = -74.89 kJ/mol. Estimated dCp = +151 J/(mol.K)
* Check Khodakovskii value
S: 4/87 VBP
115. Z: 1941PER
R: $\text{FeCl}_2:4\text{H}_2\text{O}(\text{cr}) = \text{FeCl}_2(400\text{H}_2\text{O}) + 4\text{H}_2\text{O}(\text{l})$
DV: H, -11.96 \pm 2.0 kJ
F: TN
C: Measurement at 285.7 K, dH = -10.21 kJ/mol. Estimated dCp = -130 J/(K mol). 79BER/MOR measured ϕ Cp for FeCl_2 (12.54 H_2O) to be -37 J/(mol.K) and ϕ Cp0 = -256 \pm 30 J/K.mol.
S: 4/87 VBP
116. Z: 1979BER/MOR
R: $\text{FeCl}_2(12.54\text{H}_2\text{O}) = \text{FeCl}_2(\text{ai})$
DV: H, -20.558 \pm 0.178 kJ
DV: H, 288.15 K, -17.938 \pm 0.079 kJ
DV: H, 308.15 K, -22.353 \pm 0.109 kJ
C: Also measured ϕ Cp at 288, 298 and 308 K of solution (12.54 H_2O). Calculates ϕ Cp0 = -256 \pm 30 J/(mol.K) at 298.15 K
S: 4/87 VBP
117. Z: 1889SAB
R: $\text{FeCl}_2:2\text{H}_2\text{O}(\text{cr}) = \text{FeCl}_2(450\text{H}_2\text{O}) + 2\text{H}_2\text{O}(\text{l})$
DV: H, 293 K, -36.4 \pm 2.0 kJ
DV: H, -37.5 \pm 2.2 kJ
F: TN
C: Measurement at 293 K in 300 to 600 H_2O ; dCp estimated = -220 J/(mol.K).
S: 4/87 VBP
118. Z: 87NBS
R: $\text{FeCl}_2:4\text{H}_2\text{O}(\text{cr}) = \text{FeCl}_2(\text{ai}) + 4\text{H}_2\text{O}(\text{l})$
DV: G, -16.85 \pm 0.5 kJ
C: Saturation $m=4.951$ from 85CHO/PHA; activity coeff = 2.46 \pm 0.10 and $\ln a_w = -0.522 \pm 0.10$ from 62KAN/GRO.
* Khodakovskii tabulation gives -17.5 \pm 1.0 kJ/mol. These values need to be reconciled.
S: 4/87 VBP
119. Z: 1949SCH
R: $\text{FeCl}_2:4\text{H}_2\text{O}(\text{cr}) = \text{FeCl}_2:2\text{H}_2\text{O}(\text{cr}) + 2\text{H}_2\text{O}(\text{g})$
DV: H, 108.0 \pm 4.0 kJ
DV: G, +23.62 \pm 1.0 kJ
F: TN

- C: Vapor pressure measurements 293–338 K. $\log P_{\text{atm}} = 7.389 - 2,820/T$. dC_p assumed to be 0. Calculated $dS = 33.8 \text{ cal}/(\text{mol H}_2\text{O}) \text{ K}$ is slightly low.
S: 4/87 VBP
120. Z: 1949SCH
R: $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}(\text{cr}) = \text{FeCl}_2(\text{cr}) + \text{H}_2\text{O}(\text{g})$
DV: H, 63.1 \$5.0 kJ
DV: G, 18.57 \$2.0 kJ
F: TN
C: Vapor pressure measurements 323–383 K; $dH = 62.9 \text{ kJ/mol}$ at mean $T = 333 \text{ K}$; $dC_p = -4 \text{ J}/(\text{mol.K})$ assumed.; $\log P_{\text{atm}} = 7.704 - 3,286/T$. Calculated $dS = 35.7 \text{ cal}/(\text{mol.K})$ at 298 K. $p = 1 \text{ atm}$.
S: 4/87 VBP
121. Z: 1949SCH
R: $\text{FeCl}_2 \cdot \text{H}_2\text{O}(\text{cr}) = \text{FeCl}_2(\text{cr}) + \text{H}_2\text{O}(\text{g})$
DV: H, 63.1 \$5.0 kJ
DV: G, 24.93 \$2.0 kJ
C: Vapor pressure measurements 383–444 K; $dH = 62.6 \text{ kJ/mol}$ at mean $T \sim 413 \text{ K}$; $dC_p = -4 \text{ J}/(\text{mol.K})$ assumed; $\log P_{\text{atm}} = 6.619 - 3,270/T$. Calculated $dS = 30.6 \text{ cal}/(\text{mol.K})$ is low. $p = 1 \text{ atm}$.
S: 4/87 VBP
122. Z: 88CTT
R: $= \text{FeCl}_3(\text{cr})$
DV: S, 147.80 \$0.3 J
C: From the low temp. C_p measurements (4.7–307.6 K) by 80STU/FER. $C_p = 96.942 \text{ J}/(\text{mol.K})$ and $H - H_0 = 19.440 \text{ kJ/mol}$ at 298.15 K. Low temp. results of 51TOD/COU rejected
S: 4/86 VBP, 10/88 VBP
123. Z: 71STU/PRO
R: $= \text{FeCl}_3(\text{cr})$
DV: S, 142.335 \$2.0 J
F: TN
W: 99
C: From low temp. measurements (51–298 K) by 51TOD/COU who report $S_0(51\text{K}) = 18.828 \text{ J}/(\text{mol.K})$ and $S_0(298.15) - S_0(51\text{K}) = 115.855 \text{ J}/(\text{mol.K})$. 71STU/PRO adjusts $S_0(51\text{K})$ to $26.32 \text{ J}/(\text{mol.K})$ in order to reconcile 2nd and 3rd law d_rH for $\text{FeCl}_2(\text{cr}) = \text{FeCl}_3(\text{cr})$ equilibrium and considers difference to be the the remaining magnetic entropy at 51K. Dated evaluation June 1965.
S: 4/86 VBP
124. Z: 59KOE/COU
R: $\text{Fe}(\text{cr}) + 3\text{HCl}(12.731\text{H}_2\text{O}) + 0.5\text{H}_2\text{O}_2(12.58\text{H}_2\text{O}) = \text{FeCl}_3(\text{cr}) + \text{H}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
DV: H, -102.59 \$0.30 kJ
F: TN
C: Measured $dH(303\text{K}) = -100.75 \text{ kJ/mol}$; $dC_p = 368 \text{ J}/(\text{mol.K})$. Same reaction as IVTAN equation 393 without dC_p corrections.
S: 3/86 VBP
125. Z: 82LAV/TIM
R: $\text{Fe}(\text{cr}) + 1.5\text{Cl}_2(\text{g}) = \text{FeCl}_3(\text{cr})$
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. Instit. of Ferrous Metallurgy, Moscow which had been prep'd. by vacuum meeting of $\text{Fe}(\text{CO})_5$ and then refined in H_2 in presence of ZrH_2 . Corrected for impurities.
S: VM, VBP 7/87
126. Z: 84LAV/TIM
R: $\text{Fe}(\text{cr}) + 1.5\text{Cl}_2(\text{g}) = \text{FeCl}_3(\text{cr})$
DV: H, -396.02 \$0.14 kJ
W: 99
C: See 82LAV/TIM
S: VBP 7/87
127. Z: 89EVD/EFI
R: $\text{FeCl}_2(\text{cr}) + 1/2\text{Br}_2(\text{l}) + \text{KCl}(\text{cr}) = \text{FeCl}_3(\text{cr}) + \text{KBr}(\text{cr})$
DV: H, -11.386 \$0.18 kJ
C: Calorimetric measurements at 298.15 K of all chloride components in solution of (KBr, 0.43 Br_2 , 112 HBr , 50.78 H_2O) combined with reactions from 89EFI/EVD. $dH \text{ FeCl}_3(\text{cr}) = -146.523 \text{ kJ/mol}$. Reported earlier as 88EFI/EVD.
S: 8/88 VBP, 9/91 VBP
128. *Z: 27BAG
*R: $2\text{FeCl}_3(\text{cr}) + \text{H}_2(\text{g}) = 2\text{FeCl}_2(\text{cr}) + 2\text{HCl}(\text{g})$
*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: $2\text{FeCl}_3(\text{cr}) = 2\text{FeCl}_2(\text{cr}) + \text{Cl}_2(\text{g})$
DV: H, 107.02 \$3.6 kJ
C: IVTAN 3-85 EQ. 99, readjusted (vbp) in agreement with 86ARI/BER text calculations and returning to $S(\text{FeCl}_2, \text{cr}) = 118.0 \text{ J}/(\text{mol.K})$ 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: $2\text{FeCl}_3(\text{cr}) = 2\text{FeCl}_2(\text{cr}) + \text{Cl}_2(\text{g})$
DV: H, 104.98 \$2.3 kJ
C: IVTAN 3-85 EQ. 100, readjusted (vbp) in agreement with 86ARI/BER text calculations and returning to $S(\text{FeCl}_2, \text{cr}) = 118.0 \text{ J}/(\text{mol.K})$ at 298.15 K. Transpiration; third law, 12 pts, 526–574 K.
