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, $\Delta_f H°$, $\Delta_f G°$, 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: $\Delta_f H° = -90.0\pm0.5$ kJ·mol^{-1}, $\Delta_f G° = -90.53\pm1.0$ kJ·mol^{-1}, $S° = -101.6\pm3.7$ J·mol^{-1}·K^{-1} for Fe^{2+}(ao) and $\Delta_f H° = -49.0\pm1.5$ kJ·mol^{-1}, $\Delta_f G° = -16.28\pm1.1$ kJ·mol^{-1}, $S° = -278.4\pm7.7$ J·mol^{-1}·K^{-1} for Fe^{3+}(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 FeOOH(cr, Goethite), $FeCl_2$(cr), $FeCl_3$(cr), $FeBr_2$(cr), $FeBr_3$(cr), FeI_2(cr), and $FeSO_4 \cdot 7H_2O$(cr), as well as "reconstituted" recommended process values with uncertainties involving these substances. All recommended values are also given for a standard state of $p°=1$ atm. A computer based reaction catalog of measurements accompanies the text analysis. © *1995 American Institute of Physics and American Chemical Society.*

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

Contents

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 AI.b (Reaction Catalog) and, unless otherwise specified, reaction energies are to be assumed to be at 298.15 K and are given as kJ·mol^{-1}; the energy value is for the reaction as written. For convenience to the users, E values and ΔG values given in Secs. 4 and 5 are as originally obtained using $p^\circ = 1$ atm, unless otherwise stated; calculation to

$\Delta_f G^\circ(Fe^{+2}, ao)$ and $\Delta_f G^\circ(Fe^{+3}, ao)$ 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 (AI.b), the following are used:

ai = hypothetical standard state, $m=1$ 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

250 H$_2$O, 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

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

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

$\Phi_{L(D-H)}$ = 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

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

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

$$\left. + 3 \ln (1+4BI^{1/2}) - 1 \right],$$

$\Delta z^2 = \Sigma$ (z^2 ions, products—z^2 ions, reactants),
z=charge on the ion,
at 298.15 K B=0.3285,
S_H=1.4703 kJ·mol^{-1},
W_H=$-.54183$ kJ·mol^{-1}
So that

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[a]This is a reference code used in the text and in the accompanying reaction catalog. It is keyed to the bibliographic references given in Sec. 7. A description of the reference code is given in 1.2.5 and AI.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:

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

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

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

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

K,   °C = degrees Kelvin, Celsius temperature.

All values are for the reaction as given.

1.2.7. Uncertainties

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

The 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

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, $\Delta_f H°$, $\Delta_f G°$, 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 $Fe^{2+}(ao)$ and $Fe^{3+}(ao)$ are:

$Fe_3O_4(cr)$, FeOOH(cr, Goethite), $FeCl_2(cr)$, $FeCl_2 \cdot 4H_2O(cr)$, $FeCl_3(cr)$, $FeBr_2(cr)$, $FeBr_3(cr)$, $FeI_2(cr)$, $FeSO_4 \cdot 7H_2O(cr)$, and $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O(cr)$.

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

(1) the determinations of $\Delta_f H°(FeCl_2$, cr), independent of other Fe compounds, and the $\Delta_{sol} H°$ of $FeCl_2(cr)$ in $H_2O(l)$; an initial selection is made for $\Delta_f H°(FeCl_2$, cr);

(2) the determinations of $\Delta_f H°(FeBr_2$, cr), independent of other Fe compounds, and the $\Delta_{sol} H°$ of $FeBr_2(cr)$ in $H_2O(l)$; this also requires an initial selection for $\Delta_f H°(FeBr_2$, cr);

(3) the measurements of $\Delta_f H°(FeI_2$, cr); those independent of other Fe compounds, and then that dependent upon $\Delta_f H°(FeBr_2$, cr); an initial selection is also made for $\Delta_f H°(FeI_2$, cr), as well as $\Delta_{sol} H°$;

(4) the independently determined $\Delta_f H°(FeSO_4 \cdot 7H_2O$, cr) and the $\Delta_{sol} H°$ in $H_2O(l)$;

(5) the independently arrived at $\Delta_f H°((NH_4)_2Fe(SO_4)_2$, cr) and its $\Delta_{sol} H°$ in $H_2O(l)$.