S: VM 4/87 and 10/87, 8/88 VBP
131. Z: 53SCH/OEH
R: $2\text{FeCl}_3(\text{cr}) = 2\text{FeCl}_2(\text{cr}) + \text{Cl}_2(\text{g})$
DV: H, 108.54 \$1.6 kJ
C: IVTAN 3-85 EQ. 101, readjusted (vbp) in agreement with 86ARI/BER text calculations and returning to $S(\text{FeCl}_2, \text{cr}) = 118.0 \text{ J}/(\text{mol.K})$ 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: $2\text{FeCl}_3(\text{cr}) = 2\text{FeCl}_2(\text{cr}) + \text{Cl}_2(\text{g})$
DV: H, 108.75 \$1.6 kJ

- C: IVTAN 3-85 EQ. 102, readjusted (vbp) in agreement with 86ARI/BER text calculations and returning to $S(\text{FeCl}_2, \text{cr}) = 118.0 \text{ J}/(\text{mol}\cdot\text{K})$ 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
133. Z: 52LI/GRE
R: $\text{FeCl}_3(\text{cr}) = \text{Fe} + 3(\text{ao}) + 3\text{Cl}-(\text{ao})$
DV: H, $-158.99 \text{ } \$0.84 \text{ kJ}$
C: IVTAN 3-85 EQ. 392
Molality range .00318 to .000766 moles/kg H_2O , corrected for chloride and hydroxide complexes. Experimental enthalpies range from -130.12 kJ/mol to -116.32 kJ/mol . Measurements by 85SOL/MON in molality ranged 0.007578 to 0.002236 support 52LI/GRE
- S: VM, VBP 4/87
134. Z: 87NBS
R: $\text{FeCl}_3(\text{cr}) = \text{FeCl}_3(\text{ai})$
DV: H, $-146.5 \text{ } \$3.0 \text{ kJ}$
C: Extrapolation from results as a function of concentration of HCl of 35KAN/FLU at 293 K and measurements of 76COR/OUW 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: 87NBS
R: $\text{FeCl}_3(\text{cr}) = \text{FeCl}_3(\text{HCl} + 111.0 \text{ H}_2\text{O}:\text{au})$
DV: H, $-138.78 \text{ } \$1.0 \text{ kJ}$
C: Smoothed curve from measurements as a function of concentration of HCl of 35KAN/FLU at 293 K and measurements of 76COR/OUW 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: 87NBS
R: $\text{FeCl}_3(\text{cr}) = \text{FeCl}_3(\text{HCl} + 55.51 \text{ H}_2\text{O}:\text{au})$
DV: H, $-132.85 \text{ } \$1.0 \text{ kJ}$
C: Smoothed curve from measurements as a function of concentration of HCl of 35KAN/FLU at 293 K and measurements of 76COR/OUW 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: 87NBS
R: $\text{FeCl}_3(\text{cr}) = \text{FeCl}_3(\text{HCl} + 27.75 \text{ H}_2\text{O}:\text{au})$
DV: H, $-123.77 \text{ } \$1.0 \text{ kJ}$
C: Smoothed curve from measurements as a function of concentration of HCl of 35KAN/FLU at 293 K and measurements of 76COR/OUW 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: 87NBS
R: $\text{FeCl}_3(\text{cr}) = \text{FeCl}_3(\text{HCl} + 18.50 \text{ H}_2\text{O}:\text{au})$
DV: H, $-115.12 \text{ } \$1.0 \text{ kJ}$
- C: Smoothed curve from measurements as a function of concentration of HCl of 35KAN/FLU at 293 K and measurements of 76COR/OUW 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: 87NBS
R: $\text{FeCl}_3(\text{cr}) = \text{FeCl}_3(\text{HCl} + 13.88 \text{ H}_2\text{O}:\text{au})$
DV: H, $-106.62 \text{ } \$1.0 \text{ kJ}$
C: Smoothed curve from measurements as a function of concentration of HCl of 35KAN/FLU at 293 K and measurements of 76COR/OUW 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: 87NBS
R: $\text{FeCl}_3(\text{cr}) = \text{FeCl}_3(\text{HCl} + 11.10 \text{ H}_2\text{O}:\text{au})$
DV: H, $-98.22 \text{ } \$1.0 \text{ kJ}$
C: Smoothed curve from measurements as a function of concentration of HCl of 35KAN/FLU at 293 K and measurements of 76COR/OUW and 80STU/FER at 298 K and 59KOE/COU at 303 K. Used 86KHO corrections to extrapolate to $I=0$.
- S: 3/90 VBP
141. Z: 90EFI/FUR
R: $\text{FeCl}_3(\text{cr}) = \text{Fe} + 3(\text{ao}) + 3\text{Cl}-(\text{ao})$
DV: H, $-156.78 \text{ } \$1.2 \text{ kJ}$
C: Extrapolation to $I=0$ from measurements in m $\text{HClO}_4 = 4.769, 3.61$ and 1.085 after correction for $\phi(\text{L})\text{D-H}$. See reactions listed separately. Authors' uncertainty of 0.28 kJ/mol increased.
- S: 6/89 VBP, 3/90 VBP
142. Z: 90EFI/FUR
R: $\text{FeCl}_3(\text{cr}) = \text{FeCl}_3(1390(\text{HClO}_4 + 11.64\text{H}_2\text{O}))$
DV: H, $-121.518 \text{ } \$0.5 \text{ kJ}$
C: Mean of two experimental measurements in $3.903 \text{ mol dm}^{-3} \text{ HClO}_4 (m=4.769) \text{ m} (\text{FeCl}_3) = 0.0026044$ and 0.004279 . $dH = -121.763$ and -121.273 kJ/mol respectively. $\phi(\text{L})\text{D-H}$ correction at $I=4.77$, 6.936 kJ/mol , is used in the extrapolation.
- S: 6/89 VBP
143. Z: 90EFI/FUR
R: $\text{FeCl}_3(\text{cr}) = \text{FeCl}_3(105(\text{HClO}_4 + 15.376 \text{ H}_2\text{O}))$
DV: H, $-131.806 \text{ } \$0.4 \text{ kJ}$
C: Mean of two experimental measurements in $3.08 \text{ mol dm}^{-3} \text{ HClO}_4 (m=3.610) \text{ m} (\text{FeCl}_3) = 0.004276$ and 0.002676 . $dH = -131.981$ and -131.630 kJ/mol , respectively. $\phi(\text{L})\text{D-H}$ correction at $I=3.62$ is 6.66 kJ/mol .
- S: 6/89 VBP
144. Z: 90EFI/FUR
R: $\text{FeCl}_3(\text{cr}) = \text{FeCl}_3(256(\text{HClO}_4 + 51.16 \text{ H}_2\text{O}))$
DV: H, $-144.661 \text{ } \$0.5 \text{ kJ}$

- 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 dH = -144.743, -144.885, -144.136, and -144.879 kJ/mol, respectively. Phil D-H correction at I=1.097 is 5.36 kJ.
S: 6/89 VBP
145. Z: 84NOV/BEL
R: FeCl₃(cr)=FeCl₃(42.4(HClO₄+82.24 H₂O))
DV: H, -138.22±0.27 kJ
C: Mean of measurements. Used isothermal calorimetry. Also measured dsolH 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 I=0.72 (4.37 kJ/mol) results in -142.59 kJ/mol for inclusion in extrapolation of dH' to I=0. See 90EFI/FUR measurements. Interpolation of 90EFI/FUR measurements at I=0.72 gives dH'=-152.5 kJ/mol, 10 kJ more negative.
S: 5/92 VBP
146. Z: 76COR/OUW
R: FeCl₃(cr)=FeCl₃(18HCl+1800 H₂O)
DV: H, -135.227 ±0.31 kJ
W: 99
C: See smoothed curve
S: 4/86 VBP
147. Z: 58SHC/VAS
R: FeCl₃(cr)=FeCl₃(18HCl+1800 H₂O)
DV: H, -127.90 ±1.1 kJ
F: TN
W: 99
C: See 76COR/OUW reaction for basis for rejection
S: 4/86 VBP
148. Z: 80STU/FER
R: FeCl₃(cr)=FeCl₃(80HCl+1021H₂O)
DV: H, -103.323 ±0.033 kJ
W: 99
C: Part of cycle involving dfH₀(FeOCl, cr); used in extrap. to dH₀soln FeCl₃(cr). See smoothed curve.
S: 7/87 VBP
149. Z: 59KOE/COU
R: FeCl₃(cr)=FeCl₃(243HCl+3091H₂O)
DV: H, 303.15 K, -102.341 ±0.084 kJ
DV: H, -102.106 ±0.20 kJ
W: 99
C: Measured at 303.15 K. Used dC_p=-47 J/(mol.K); part of cycle used to detn. dfH₀(FeCl₃, cr). See smoothed curve.
S: 7/87 VBP
150. Z: 35KAN/FLU
R: FeCl₃(cr)=FeCl₃(2000 H₂O)
DV: H, -134.77 ±1.0 kJ
C: Measured dsoln H (293K)=-132.26 kJ; estimated dC_p=-0.50 kJ/(mol.K)
S: 4/86 VBP
151. Z: 50BOB/LAI
R: FeCl₃(cr)=FeCl₃(600 H₂O)
DV: H, -131.38 ±0.6 kJ
F: TN
- C: dH=-130.96 kJ/mol at 297 K
S: VBP 4/86
152. Z: 84NOV/BEL
R: FeCl₃:2H₂O(cr)=FeCl₃(42.4(HClO₄+82.24 H₂O))+2 H₂O(l)
DV: H, -94.40±0.29 kJ
C: Used isothermal calorimeter. Mean of 6 measurements. Also measured dsolH FeCl₃(cr), FeCl₃:2.5 H₂O(cr), FeCl₃:3.5 H₂O(cr), and FeCl₃:6 H₂O(cr) in 0.65 mol dm⁻³ HClO₄. Diln correction considered negligible.
S: 5/92 VBP
153. Z: 84NOV/BEL
R: FeCl₃:2.5 H₂O(cr)=FeCl₃(42.4(HClO₄+82.24 H₂O))+2.5 H₂O(l)
DV: H, -86.37±0.42 kJ
C: Used isothermal calorimeter. Mean of 6 measurements. Also measured dsolH FeCl₃(cr), FeCl₃:2 H₂O(cr), FeCl₃:3.5 H₂O(cr), and FeCl₃:6 H₂O(cr) in 0.65 mol dm⁻³ HClO₄. Diln correction considered negligible.
S: 5/92 VBP
154. Z: 84NOV/BEL
R: FeCl₃:3.5 H₂O(cr)=FeCl₃(42.4(HClO₄+82.24 H₂O))+3.5 H₂O(l)
DV: H, -61.16±0.32 kJ
C: Used isothermal calorimeter. Mean of 6 measurements. Also measured dsolH FeCl₃(cr), FeCl₃:2 H₂O(cr), FeCl₃:2.5 H₂O(cr), and FeCl₃:6 H₂O(cr) in 0.65 mol dm⁻³ HClO₄. Diln correction considered negligible.
S: 5/92 VBP
155. Z: 84NOV/BEL
R: FeCl₃:6H₂O(cr)=FeCl₃(42.4(HClO₄+82.24 H₂O))+6 H₂O(l)
DV: H, -27.21±0.28 kJ
C: Used isothermal calorimeter. Mean of 6 measurements. Also measured dsolH FeCl₃(cr), FeCl₃:2 H₂O(cr), FeCl₃:2.5 H₂O(cr), and FeCl₃:3.5 H₂O(cr) in 0.65 mol dm⁻³ HClO₄. Diln correction considered negligible.
S: 5/29 VBP
156. Z: 50BOB/LAI
R: FeCl₃:6H₂O(cr)=FeCl₃(cr)+6H₂O(l)
DV: H, +109.75 ±0.6 kJ
F: TN
C: dH for soln of FeCl₃:6H₂O(cr) in 435 H₂O(l) at 297 K=-21.42 kJ/mol
S: VBP 4/86
157. Z: 1881SAB
R: FeCl₃:6H₂O(cr)=FeCl₃(1200H₂O)+6H₂O(l)
DV: H, -24.27 ±5 kJ
C: dH (294K)=-23.60 kJ/mol
S: VBP 4/86
158. Z: 89CTT
R: =FeOCl (cr)
DV: S, 82.550 ±0.13 J
C: Based on measurements by 80STU/FER in T range 6 to 305 K. H-H₀=12.940 kJ, C_p=70.50 J/(mol.K).
S: 7/89 VBP
159. Z: 56SCH/WIT

- R: $\text{FeCl}_3(\text{cr}) + \text{H}_2\text{O}(\text{l}) = \text{FeOCl}(\text{cr}) + 2 \text{HCl}(3.221 \text{ H}_2\text{O})$
 DV: H, -24.31 \$1.4 kJ
 C: $\text{dsolnH FeOCl}(\text{cr})$ in excess HCl = -48.49 kJ. Correction for excess HCl = -9.18 kJ.
 S: VM 10/87, 7/89 VBP
160. Z: 80STU/FER
 R: $\text{FeCl}_3(\text{cr}) + \text{H}_2\text{O}(\text{l}) = \text{FeOCl}(\text{cr}) + 2\text{HCl}(12.731 \text{ H}_2\text{O})$
 DV: H, -50.513 \$0.080 kJ
 C: $\text{dsolnH FeOCl}(\text{cr})$ in excess HCl = -61.296 \$0.065 kJ/mol.
 S: 7/87 VBP
161. Z: 83GRE
 R: $6\text{FeOCl}(\text{cr}) = 2\text{Fe}_2\text{O}_3(\text{cr}) + \text{Fe}_2\text{Cl}_6(\text{g})$
 DV: H, 136.45 \$9.1 kJ
 C: Equation, from spectrometric measurements, 465 to 560 K, and membrane 580 to 670 K, merged with data from 25STI, manometric 660 to 770 K; Third Law value. Second Law value 134.3 \$5.0 kJ. Adjusted from IVTAN 12/89 catalog value (136.247 \$9.1) for change in thermal functions $\text{Fe}_2\text{O}_3(\text{cr})$.
 S: 5/89 and 12/89 EME, 10/89 and 1/90 VBP
162. Z: 49SCH
 R: $\text{Fe}_2\text{O}_3(\text{cr}) + 2 \text{HCl}(\text{g}) = \text{Fe}_2\text{Cl}_6(\text{g}) + 3 \text{H}_2\text{O}(\text{g})$
 DV: H, -2.17 \$8.7 kJ
 C: Transpiration, 523-623 K, equation, third law; second law value 5.1 kJ.
 *** IVTAN reaction catalog 12/89 EME gives -2.66 kJ and T range as 573-723 K. Second law value given in 86ARI/BER +7.9 kJ is in error. $\text{dH}(600 \text{ K}) = -340 \text{ cal}$, not +340 cal.)
 S: 5/89, 12/89 EME, 10/89, 1/90 VBP
163. Z: 50KAN/PET
 R: $2\text{FeCl}_2(\text{cr}) + \text{Cl}_2(\text{g}) = \text{Fe}_2\text{Cl}_6(\text{g})$
 DV: H, 23 \$12 kJ
 C: Static; 606-970 K; 11 points; third law. Second law 54 \$16 kJ.
 S: 5/89 EME, 11/89 VBP
164. Z: 58WIL/GRE
 R: $2\text{FeCl}_2(\text{cr}) + \text{Cl}_2(\text{g}) = \text{Fe}_2\text{Cl}_6(\text{g})$
 DV: H, 23.3 \$7.6 kJ
 C: Transpiration, 500-673 K; equation; third law. Second law 33.0 kJ.
 S: 5/89 EME, 11/89 VBP
165. Z: 89EFI/EVD
 R: $\text{Fe}(\text{cr}) + \text{Br}_2(\text{l}) = \text{FeBr}_2(\text{cr})$
 DV: H, -244.737 \$0.22 kJ
 C: Calorimetric measurements at 298.15 K of all components in solution of (KBr, 0.43 Br₂, 112 HBr, 50.78 H₂O). $\text{Fe}(\text{cr})$ $\text{dH} = -395.43$ \$0.15 kJ/mol; $\text{Br}_2(\text{l})$, -7.777 \$0.089; $\text{FeBr}_2(\text{cr})$ -158.47 \$0.13. Reported earlier as 88EFI/EVD.
 S: 8/88 VBP, 9/91 VBP
166. Z: 89EVD/EFI
 R: $\text{FeBr}_2(\text{cr}) + 2\text{KCl}(\text{cr}) = \text{FeCl}_2(\text{cr}) + 2\text{KBr}(\text{cr})$
 DV: H, -10.032 \$0.21 kJ
 C: Calorimetric measurements at 298.15 K of all components in solution of (KBr, 0.43 Br₂, 112 HBr, 50.78 H₂O) combined with measurements from 89EFI/EVD. $\text{KBr}(\text{cr})$ $\text{dH} = 18.123$ \$0.039 kJ/mol, $\text{KCl}(\text{cr})$ 16.262 \$0.079, $\text{FeCl}_2(\text{cr})$ -152.16 \$0.13. See other 89EFI/EVD and 89EVD/EFI reactions on $\text{FeBr}_2(\text{cr})$, $\text{FeCl}_3(\text{cr})$, $\text{FeBr}_3(\text{cr})$ and $\text{FeI}_2(\text{cr})$. Reported earlier as 88EFI/EVD.
 S: 8/88 VBP, 9/91 VBP
167. Z: 34HIE/WOE
 R: $\text{Fe}(\text{cr}) + \text{Br}_2(\text{l}) = \text{FeBr}_2(\text{cr})$
 DV: H, -251.44 kJ
 DV: H, 273.15 K, -250.91 kJ
 C: Enthalpies of reaction of all components in $\text{Br}_2(\text{KBr})$ solutions at 273 K. dCp correction = -21 J/mol. Enthalpies for components at 273 K are $\text{Fe}(\text{cr})$ -408.86, $\text{Br}_2(\text{l})$ -7.74, and $\text{FeBr}_2(\text{cr})$ -165.69 kJ/mol respectively.
 S: 6/89 VBP
168. Z: 34HIE/APP
 R: $\text{FeCl}_2(\text{cr}) + \text{FeBr}_2(\text{D:HCl} + 27 \text{ H}_2\text{O}) = \text{FeBr}_2(\text{cr}) + \text{FeCl}_2(\text{D:HCl} + 27 \text{ H}_2\text{O})$
 DV: H, 273.15 K, 4.69 kJ
 DV: H, 4.99 kJ
 C: Measurements of enthalpies of solution of $\text{FeCl}_2(\text{cr})$ (-68.20 kJ/mol) and $\text{FeBr}_2(\text{cr})$ (-72.89 kJ/mol) in 2N HCl at 273 K. $\text{dCp} = 12$ J/mol
 S: 6/89 VBP
169. Z: 89NBS
 R: $\text{FeCl}_2(\text{D:HCl} + 27 \text{ H}_2\text{O}) + 2\text{HBr}(\text{ai}) = \text{FeBr}_2(\text{D:HCl} + 27 \text{ H}_2\text{O}) + 2 \text{HCl}(\text{ai})$
 DV: H, -1.96 \$0.4 kJ
 C: Correction to standard state based on L2 HCl and HBr from 89PAR
 W: -1
 S: 7/89 VBP
170. Z: 34HIE/APP
 R: $\text{FeBr}_2(\text{cr}) = \text{FeBr}_2(1650 \text{ H}_2\text{O})$
 DV: H, -86.86 \$3.0 kJ
 DV: H, 293.15 K, -85.19 kJ
 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: $\text{FeBr}_2(1650 \text{ H}_2\text{O}) = \text{FeBr}_2(\text{ai})$
 DV: H, -1.44 ± 0.2 kJ
 C: Estimated.
 S: 7/89 VBP
172. Z: 52LI/GRE
 R: $\text{FeBr}_2(\text{cr}) = \text{FeBr}_2(11,500 \text{ H}_2\text{O})$
 DV: H, -84.1 \$1.7 kJ
 C: Average of five measurements at $m = 0.00828$, 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: 52LI/GRE
 R: $\text{FeBr}_2(\text{cr}) = \text{FeBr}_2(\text{ai})$

- DV: H, -86.53 \$2.0 kJ
C: Extrapolation of five measurements (corrected for ϕ LiL D-H). ϕ LiL D-H at $I=0.025$ is 543 J/mol.