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

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

(1) the determinations for $\Delta_f H°(FeCl_3$, cr), those independent of other Fe compounds as well as those linked to $FeCl_2(cr)$, combined with a selection for $\Delta_{sol} H°(FeCl_3$, cr) which in itself requires a working value;

(2) the direct determination of $\Delta_f H°(Fe^{3+}$, ao) through oxidation of Fe(cr);

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

In Sec. 3.4 we summarize the various possibilities and select a value for $\Delta_f H°(Fe^{3+}$, ao), modify our initial selection for $\Delta_f H°(FeCl_3$, cr), and also select a value for $\Delta_f H°(FeBr_3$, cr). These selections will eventually become our final recommended values.

Section 4—The $\Delta_f G°(Fe^{2+}$, 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 $\Delta_f G°$ independent of other Fe species;

(2) equilibrium measurements involving solubilities of $Fe_3O_4(cr$, magnetite) (Sec. 4.2.2) and $FeSO_4 \cdot 7H_2O(cr)$ (Sec. 4.2.3) and $FeCl_2 \cdot 4H_2O(cr)$ (Sec. 4.2.4) which also involves its vapor pressure.

In Sec. 4.3 a tentative selection is made ($p° = 1$ atm).
Section 5—The $\Delta_f G°(Fe^{3+}$, ao) is evaluated by:

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

(2) by obtaining values for $\Delta_fG°(Fe^{3+}$, ao)$-\Delta_fG°(Fe^{2+}$, 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 $\Delta_fG°(Fe^{2+}$, ao) to obtain other values for $\Delta_fG°(Fe^{3+}$, ao).

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

Section 6—All final recommended property values and uncertainties are tabulated ($p° = 1$ atm and $p° = 1$ bar). Predicted (calculated) process values and uncertainties for many of the reactions used in this evaluation are also tabulated. 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+}, $\Delta_fH°(Fe^{2+}$, ao)

Here we evaluate the measurements leading to $\Delta_fH°(Fe^{2+}$, ao) beginning with:

(1) the determinations of $\Delta_fH°(FeCl_2$, cr), independent of other Fe compounds, and the $\Delta_{sol}H°$ of $FeCl_2(cr)$ in $H_2O(l)$; an initial selection is made for $\Delta_fH°(FeCl_2$, cr);

(2) the determinations of $\Delta_fH°(FeBr_2$, cr), independent of other Fe compounds, and the $\Delta_{sol}H°$ of $FeBr_2(cr)$ in $H_2O(l)$; this also requires an initial selection for $\Delta_fH°(FeBr_2$, cr);

(3) the measurements of $\Delta_fH°(FeI_2$, cr); those values independent of other Fe compounds, and then that dependent upon $\Delta_fH°(FeBr_2$, cr); an initial selection is also made for $\Delta_fH°(FeI_2$, cr), as well as $\Delta_{sol}H°$;

(4) the independently determined $\Delta_fH°(FeSO_4 \cdot 7H_2O$, cr) and the $\Delta_{sol}H°$ in $H_2O(l)$;

(5) the independently arrived at $\Delta_fH°((NH_4)_2Fe(SO_4)_2$, cr) and its $\Delta_{sol}H°$ in $H_2O(l)$.

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

2.1. The Chloride System

2.1.1. $\Delta_fH°(FeCl_2$, cr)

2.1.1.1. Calorimetric measurements of the enthalpies of the reaction of Fe(cr) and FeCl₂(cr) in HCl solutions

There are two determinations for the enthalpy of the reaction:

$$Fe(cr)+2(HCl \cdot nH_2O)=FeCl_2(cr)+H_2(g)$$
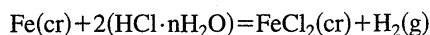
$\Delta_rH=-17.04\pm0.21$ kJ·mol^{-1} ($n=12.731$)[59KOE/COU (No. 90)]

and

$\Delta_rH=-12.85\pm2.0$ kJ·mol^{-1} ($n=200$)[1882THO (No. 89)].

Correction to the standard state of HCl(aq), using ϕ_L from 65PAR, results in $\Delta_rH° = -7.50\pm0.21$ and -11.08 ± 2.0 kJ·mol^{-1}, respectively, for

$$Fe(cr)+2HCl(ai)=FeCl_2(cr)+H_2(g)$$
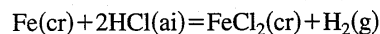
and $\Delta_fH°(FeCl_2$, cr)$= -341.66\pm0.25$ and -345.24 ± 2.0 kJ mol^{-1}, respectively.