S: 7/89 VBP
174. Z: 65PAO
R: $\text{FeBr}_2(\text{cr})=\text{FeBr}_2(2000 \text{ H}_2\text{O})$
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: $\text{FeBr}_2(2000 \text{ H}_2\text{O})=\text{FeBr}_2(\text{ai})$
DV: H, -1.4 \$0.2 kJ
C: Estimated; based on ϕ LiL D-H=1.21 kJ and ϕ LiL m=0.2 kJ/mol.
S: 7/89 VBP
176. Z: 89PAR
R: $\text{FeBr}_2(2000 \text{ H}_2\text{O})=\text{FeBr}_2(4000 \text{ H}_2\text{O})$
DV: H, -0.20±0.20 kJ
C: Estimated from comparison of divalent bromides
S: 7/89 VBP
177. Z: 67CHR/GRE
R: $\text{Fe}_2\text{O}_3(\text{cr})+6 \text{HBr}(\text{g})=2 \text{FeBr}_2(\text{cr})+3 \text{H}_2\text{O}(\text{g})+\text{Br}_2(\text{g})$
DV: H, -150.5 \$8 kJ
C: Third law; Spectrometric study; T range 468-598 K; second law $\text{dH}=-150.8$ kJ/mol. Used thermal functions for $\text{FeBr}_2(\text{cr})$ from 85CHA/DAV which gives S (FeBr_2, cr)=140.7 \$1.3 J at 298.15 K from a private communication (Westrum).
S: 7/89 VBP
178. Z: 90EFI/FUR
R: $\text{FeBr}_2(\text{cr})=\text{Fe}+2(\text{ao})+2 \text{Br}(\text{ao})$
DV: H, -86.85 \$0.12 kJ
C: Author's extrapolation after correction for ϕ LiL D-H from measurements in 0.001 mol dm⁻³ HClO_4 . Measured values are -86.803, -86.442, and -86.116 kJ/mol for $m=0.004958, 0.004273$, and 0.007585 moles/(kg H_2O) respectively. ϕ LiL 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 HClO_4 solutions. See other reactions.
*** This is really an average of the three measurements. A plot of dH vs
*** I or $I(1/2)$ using measurements in 0.01, 0.10, and 1.0 mol dm⁻³ HClO_4 (corrected for ϕ LiL D-H) shows high curvature.
S: 5/89 VBP, 11/89 VBP
179. Z: 90EFI/FUR
R: $\text{FeBr}_2(\text{cr})=\text{FeBr}_2(0.18(\text{HClO}_4+55,500 \text{ H}_2\text{O}))$
DV: H, -86.214 \$0.20 kJ
C: Average of three measurements in 0.001 mol dm⁻³ HClO_4 . See extrapolated value.
S: 5/89 VBP
180. Z: 90EFI/FUR
R: $\text{FeBr}_2(\text{cr})=\text{FeBr}_2(182(\text{HClO}_4+51.16 \text{ H}_2\text{O}))$
DV: H, -82.611 \$0.01 kJ
C: Average of two measurements in 1.085 molal HClO_4 . $m \text{FeBr}_2=0.00567$ and 0.00618 mol/(kg H_2O). ϕ LiL D-H correction would be 2.674 kJ/mol for extrapolation.
S: 5/89 VBP
181. Z: 90EFI/FUR
R: $\text{FeBr}_2(\text{cr})=\text{FeBr}_2(28.7(\text{HClO}_4+512 \text{ H}_2\text{O}))$
DV: H, -84.322 kJ
C: Experimental measurements in 0.1085 molal HClO_4 . $m \text{FeBr}_2=0.003777$. ϕ LiL D-H correction would be 1.28 kJ/mol for extrapolation.
S: 5/89 VBP
182. Z: 90EFI/FUR
R: $\text{FeBr}_2(\text{cr})=\text{FeBr}_2(2.13(\text{HClO}_4+5290 \text{ H}_2\text{O}))$
DV: H, -85.960 kJ
C: Experimental measurements in 0.0105 m HClO_4 . $m \text{FeBr}_2=0.004918$. ϕ LiL D-H correction would be 0.776 kJ/mol for extrapolation.
S: 5/89 VBP
183. Z: 89WES
R: $=\text{FeBr}_2(\text{cr})$
DV: S, 140.67 \$0.20 J
C: Calorimetric Cp measurements 4-303 K. $\text{H}-\text{H}_0(298.15 \text{ K})=18.092$ \$??? kJ/mol and $\text{Cp}=79.747$ \$0.20 J/(mol.K).
S: 7/89 VBP
184. Z: 89EFI/EVD
R: $\text{FeBr}_2(\text{cr})+1/2\text{Br}_2(\text{l})=\text{FeBr}_3(\text{cr})$
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 H_2O). $\text{dH FeBr}_3(\text{cr})=-144.463$ kJ/mol, see other 89EFI/EVD reaction. Reported earlier as 88EFI/EVD.
S: 8/88 VBP, 9/91 VBP
185. Z: 50GRE/THA
R: $2\text{FeBr}_3(\text{cr})=2\text{FeBr}_2(\text{cr})+\text{Br}_2(\text{g})$
DV: H, 67.1 \$2.0 kJ
DV: H, 375 K, 66.60 \$1.7 kJ
DV: S, 161.8 \$7 J
F: TN
C: Vapor pressure measurements 338 to 413 K. $\log P \text{ mm}=-3,478.6/T+11.327$. Corrected using estimated $\text{dCp}=-6$ J/(mol Br₂).
S: 7/89 VBP
186. Z: 52LI/GRE
R: $\text{FeBr}_3(\text{cr})=\text{FeBr}_3(40,000 \text{ H}_2\text{O})$
DV: H, -104.0 kJ
C: From smoothed experimental curve. Measurements at 7 concentrations, 0.0074 to 0.00098 mol/(kg H_2O). dH varies from -121.3 to -101.7 kJ/mol. See other reactions.
S: 7/89 VBP
187. Z: 52LI/GRE
R: $\text{FeBr}_3(\text{cr})=\text{FeBr}_3(20,000 \text{ H}_2\text{O})$
DV: H, -119.7 kJ
C: From smoothed experimental curve. Measurements at 7 concentrations, 0.0074 to 0.00098 mol/(kg H_2O). dH varies from -121.3 to -101.7 kJ/mol. See other reactions.

188. S: 7/89 VBP
Z: 52LI/GRE
R: $\text{FeBr}_3(\text{cr}) = \text{FeBr}_3(10,000 \text{ H}_2\text{O})$
DV: H, -122.3 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.
189. S: 7/89 VBP
Z: 52LI/GRE
R: $\text{FeBr}_3(\text{cr}) = \text{FeBr}_3(\text{ai})$
DV: H, -146.9 \$5.0 kJ
C: Authors correct for formation of $\text{FeOH} + 2(\text{ao})$ and $\text{FeBr} + 2(\text{ao})$.
190. S: 7/89 VBP
Z: 90EFI/FUR
R: $\text{FeBr}_3(\text{cr}) = \text{Fe} + 3(\text{ao}) + 3\text{Br}(\text{ao})$
DV: H, -150.4 \$1.3 kJ
C: Extrapolation to I=0 from measurements in m $\text{HClO}_4 = 4.769, 3.651, \text{ and } 1.085 \text{ mol}/(\text{kg H}_2\text{O})$ after correction for Phi L D-H. See reactions listed separately. Value revised by authors from -151.4 \$3.8 kJ.
191. S: 6/89 VBP, 10/89 VBP
Z: 90EFI/FUR
R: $\text{FeBr}_3(\text{cr}) = \text{FeBr}_3(768(\text{HClO}_4 + 11.64 \text{ H}_2\text{O}))$
DV: H, -119.416 \$1.2 kJ
C: Mean of two experimental measurements in 3.903 mol dm⁻³ HClO_4 (m=4.769). m $\text{FeBr}_3 = 0.00576 \text{ and } 0.00629 \text{ mol}/(\text{kg H}_2\text{O})$. dH = -118.813 and -120.018 kJ/mol respectively. Phi L D-H correction at I=4.787 is 6.948 kJ.
192. S: 6/89 VBP
Z: 90EFI/FUR
R: $\text{FeBr}_3(\text{cr}) = \text{FeBr}_3(530(\text{HClO}_4 + 15.376 \text{ H}_2\text{O}))$
DV: H, -128.238 \$0.2 kJ
C: Mean of two experimental measurements in 3.11 mol dm⁻³ HClO_4 (m=3.651). m $\text{FeBr}_3 = 0.00659 \text{ and } 0.00719 \text{ mol}/(\text{kg H}_2\text{O})$. dH = -128.230 and -128.246 kJ/mol respectively. Phi L D-H correction at I=3.672 is 6.70 kJ.
193. S: 6/89 VBP
Z: 90EFI/FUR
R: $\text{FeBr}_3(\text{cr}) = \text{FeBr}_3(183(\text{HClO}_4 + 51.16 \text{ H}_2\text{O}))$
DV: H, -139.324 \$0.08 kJ
C: Mean of three experimental measurements in 1.0257 mol dm⁻³ HClO_4 (m=1.085). m FeBr_3 is 0.00504, 0.00431, and 0.00841 mol/(kg H₂O). dH = -139.301, -139.360, and -139.312 kJ, respectively. Phi L D-H at I=1.12 is 5.376 kJ.
194. S: 6/89 VBP
Z: 90EFI/EVD
R: $\text{Fe}(\text{cr}) + \text{I}_2(\text{cr}) = \text{FeI}_2(\text{cr})$
DV: H, -118.079 \$0.27 kJ
C: Calorimetric measurements at 298.15 of components in solution (KBr, 0.43Br₂, 112 HBr + 50.78H₂O). dHI₂(cr) = -23.38 \$0.20 kJ/mol, FeI₂(cr) -300.731 \$0.095. See other 89EFI/EVD reactions. Reported earlier as 88EFI/EVD.