2.1.1.2. Calorimetric measurements of the enthalpies of the reaction of Fe(cr), FeBr₂(cr) and FeCl₂(cr) in aqueous (KBr, Br₂) solutions.

Recently, 89EFI/EVD and 89EVD/EFI (Nos. 115 and 166) measured the enthalpies of reaction of Fe(cr), $FeBr_2(cr)$, and $FeCl_2(cr)$ in (KBr, Br_2) solutions, as well as the enthalpies of solution of KCl(cr) and KBr(cr) in the same medium to result in the following summations:

1. $Fe(cr)+Br_2(l)=FeBr_2(cr)$;

$$\Delta_rH°=-244.737\pm0.22 \text{ kJ·mol}^{-1}$$

2. $FeBr_2(cr)+2KCl(cr)=FeCl_2(cr)+2KBr(cr)$;
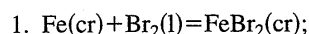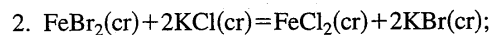
$$\Delta_rH°=-10.032\pm0.21 \text{ kJ·mol}^{-1}$$

Using the following:

3a. $KCl(cr)=K^+(ao)+Cl^-(ao)$;
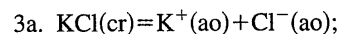
$$\Delta_rH°=17.245\pm0.045 \text{ kJ·mol}^{-1}[87GAR/PAR]$$

and

3b. $KBr(cr)=K^+(ao)+Br^-(ao)$;
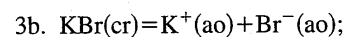
$$\Delta_rH°=19.75\pm0.05 \text{ kJ·mol}^{-1}[89PAR],^b$$

we obtain

4. $FeBr_2(cr)+2Cl^-(ao)=FeCl_2(cr)+2Br^-(ao)$;
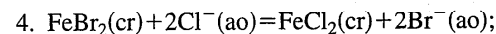
$$\Delta_rH°=-5.032\pm0.22 \text{ kJ·mol}^{-1}.$$

Thus, $\Delta_fH°(FeCl_2$, cr)$-\Delta_fH°(FeBr_2$, cr) $= -96.372 \pm0.24$ kJ·mol^{-1}, and using $\Delta_rH°(1)$, $\Delta_fH°(FeCl_2$, cr) $=-341.109\pm0.22$ kJ·mol^{-1}, in support of 59KOE/COU (Sec. 2.1.1.1). Similar measurements were made by 34HIE/WOE (No. 167) at 273.15 K for Fe(cr), $Br_2(l)$ and $FeBr_2(cr)$ to obtain (corrected to 298.15 K) $\Delta_fH°(FeBr_2$, cr) or $\Delta_rH°(1)= -251.44\pm5.0$ kJ·mol^{-1}. Since 34HIE/APP (No. 168) measured the enthalpies of solution of $FeCl_2(cr)$ and $FeBr_2(cr)$ in 2 mol·dm^{-3} HCl (see 8.2 for all details) we have, in place of the above reaction (2):

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

TABLE 1. The enthalpy of formation of $FeCl_2$ (cr) from the reaction, $FeCl_2(cr)+H_2(g)=Fe(cr)+2HCl(g)$

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

5. $FeCl_2(cr)+FeBr_2(D·HCl+27H_2O)$

$=FeBr_2(cr)+FeCl_2(D·HCl+27H_2O);$
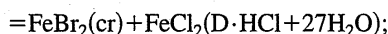
$\Delta_r H=4.99±1.6$ kJ·mol^{-1}.

An estimate for

6. $FeCl_2(D·HCl+27H_2O)+2HBr(ai)$

$=FeBr_2(D·HCl+27H_2O)+2HCl(ai);$

$\Delta_r H=-1.96±0.4$ kJ·mol^{-1}

based on the $\overline{L}_2$ values for HCl (in $27H_2O$) and HBr (in $27H_2O$) from 65PAR results in $\Delta_r H°(4)=-3.03±1.6$ kJ·mol^{-1}, $\Delta_f H°(FeCl_2,$ cr) $-\Delta_f H°(FeBr_2,$ cr) $=-94.37±1.6$ kJ·mol^{-1} and $\Delta_f H°(FeCl_2,$ cr) $=-345.81$ ±5.3 kJ·mol^{-1}, in support of 1882THO. It should be pointed out that the $\Delta(\Delta_f H°)$'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 $FeCl_2(cr)$ by $H_2(g)$

For the reaction: $FeCl_2(cr)+H_2(g)=Fe(cr)+2HCl(g)$, we tabulate (Table 1) the second (II) and third (III) law results from six studies considered in this analysis (see Sec. 8.2 entries for details) and the weighted average of the third law values.