195. S: 8/88 VBP, 9/91 VBP
Z: 90EFI/EVD
- S: 8/88 VBP, 9/91 VBP
DV: H, -167.7 \$0.19 kJ
C: Calorimetric measurements on FeBr₃ and components in solution (KBr, 0.43Br₂, 112 HBr, 50.78 H₂O) at 298.15 K. dHI₂(cr) = -23.38 \$0.20 kJ/mol. See other 89EFI/EVD reactions. Reported earlier as 88EFI/EVD.
196. S: 8/88 VBP, 9/91 VBP
Z: 66ZAI/GRE
R: $\text{FeI}_2(\text{cr}) = \text{Fe}(\text{cr}) + \text{I}_2(\text{g})$
DV: H, 166.1 \$5.0 kJ
DV: H, 813 K, 152.7 \$3.0 kJ
DV: S, 813 K, 95.8 \$3.5 J
C: Decomposition pressure measurements, 771 K to 858 K; corrects for formation of FeI₃(g) and Fe₂I₆(g). Corrected to 298.15 K using 85CHA/DAV estimated thermal functions for FeI₂(cr) with S (298.15 K) = 167.4 \$8.4 J/(mol.K). third Law value.
197. S: 7/89 VBP
Z: 56SCH/ORR
R: $\text{FeI}_2(\text{cr}) = \text{Fe}(\text{cr}) + \text{I}_2(\text{g})$
DV: H, 193.9 \$20 kJ
C: Decomposition $\text{FeI}_2(\text{l})$; log P(atm) = 4.14 - 6790/T. Second law value. Third law value = 149.4 kJ/mol.
198. S: 7/89 VBP
Z: 34HIE/WOE
R: $\text{Fe}(\text{cr}) + \text{I}_2(\text{cr}) = \text{FeI}_2(\text{cr})$
DV: H, 273.15 K, -126.06 kJ
DV: H, -125.9 \$5.0 kJ
C: From measurements of all components in Br₂, KBr solutions at 273.15 K. dCp correction used = 4J/(mol.K).
199. S: 7/89 VBP
Z: 34HIE/APP
R: $\text{FeCl}_2(\text{cr}) + \text{FeI}_2(\text{D: HCl} + 27 \text{ H}_2\text{O}) = \text{FeI}_2(\text{cr}) + \text{FeCl}_2(\text{D: HCl} + 27 \text{ H}_2\text{O})$
DV: H, +9.2 \$2.0 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 FeI₂(cr) (-77.86 kJ) at 293 K. dCp = -20 J/mol K.
200. S: 7/89 VBP
Z: 89PAR
R: $\text{FeCl}_2(\text{D: HCl} + 27 \text{ H}_2\text{O}) + 2\text{HI}(\text{ai}) = \text{FeI}_2(\text{D: HCl} + 27 \text{ H}_2\text{O}) + 2\text{HCl}(\text{ai})$
DV: H, -4.68 kJ
C: Correction to standard state based on L2's for HCl and HI from 89PAR.
201. S: 7/89 VBP
Z: 65PAO/SAB
R: $\text{FeI}_2(\text{cr}) = \text{FeI}_2(4000\text{H}_2\text{O})$
DV: H, -81.42 \$0.25 kJ
C: Sample prepared from elements at 773 K. Analysis indicated 82.03% Iodine (calculated 81.97%).
202. S: 7/89 VBP
Z: 34NAE
R: $\text{Fe}(\text{cr}) + \text{KI}_3(\text{au}) = \text{FeI}_2(\text{au}) + \text{KI}(\text{au})$
DV: H, -217.0 \$10 kJ
203. S: 7/89 VBP
Z: 97MOS

- R: $\text{FeI}_2(\text{cr})=\text{FeI}_2(\text{au})$
 DV: H, -97.1 kJ
 S: 7/89 VBP
204. Z: 42MOO/KEL
 R: $=\text{FeSO}_4(\text{cr})$
 DV: S, 25.70 \$0.30 cal
 F: TN
 C: Low temp Cp measurements (53-295 K). S(298.15 K)-S(50.12 K)=23.60 cal/(mol.K) and S(50.12 K)=2.10 (extrapolated). Also reported in 61KEL/KIN.
 S: 5/86 VBP
205. Z: 71STU/PRO
 R: $=\text{FeSO}_4(\text{cr})$
 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: $\text{Fe}(\text{cr})+\text{Hg}_2\text{SO}_4(\text{cr})=\text{FeSO}_4(\text{ai})+2\text{Hg}(\text{l})$
 DV: G, -197.740 \$0.060 kJ
 C: $E_0=1.0247$ \$0.0003 V. See reaction with Hg_2Cl_2 for comments. Mean of 4 meas. Concentration FeSO_4 solution, m=0.022 to 0.0718. Activity coef. used are given by above authors from meas. by 41DEM/FED. Comparison with activity coefficients of CuSO_4 by 80MIL/MAR in dilute region indicates values are reasonable.
 S: 5/86 VBP
207. Z: 53PAT/THO
 R: $\text{Fe}(\text{cr})+\text{PbSO}_4(\text{cr})=\text{FeSO}_4(\text{ai})+2\text{Pb}(\text{cr})$
 DV: G, -10.520 \$0.038 kJ
 C: $E_0=0.05452$ \$0.0002 V mean of 2 meas. m $\text{FeSO}_4=0.0677$ and 0.030 mol/kg H_2O . $\gamma=0.198$ and 0.281 used to correct. See reaction with Hg_2SO_4 and Hg_2Cl_2 .
 S: 5/86 VBP
208. Z: 49LYO/GIA
 R: $=\text{FeSO}_4\cdot 7\text{H}_2\text{O}(\text{cr})$
 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 $S_0(1\text{ K})=0.2$ cal/(mol.K); $S_0(1-10\text{ K})=1.4$ \$0.07; $S(10-20\text{ K})=1.7$ \$0.08 and $S(20-298.15\text{ K})=94.5$ \$0.15. S associated with magnetic system from integration (Cp total-Cp lattice)=2.8 cal/(mol.K) VBP 5/86
209. Z: 86NBS
 R: $\text{FeSO}_4\cdot 7\text{H}_2\text{O}(\text{cr})=\text{FeSO}_4(\text{ai})+7\text{H}_2\text{O}(\text{l})$
 DV: G+14.116 \$0.50 kJ
 F: TN
 C: Calculated from solubility=1.944 \$0.007 mol/kg H_2O from 58LIN and estimated $\gamma=0.0344$ and $\phi=0.578$ on basis of NiSO_4 from 59ROB/STO. IVTAN evaluation uses $dG_0=14.07$ \$0.51 kJ.
 S: 3/86 VBP
210. Z: 87REA/BEC
 R: $\text{FeSO}_4\cdot 7\text{H}_2\text{O}(\text{cr})=\text{FeSO}_4(\text{ai})+7\text{H}_2\text{O}(\text{l})$
 DV: G, +12.58 \$0.30 kJ
 C: Reanalysis of isopiestic meas. of 74OYK/BAL activity coefficients; uses γ at 0.1 m=0.161 and $\phi=0.556$. Uses $m_{\text{sat}}=1.94$ \$0.02, $\gamma=0.048$, $a_w=0.952$ \$0.003.
 S: 7/87 VBP
211. Z: 63ADA/KEL
 R: $\text{Fe}(\text{cr})+\text{H}_2\text{SO}_4(7.068\text{ H}_2\text{O})+7\text{H}_2\text{O}(\text{l})=\text{FeSO}_4\cdot 7\text{H}_2\text{O}(\text{cr})+\text{H}_2(\text{g})$
 DV: H, -137.09 \$0.40 kJ
 F: TN
 C: Measurements on $\text{FeSO}_4\cdot 6.952\text{ H}_2\text{O}(\text{cr})$ at 303.15 K combined with measurement by 59KOE/COU on $\text{Fe}(\text{cr})$; Composite dH=-137.737 \$0.25 kJ/mol corrected to 298.15 K ($dC_p=-184$ J/(mol.K)) and to stoichiometric $\text{FeSO}_4\cdot 7\text{H}_2\text{O}(\text{cr})$ assuming presence of 0.008 $\text{FeSO}_4\cdot \text{H}_2\text{O}(\text{cr})$. Correction for this=-0.46 kJ/mol.
 S: 3/86 VBP
212. Z: 63ADA/KEL
 R: $\text{Fe}(\text{cr})+\text{H}_2\text{SO}_4(7.068\text{ H}_2\text{O})+\text{H}_2\text{O}(\text{l})=\text{FeSO}_4\cdot \text{H}_2\text{O}(\text{cr})+\text{H}_2(\text{g})$
 DV: H, -79.72 \$0.40 kJ
 F: TN
 C: Measurements on $\text{FeSO}_4\cdot 1.008\text{ H}_2\text{O}(\text{cr})$ at 303.15K combined with measurements by 59KOE/COU on $\text{Fe}(\text{cr})$; Composite dH=-81.714 \$0.29 kJ/mol. corrected to 298.15 K ($dC_p=-52.7$ J/(mol.K)) and to stoichiometric $\text{FeSO}_4\cdot \text{H}_2\text{O}(\text{cr})$, assuming presence of 0.0013 $\text{FeSO}_4\cdot 7\text{H}_2\text{O}(\text{cr})$ (correction=+1.68 kJ/mol).
 S: 3/86 VBP
213. Z: 64KOH/ZAS
 R: $\text{FeSO}_4\cdot 4\text{H}_2\text{O}(\text{cr})=\text{FeSO}_4\cdot \text{H}_2\text{O}(\text{cr})+3\text{H}_2\text{O}(\text{g})$
 DV: H, 140.7 \$2.0 kJ
 F: TN
 DV: G, 27.44 \$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 H_2O) is low. dG at $p=1$ bar.
 S: 3/86 VBP
214. Z: 64KOH/ZAS
 R: $\text{FeSO}_4\cdot 7\text{H}_2\text{O}(\text{cr})=\text{FeSO}_4\cdot 4\text{H}_2\text{O}(\text{cr})+3\text{H}_2\text{O}(\text{g})$
 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)=-2719T-1+10.30 (40-54 °C) for dehydration to tetrahydrate. Calculated $dS=34.0$ cal/(K.mol H_2O). dG at $p=1$ bar.
 S: 3/86 VBP
215. Z: 79MAL/DRA
 R: $\text{FeSO}_4\cdot 7\text{H}_2\text{O}(\text{cr})=\text{FeSO}_4\cdot 4\text{H}_2\text{O}(\text{cr})+3\text{H}_2\text{O}(\text{g})$
 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: $\text{FeSO}_4\cdot 7\text{H}_2\text{O}(\text{cr})=\text{FeSO}_4\cdot 4\text{H}_2\text{O}(\text{cr})+3\text{H}_2\text{O}(\text{g})$
 DV: H, 166.4 \$6.0 kJ

- F: TN
 C: Data of 01COH/VIS.
 S: 3/86 VBP
 Z: 14FOR
 R: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{cr}) = \text{FeSO}_4(\text{au}) + 7\text{H}_2\text{O}(\text{l})$
 DV: H, +18.0 \$2.5 kJ
 F: TN
 C: Measurements at 286 K; $\text{dH} = 18.13$ kJ/mol
 ($\text{dCp} = -8$ J/(mol.K))
- S: 3/86 VBP
 Z: 14FOR
 R: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{cr}) = \text{FeSO}_4 \cdot \text{H}_2\text{O}(\text{cr}) + 6\text{H}_2\text{O}(\text{l})$
 DV: H, 52.18 \$1.5 kJ
 F: TN
 C: dsolnH (286 K) of $\text{FeSO}_4 \cdot \text{H}_2\text{O}(\text{cr}) = -31.54$ kJ/mol combined with dsolnH heptahydrate;
 dCp for composite = +209 J/(mol.K)
- S: 3/86 VBP
 Z: 14FOR
 R: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{cr}) = \text{FeSO}_4 \cdot 4\text{H}_2\text{O}(\text{cr}) + 3\text{H}_2\text{O}(\text{l})$
 DV: H, +26.18 \$1.5 kJ
 C: dsolnH (286 K) of $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}(\text{cr}) = -6.69$ kJ/mol; dCp for composite = 113 J/(mol.K)
- S: 3/86 VBP
 Z: 14FOR
 R: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{cr}) = \text{FeSO}_4(\text{cr}) + 7\text{H}_2\text{O}(\text{l})$
 DV: H, 83.28 \$2.0 kJ
 F: TN
 C: dsolnH (286 K) of $\text{FeSO}_4(\text{cr}) = -62.34$ kJ/mol;
 dCp for composite = 392 J/(mol.K).
- S: 3/86 VBP 221.
 Z: 85VAS/DMI2
 R: $\text{Fe}(\text{cr}) + \text{H}_2\text{O}_2(3.5\text{H}_2\text{O}) + 5\text{H}_2\text{O}(\text{l})$
 $+ \text{H}_2\text{SO}_4(0.3\text{H}_2\text{O}) = \text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{cr})$
 DV: H, -569.96 \$0.28 kJ
 C: Measurements of components,
 H_2SO_4 , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{cr})$ and H_2O_2 in 2,3,
 and 4N HClO_4 solutions combined with $\text{Fe}(\text{cr})$
 measurements from 83DMI and 78VAS/VAS.
 Authors' calculated value for dH
 $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{cr}) \sim -3014.6$.
- S: Joint, 6/86 VBP and 4/87 O.D and I.Kh.
 Z: 85VAS/DMI
 R: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{cr}) + \text{H} + (\text{ao}) = \text{Fe} + 2(\text{ao}) + \text{HSO}_4$
 $- (\text{ao}) + 7\text{H}_2\text{O}(\text{l})$
 DV: H, +33.58 \$0.50 kJ
 W: 99
 C: Extrapolation of enthalpies of solution of
 $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{cr})$ in 2N, 3N and 4N HClO_4 as
 a function of $m(1/2)$ to $m(\text{Fe} + 2(\text{ao})) = 0$ and to
 ionic strength solution = 0 using corrections
 from 78VAS/YAS. See 83DMI.
- S: 6/86 VBP
 Z: 83DMI
 R: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{cr}) + \text{H} + (\text{ao}) = \text{Fe} + 2(\text{ao})$
 $+ \text{HSO}_4 - (\text{ao}) + 7\text{H}_2\text{O}(\text{l})$
 DV: H, +35.50 \$0.10 kJ
 C: Recalc. to correct for $\text{SO}_4 = (\text{ao})$ in solution.
 Ionic strength corrections from Khod.
- S: 3/87 VBP, I.Kh., O.D.
 Z: 85VAS/DMI
 R: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{cr}) = \text{FeSO}_4(\text{ai}) + 7\text{H}_2\text{O}(\text{l})$
 DV: H, +11.99 \$0.20 kJ
- W: 99
 C: 16 measurements, extrapolation; equation only.
 $\text{dsolnH}(\text{m}) = 11.99$ (\$0.09) + 36.33 (\$0.48) $m(1/2)$.
 Recalc. gives much higher value. See
 83DMI.
- S: 6/86 VBP
 Z: 78VAS/VAS
 R: $(\text{NH}_4)_2 \text{SO}_4(\text{cr}) + \text{Fe}(\text{cr}) + \text{H}_2\text{O}_2(4.95\text{H}_2\text{O})$
 $+ \text{H}_2\text{SO}_4(0.43\text{H}_2\text{O}) + 4\text{H}_2\text{O}(\text{l}) = (\text{NH}_4)_2$
 $\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}(\text{cr})$
 DV: H, -579.78 \$0.87 kJ
 W: 99
 C: Summation from meas of dsolnH of all compo-
 nents in 4.0, 3.0, 2.0, 1.0 mol dm⁻³ HClO_4 so-
 lutions. Assume all solutions formed are
 equivalent so that no corrections for $\text{SO}_4 = \text{ao}$
 are necessary. Meas. in 1.0 mol dm⁻³ HClO_4 not
 used. Mean of 6 meas. See 83DMI.
- S: VBP Aug. 85, 3/87 VBP
 Z: 83DMI
 R: $(\text{NH}_4)_2 \text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}(\text{cr}) + 2\text{H} + (\text{ao}) =$
 $2\text{NH}_4 + (\text{ao}) + \text{Fe} + 2(\text{ao}) + 2\text{HSO}_4 - (\text{ao})$
 $+ 6\text{H}_2\text{O}(\text{l})$
 DV: H, 69.40 \$0.20 kJ
 C: Extrap. from dsolnH meas. in 2.0, 3.0, 4.0 mol
 dm⁻³ HClO_4 aqueous solutions. m salt = 0.01 to
 0.04. Correct for $\text{SO}_4 = \text{in HClO}_4$ soln., and to
 ionic strength = 0 using Khodakhovskii equa-
 tion with 1986 constants. Supersedes 78VAS/
 VAS.
- S: VBP Aug. 85, 3/87 VBP
 Z: 83DMI
 R: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{cr}) = \text{FeSO}_4(\text{ai}) + 7\text{H}_2\text{O}(\text{l})$
 DV: H, 12.90 \$0.10 kJ
 C: Experimental points refit to Khodakhovskii
 equation with extrapolation to $m = 0$. $\text{dH}(\text{l})$
 $- \text{dH}(\text{DH})/\text{kJ/mol} = (12.895 \text{ } \$0.096) + (35.572$
 $\$2.372) \text{ I}$
- S: VBP, O.D., I.Kh 5/87
 Z: 83DMI
 R: $\text{Fe}(\text{cr}) + \text{H}_2\text{O}_2(4.95\text{H}_2\text{O}) + (\text{NH}_4)_2 \text{SO}_4(\text{cr})$
 $+ \text{H}_2\text{SO}_4(0.3\text{H}_2\text{O}) + 4\text{H}_2\text{O}(\text{l})$
 $= (\text{NH}_4)_2 \text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}(\text{cr})$
 DV: H, -579.68 \$0.44 kJ
 C: Supersedes 78VAS/VAS. Meas. in 1N HClO_4
 not used. Concentration H_2SO_4 is 0.3H₂O,
 rather than 0.43H₂O.
- S: O.D., I.Kh., VBP 4/87
 Z: 68LAR/CER
 R: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{cr}) = \text{FeSO}_4(\text{ai}) + 7\text{H}_2\text{O}(\text{l})$
 DV: H, +11.80 \$0.42 kJ
 C: From meas of dsolnH of hydrated salts with
 compositions $\text{FeSO}_4 \cdot 6.92 \text{ H}_2\text{O}$, $\text{FeSO}_4 \cdot 6.78$
 H_2O , $\text{FeSO}_4 \cdot 5.32 \text{ H}_2\text{O}$, $\text{FeSO}_4 \cdot 3.98 \text{ H}_2\text{O}$, and
 $\text{FeSO}_4 \cdot 2.46 \text{ H}_2\text{O}$. Measured concentrations
 0.005 to 0.05 m. Authors correct to std state
 using $\phi_{\text{H}_2\text{O}}$ from 56LAN/MIE for NiSO_4 . More
 details in 68LAR.