2.1.1.4. Summary

The considered values for $\Delta_f H°(FeCl_2,$ cr)/kJ·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 $-345.24±2.0$ kJ·mol^{-1}) from which we initially select $-341.66±0.25$ kJ·mol^{-1} and which we will use in Sec. 2.1.2.

2.1.2. The Standard Enthalpy of Solution of FeCl₂(cr) in H₂O(l), and Δ_f H°(Fe²⁺, ao)

For the process: $FeCl_2(cr)=Fe^{2+}(ao)+2Cl^-(ao)$, the measurements lead to the following:

	$\Delta_f H°$, kJ·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 $\Delta_{sol}H$ of $FeCl_2(cr)$ as a function of molality in the range 0.0002 to 0.011 mol·kg^{-1} (total ionic strength 0.01155 to 0.03713 mol·kg^{-1}) and the direct enthalpies of dilution of a $FeCl_2$ solution by 79BER/MOR (No. 116) ($m=4.43$ mol·kg^{-1}) to final solutions in the range 0.0016 to 0.0052 mol·kg^{-1} (total ionic strength 0.0049 to 0.0157 mol·kg^{-1}).

We accept for a "tentative" or working value, $\Delta_{sol}H°=-83.00±0.10$ kJ·mol^{-1}. With the initial value $\Delta_f H°(FeCl_2,$ cr)$=-341.66±0.25$ kJ·mol^{-1} and $\Delta_{sol}H°$ $=-83.00±0.10$ kJ·mol^{-1} we obtain $\Delta_f H°(FeCl_2,$ ai) $=-424.66±0.15$ kJ·mol^{-1} and $\Delta_f H°(Fe^{2+},$ ao) $=-90.50±0.25$ kJ·mol^{-1}. It is obvious, however, from the spread in values for $\Delta_f H°(FeCl_2,$ cr): $-340.4±2.0$ to $-345.24±2.0$ kJ·mol^{-1}, that the range of values for $\Delta_f H°(Fe^{2+},$ aq) is -89.4 to -94.08 kJ·mol^{-1}.

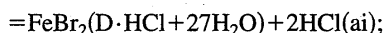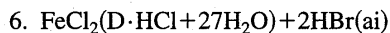In addition, the combination of 89EFI/EVD and 89EVD/EFI for $\Delta_f H°(FeCl_2,$ cr)$(-341.11±0.22$ kJ·mol$^{-1})$ and $\Delta_{sol}H°(-83.11±0.10$ kJ·mol$^{-1})$ from 90EFI/FUR results in a direct path to $\Delta_f H°(Fe^{2+},$ ao)$=-90.06±0.25$ kJ·mol^{-1}.

2.2. The Bromide System

2.2.1. Δ_f H°(FeBr₂, cr)

2.2.1.1. Calorimetric measurements of the enthalpies of reaction of Fe(cr) and FeBr₂(cr) in aqueous (KBr, Br₂) solutions

In Sec. 2.1.1.2 we obtain two values for $\Delta_f H°(FeBr_2,$ cr), $-244.74±0.22$ kJ·mol^{-1} [89EFI/EVD] and $-251.44±5.2$ kJ·mol^{-1} [34HIE/WOE], although the $\Delta_f H°(FeCl_2,$ cr)$-\Delta_f H°(FeBr_2,$ cr)'s are in closer agreement, $-96.37±0.24$ [89EVD/EFI] and $-94.37±1.6$ kJ·mol^{-1}, respectively.[c] We initially select $\Delta_f H°(FeBr_2,$ cr) $=-245.00±0.25$ kJ·mol^{-1}.