- S: 8/85 VBP
 Z: 68LAR/CER
 R: $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}(\text{cr}) = \text{FeSO}_4(\text{ai}) + 4\text{H}_2\text{O}(\text{l})$
 DV: H, -13.81 \$0.42 kJ

- C: From meas of dsolnH of hydrated salts with compositions $\text{FeSO}_4\cdot 6.92 \text{ H}_2\text{O}$, $\text{FeSO}_4\cdot 6.78 \text{ H}_2\text{O}$, $\text{FeSO}_4\cdot 5.32 \text{ H}_2\text{O}$, $\text{FeSO}_4\cdot 3.98 \text{ H}_2\text{O}$, and $\text{FeSO}_4\cdot 2.46 \text{ H}_2\text{O}$. Measured concentrations 0.005 to 0.05m. Authors correct to std state using $\phi_{\text{H}_2\text{O}}$ from 56LAN/MIE for NiSO_4 . More details in 68LAR
- S: 8/85 VBP
231. Z: 68LAR/CER
R: $\text{FeSO}_4\cdot \text{H}_2\text{O}(\text{cr}) = \text{FeSO}_4(\text{ai}) + \text{H}_2\text{O}(\text{l})$
DV: H, -44.35 \$0.84 kJ
C: From meas of dsolnH of hydrated salts with compositions $\text{FeSO}_4\cdot 6.92 \text{ H}_2\text{O}$, $\text{FeSO}_4\cdot 6.78 \text{ H}_2\text{O}$, $\text{FeSO}_4\cdot 5.32 \text{ H}_2\text{O}$, $\text{FeSO}_4\cdot 3.98 \text{ H}_2\text{O}$, and $\text{FeSO}_4\cdot 2.46 \text{ H}_2\text{O}$. Measured concentrations 0.005 to 0.05m. Authors correct to std state using $\phi_{\text{H}_2\text{O}}$ from 56LAN/MIE for NiSO_4 . More details in 68LAR.
- S: VBP Aug. 85
232. Z: 41PER
R: $\text{FeSO}_4\cdot 7\text{H}_2\text{O}(\text{cr}) = \text{FeSO}_4(1500 \text{ H}_2\text{O}) + 7 \text{ H}_2\text{O}(\text{l})$
DV: H, 17.10 \$1.0 kJ
C: Measurements at 282–293 K over range 1550 H_2O to 32.7 H_2O . Corrected to 298 K using 41PER Cp measurements of aqueous solutions at 293 K.
- S: 10/90 VBP
233. Z: 41PER
R: $\text{FeSO}_4\cdot 7\text{H}_2\text{O}(\text{cr}) = \text{FeSO}_4(1000 \text{ H}_2\text{O}) + 7 \text{ H}_2\text{O}(\text{l})$
DV: H, 17.35 \$1.0 kJ
C: Measurements at 282–293 K over range 1550 H_2O to 32.7 H_2O . Corrected to 298 K using 41PER Cp measurements of aqueous solutions at 293 K.
- S: 10/90 VBP
234. Z: 41PER
R: $\text{FeSO}_4\cdot 7\text{H}_2\text{O}(\text{cr}) = \text{FeSO}_4(300 \text{ H}_2\text{O}) + 7 \text{ H}_2\text{O}(\text{l})$
DV: H, 18.30 \$1.0 kJ
C: Measurements at 282–293 K over range 1550 H_2O to 32.7 H_2O . Corrected to 298 K using 41PER Cp measurements of aqueous solutions at 293 K.
- S: 10/90 VBP
235. Z: 41PER
R: $\text{FeSO}_4\cdot 7\text{H}_2\text{O}(\text{cr}) = \text{FeSO}_4(200 \text{ H}_2\text{O}) + 7 \text{ H}_2\text{O}(\text{l})$
DV: H, 18.70 \$1.0 kJ
C: Measurements at 282–293 K over range 1550 H_2O to 32.7 H_2O . Corrected to 298 K using 41PER Cp measurements of aqueous solutions at 293 K.
- S: 10/90 VBP
236. Z: 41PER
R: $\text{FeSO}_4\cdot 7\text{H}_2\text{O}(\text{cr}) = \text{FeSO}_4(100 \text{ H}_2\text{O}) + 7 \text{ H}_2\text{O}(\text{l})$
DV: H, 19.35 \$1.0 kJ
C: Measurements at 282–293 K over range 1550 H_2O to 32.7 H_2O . Corrected to 298 K using 41PER Cp measurements of aqueous solutions at 293 K.
- S: 10/90 VBP
237. Z: 41PER
R: $\text{FeSO}_4\cdot 7\text{H}_2\text{O}(\text{cr}) = \text{FeSO}_4(75 \text{ H}_2\text{O}) + 7 \text{ H}_2\text{O}(\text{l})$
DV: H, 19.65 \$1.0 kJ
C: Measurements at 282–293 K over range 1550 H_2O to 32.7 H_2O . Corrected to 298 K using 41PER Cp measurements of aqueous solutions at 293 K.
- S: 10/90 VBP
238. Z: 41PER
R: $\text{FeSO}_4\cdot 7\text{H}_2\text{O}(\text{cr}) = \text{FeSO}_4(50 \text{ H}_2\text{O}) + 7 \text{ H}_2\text{O}(\text{l})$
DV: H, 20.05 \$1.0 kJ
C: Measurements at 282–293 K over range 1550 H_2O to 32.7 H_2O . Corrected to 298 K using 41PER Cp measurements of aqueous solutions at 293 K.
- S: 10/90 VBP
239. Z: 41PER
R: $\text{FeSO}_4\cdot 7\text{H}_2\text{O}(\text{cr}) = \text{FeSO}_4(40 \text{ H}_2\text{O}) + 7 \text{ H}_2\text{O}(\text{l})$
DV: H, 20.30 \$1.0 kJ
C: Measurements at 282–293 K over range 1550 H_2O to 32.7 H_2O . Corrected to 298 K using 41PER Cp measurements of aqueous solutions at 293 K.
- S: 10/90 VBP
240. Z: 41PER
R: $\text{FeSO}_4\cdot 7\text{H}_2\text{O}(\text{cr}) = \text{FeSO}_4(35 \text{ H}_2\text{O}) + 7 \text{ H}_2\text{O}(\text{l})$
DV: H, 20.45 \$1.0 kJ
C: Measurements at 282–293 K over range 1550 H_2O to 32.7 H_2O . 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: $= \text{FeCO}_3(\text{cr})$
DV: S, 22.25 \$0.4 C
F: TN
C: measured by 34AND, 54–297 K. $C_p = 19.63 \text{ cal}/(\text{mol}\cdot\text{K})$ at 298.15
- S: VBP Aug. 85
242. Z: 64KOS/KAL
R: $= \text{FeCO}_3(\text{cr})$
DV: S, 96.1 \$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. $S(0-70 \text{ K}) = 16.8 \text{ J}/(\text{mol}\cdot\text{K})$
- S: VBP Aug. 85
243. Z: 35KRU
R: $\text{FeCO}_3(\text{cr}) = \text{FeO}(\text{cr}) + \text{CO}_2(\text{g})$
DV: H, 127 \$20 kJ
F: TN
W: 99
C: Third law value. Decomp. to FeO occurs at approx. 710 K. Not considered. Mechanism. of decomp. complex. See 71FRE
- S: VBP Aug. 85
244. Z: 81REI/JOH
R: $\text{FeCO}_3(\text{cr}) + 2\text{H} + (\text{ao}) = \text{Fe} + 2(\text{ao}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}$
DV: G, 323.15 K, -45.84 \$0.5 kJ
DV: G, -44.75 \$1.0 kJ

- 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 kJ
F: TN,
W: 99
C: Corrected from 18 C; no analysis of products. Assumed oxidation goes completely to Fe₃O₄(cr). Same as 29ROT1. Rejected in TN evaluation.
S: VBP Aug. 85
246. Z: 1875BER
R: FeSO₄(220 H₂O)+K₂CO₃(220 H₂O)=FeCO₃(cr)+K₂SO₄(440 H₂O)
DV: H, 4.36 \$0.5 kC
C: 16 C measurement, est'd dCp=100 cal/(mol.K)
S: 8/85 VBP
247. Z: 1875BER
R: FeSO₄(220H₂O)+Na₂CO₃(220 H₂O)=FeCO₃(cr)+Na₂SO₄(440H₂O)
DV: H, 4.64 \$0.5 kC
C: 16 C measurement, est'd dCp=100 cal/(mol.K)
S: VBP Aug. 85
248. Z: 18SMI
R: FeCO₃(cr)+H₂CO₃(ao)=Fe(HCO₃)₂(ai)
DV: G, 14.01 \$0.5 kJ
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)=Fe+2(ao)+CO₃-2(ao)
DV: G, 59.96 \$0.84 kJ
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)=FeCO₃(ai)
DV: G, 60.22 \$0.60 kJ
C: pK=10.55 \$0.03 based on three measurements.
S: 3/89 VBP
251. Z: 78JOH/BAU
R: Fe+2(ao)+HCO₃-(ao)=FeHCO₃+(ao)
DV: G, -7.4 \$1.1 kJ
C: K lies between 10 and 30 at 298 K
S: 5/86 VBP
- DV: H, 41.3 \$6.0 kJ
C: IVTAN 3-85 EQ. 229
Corrected for S₀(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 S₀(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 kJ
C: IVTAN 3-85 EQ. 235
Corrected for S₀(FeCl₂, g)=293.803 (1 atm) and FeCl₂(cr), S₀=118.0 and H-H(0)=16.27
C: Transpiration; third law, 6 pts, 981-1107 K, second law 201 \$18
S: VM 4/87, 10/88 VBP
4. Z: 55SCH/BAY
R: FeCl₂(cr)=FeCl₂(g)
DV: H, 194 \$8.26 kJ
W: 99
C: IVTAN 3-85 EQ. 236
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
5. Z: 58SCH/POR
R: FeCl₂(cr)=FeCl₂(g)
DV: H, 199.17 \$4.0 kJ
W: 99
C: IVTAN 3-85 EQ. 237
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, 2 pts 671 K and 701 K
S: VM 4/87, 10/88 VBP
6. Z: 58SCH/POR
R: FeCl₂(cr)=FeCl₂(g)
DV: H, 196.73 \$4.0
C: IVTAN 3-85 EQ. 238
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, 7 pts, 621-701 K; Second law 172 \$15 kJ
S: VM 4/87, 10/88 VBP
7. Z: 60SIM/GRE
R: FeCl₂(cr)=FeCl₂(g)
DV: H, 199.03 \$4.0 kJ
C: IVTAN 3-85 EQ. 239
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, 670-740 K equation only, second law 196 kJ

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)

- S: VM 4/87, 10/88 VBP
 8. Z: 69KAN/MCC
 R: $\text{FeCl}_2(\text{cr})=\text{FeCl}_2(\text{g})$
 DV: H, 198.81 \$4.0 kJ
 C: IVTAN 3-85 EQ. 240
 Corrected for $S_0(\text{FeCl}_2, \text{g})=293.803$ (1 atm) and $\text{FeCl}_2(\text{cr})$, $S_0=118.0$ and $\text{H}-\text{H}(0)=16.27$
 C: Effusion; third law, 725–825 equation only, second law 210 kJ
 S: VM 4/87, 10/88 VBP
 9. Z: 69KAN/MCC
 R: $\text{FeCl}_2(\text{cr})=\text{FeCl}_2(\text{g})$
 DV: H, 198.31 \$4.0
 C: IVTAN 3-85 EQ. 241
 Corrected for $S_0(\text{FeCl}_2, \text{g})=293.803$ (1 atm) and $\text{FeCl}_2(\text{cr})$, $S_0=118.0$ and $\text{H}-\text{H}(0)=16.27$
 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: $\text{FeCl}_2(\text{cr})=\text{FeCl}_2(\text{g})$
 DV: H, 198.68 \$6.00 kJ
 C: IVTAN 3-85 EQ. 242
 Corrected for $S_0(\text{FeCl}_2, \text{g})=293.803$ (1 atm) and $\text{FeCl}_2(\text{cr})$, $S_0=118.0$ and $\text{H}-\text{H}(0)=16.27$
 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: $\text{FeCl}_2(\text{cr})=\text{FeCl}_2(\text{g})$
 DV: H, 199.75 \$4.0
 C: IVTAN 3-85 EQ. 243
 Corrected for $S_0(\text{FeCl}_2, \text{g})=293.803$ (1 atm) and $\text{FeCl}_2(\text{cr})$, $S_0=118.0$ and $\text{H}-\text{H}(0)=16.27$
 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: $\text{FeCl}_2(\text{cr})=\text{FeCl}_2(\text{g})$
 DV: H, 193.23 \$4.00 kJ
 C: IVTAN 3-85 EQ. 244
 Corrected for $S_0(\text{FeCl}_2, \text{g})=293.803$ (1 atm) and $\text{FeCl}_2(\text{cr})$, $S_0=118.0$ and $\text{H}-\text{H}(0)=16.27$
 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: $\text{FeCl}_2(\text{cr})=\text{FeCl}_2(\text{g})$
 DV: H, 196.41 \$4.0
 C: IVTAN 3-85 EQ. 245
 Corrected for $S_0(\text{FeCl}_2, \text{g})=293.803$ (1 atm) and $\text{FeCl}_2(\text{cr})$, $S_0=118.0$ and $\text{H}-\text{H}(0)=16.27$
 C: Effusion; third law, 624–952 K equation only; second law 215 kJ
 S: VM 4/87, 10/88 VBP
 14. Z: 78NOV
 R: $\text{FeCl}_2(\text{cr})=\text{FeCl}_2(\text{g})$
 DV: H, 202.419 \$4.14 kJ
 W: 99
 C: IVTAN 3-85 EQ. 246
 Corrected for $S_0(\text{FeCl}_2, \text{g})=293.803$ (1 atm) and $\text{FeCl}_2(\text{cr})$, $S_0=118.0$ and $\text{H}-\text{H}(0)=16.27$
 S: VM 4/87, 10/88 VBP
 15. Z: 88CTT
 R: $=\text{FeCl}_2(\text{g})$
 DV: S, 293.915 \$4.0 J
 C: at 1 bar, $S_0(1 \text{ atm})=293.806$ kJ/mol
 ** or 293.912 and 293.803 (6/90 EME)
 S: 8/88 VBP
 16. Z: 88CTT
 R: $=\text{Fe}_2\text{Cl}_4(\text{g})$
 DV: S, 439.872 \$10.0
 C: at 1 bar
 ** or 439.868 (6/90 EME)
 S: 10/88 VBP
 17. Z: 89CTT
 R: $=\text{Fe}_2\text{Cl}_6(\text{g})$
 DV: S, 528.066\$
 C: at 1 bar, $\text{H}-\text{H}(0)=37.30$ kJ/mol
 S: 10/88 VBP, 10/90 VBP
 18. Z: 88CTT
 R: $\text{FeCl}_3(\text{g})$
 DV: S, 344.827\$
 C: at 1 bar, $\text{H}-\text{H}(0)=17.815$ kJ/mol.K
 S: 10/88 VBP
 19. Z: 25MAI
 R: $2\text{FeCl}_3(\text{cr})=\text{Fe}_2\text{Cl}_6(\text{g})$
 DV: H, 133.36 \$6.7 kJ
 C: Revised 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: $2\text{FeCl}_3(\text{cr})=\text{Fe}_2\text{Cl}_6(\text{g})$
 DV: H, 132.67 \$6.8 kJ
 C: Revised from IVTAN 3-85 EQ.104 and 86ARI/BER values (at 0 K). Static; 526–568 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.
 21. Z: 29JEL/KOO
 R: $2\text{FeCl}_3(\text{cr})=\text{Fe}_2\text{Cl}_6(\text{g})$
 DV: H, 130.1 \$7.1 kJ
 C: Revised 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 $2\text{FeCl}_3(\text{cr})=2\text{FeCl}_3(\text{g})$. Measurements were recalculated for $\text{Fe}_2\text{Cl}_6(\text{g})$ as a reaction product.
 S: VM 10/87, 10/88 VBP, 12/89 EME and VBP
 22. Z: 38SAN2
 R: $2\text{FeCl}_3(\text{cr})=\text{Fe}_2\text{Cl}_6(\text{g})$
 DV: H, 134.6 \$6.8 kJ
 C: Revised 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

- S: VM 10/87, 10/88 VBP, 12/89 EME and VBP
 23. Z: 42JOH/WEI
 R: $2\text{FeCl}_3(\text{cr})=\text{Fe}_2\text{Cl}_6(\text{g})$
 DV: H, 132.7 \$6.7 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 kJ
 S: VM 10/87, 10/88 VBP, 12/89 EME and VBP
 24. Z: 58WIL/GRE
 R: $2\text{FeCl}_3(\text{cr})=\text{Fe}_2\text{Cl}_6(\text{g})$
 DV: H, 134 \$11 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 kJ
 S: VM 10/87, 10/88 VBP
 25. Z: 62HAM/GRE
 R: $2\text{FeCl}_3(\text{cr})=\text{Fe}_2\text{Cl}_6(\text{g})$
 DV: H, 135.0 \$4.2 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 kJ
 S: VM 10/87, 10/88 VBP, 12/89 EME and VBP
 26. Z: 62COO
 R: $2\text{FeCl}_3(\text{cr})=\text{Fe}_2\text{Cl}_6(\text{g})$
 DV: H, 127.61 \$11.00 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 kJ
 S: VM 10/87, 10/88 VBP, 12/89 EME and VBP
 27. Z: 65CHR
 R: $2\text{FeCl}_3(\text{cr})=\text{Fe}_2\text{Cl}_6(\text{g})$
 DV: H, 120.8 kJ
 W: 99
 C: Spectrophotometric, only vsH0(440 K)=115.5 \$2.5 kJ calculated by the 2nd law is known.
 S: VM 10/87, 10/88 VBP, 12/89 EME and VBP
 28. Z: 68GAL
 R: $2\text{FeCl}_3(\text{cr})=\text{Fe}_2\text{Cl}_6(\text{g})$
 DV: H, 132.1 \$6.8 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 kJ
 S: VM 10/87, 11/88 VBP, 12/89 EME and VBP
 29. Z: 68MAP/GRE
 R: $2\text{FeCl}_3(\text{cr})=\text{Fe}_2\text{Cl}_6(\text{g})$
 DV: H, 139.32 \$6.3 kJ
 DV: H, 550 K, 128.0 \$5.4 kJ
 C: Calorimetric dsH0(550 K)=128.0 \$5.4 kJ. Five measurements.
 S: VM 10/87, 11/88 VBP, 12/89 VBP
 30. Z: 68MAP/GRE
 R: $2\text{FeCl}_3(\text{cr})=\text{Fe}_2\text{Cl}_6(\text{g})$
 DV: H, 151.51 \$7.6 kJ
 C: Calorimetric ddH0(583 K)=51.8 \$2.5 kJ. Three measurements.
 S: VM 10/87, 11/88 VBP, 12/89
 31. Z: 68MAP/GRE
 R: $2\text{FeCl}_3(\text{l})=\text{Fe}_2\text{Cl}_6(\text{g})$
 DV: H, 583 K, 51.8 \$2.5 kJ
 C: Calorimetric, three measurements
 S: VM 10/87, 11/88 VBP
 32. Z: 69POL/KOM
 R: $2\text{FeCl}_3(\text{cr})=\text{Fe}_2\text{Cl}_6(\text{g})$
 DV: H, 131.9 \$7.2 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 kJ
 S: VM 10/87, 11/88 VBP, 12/89 EME and VBP
 33. Z: 77LAN/ADA
 R: $2\text{FeCl}_3(\text{cr})=\text{Fe}_2\text{Cl}_6(\text{g})$
 DV: H, 139.8 \$5.0 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 103.2 kJ
 S: VM 10/87, 11/88 VBP, 12/89 EME and VBP
 34. Z: 77LAN/ADA
 R: $2\text{FeCl}_3(\text{cr})=\text{Fe}_2\text{Cl}_6(\text{g})$
 DV: H, 133.6 \$6.1 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 kJ
 S: VM 10/87, 11/88 VBP, 12/89 EME and VBP
 35. Z: 83RUS/GRE
 R: $2\text{FeCl}_3(\text{cr})=\text{Fe}_2\text{Cl}_6(\text{g})$
 DV: H, 154.1 kJ
 W: 99
 C: Spectrophotometric, dsH0(550 K)=147.2 kJ, second law
 S: VM 10/87, 11/88 VBP, 12/89 VBP