2.2.2. The Standard Enthalpy of Solution of FeBr₂(cr) in H₂O(l) and Δ_f H°(Fe²⁺, ao)

From AI.b, we have $\Delta_{sol}H°(FeBr_2,$ cr)/kJ·mol$^{-1}=-86.85$ ±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 $\Delta_{sol}H°=-86.85±0.12$ kJ·mol^{-1}, resulting in $\Delta_f H°(Fe^{2+},$ ao)$=-89.03±0.28$ kJ·mol^{-1}. However, com-

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[c]One can also obtain $\Delta_f H°(FeCl_2,$ cr)$-\Delta_f H°(FeBr_2,$ cr)$=-95.08±0.5$ kJ·mol^{-1} from the difference in the standard enthalpies of solution of both salts in H_2O (-83.11 and -86.85 kJ·mol^{-1}, respectively) [90EFI/FUR (Nos. 94 and 178)] and the difference in the $\Delta_f H°$s of the Cl$^-$(ao) and Br$^-$(ao).

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

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

2.3. The Iodide System

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

2.3.1.1. Calorimetric measurements of the enthalpies of reactions of Fe(cr), FeI$_2$(cr), and I$_2$(cr) in aqueous (KBr, Br$_2$) solutions.

The measurements of 90EFI/EVD and 89EFI/EVD (No. 194) on the $\Delta_{sol}H$ of all three components in aqueous KBr, Br$_2$ solutions lead to:

$$\text{Fe(cr)}+\text{I}_2(\text{cr})=\text{FeI}_2(\text{cr}); \quad \Delta_f H°=-118.079\pm0.27 \text{ kJ·mol}^{-1}.$$
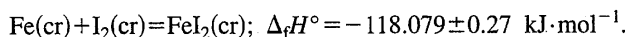
From the results of 34HIE/WOE (No. 198), we obtain $\Delta_f H°=-125.9\pm5.0$ kJ·mol^{-1}.

2.3.1.2. Decomposition of FeI$_2$(cr)

The measurements of 66ZAI/GRE (No. 196) on the decomposition pressure of FeI$_2$(cr) lead to a third law $\Delta H°=166.1\pm5.0$ kJ·mol^{-1} for
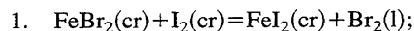
$$\text{FeI}_2(\text{cr})=\text{Fe(cr)}+\text{I}_2(\text{g})$$
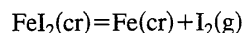
and $\Delta_f H°=-103.7\pm5.1$ kJ·mol^{-1}.

The measurements of 56SCH/ORA (No. 197) on the decomposition of FeI$_2$(l) yield widely different values, a second law $\Delta H°=193.9\pm20$ kJ·mol^{-1} and a third law $\Delta H°=149.4$ kJ·mol^{-1} which result in $\Delta_f H°=-131$ and -87 kJ·mol^{-1}, respectively.

We reject the values obtained from the decomposition of FeI$_2$(cr) and FeI$_2$(l).

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

The measurements of 89EFI/EVD (Nos. 165 and 194) and 90EFI/EVD (No. 195) on the $\Delta_{sol}H$ of all components in aqueous KBr, Br$_2$, lead to:

1. $\text{FeBr}_2(\text{cr})+\text{I}_2(\text{cr})=\text{FeI}_2(\text{cr})+\text{Br}_2(\text{l})$;

$$\Delta_r H°=126.658\pm0.24 \text{ kJ·mol}^{-1},$$

and

2. $\text{FeBr}_2(\text{cr})+2\text{KI(cr)}=\text{FeI}_2(\text{cr})+2\text{KBr(cr)}$;
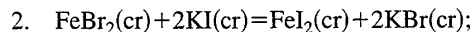
$$\Delta_r H°=-1.677\pm0.19 \text{ kJ·mol}^{-1}.$$

Reaction (1) yields $\Delta_f H°(\text{FeI}_2,\ \text{cr})-\Delta_f H°(\text{FeBr}_2,\ \text{cr})=126.658\pm0.24$ kJ·mol^{-1}. Since $\Delta_{sol}H°(\text{KBr, cr})=19.75\pm0.05$ kJ·mol$^{-1\ e}$ and $\Delta_{sol}H°(\text{KI, cr})=20.28\pm0.10$ kJ·mol^{-1},^{e} we can obtain from reaction (2)

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^{e}Selected from sources cited and used by 89COX/WAG in developing the key values of thermodynamic property values of the ions.

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3. $\text{FeBr}_2(\text{cr})+2\text{I}^-(\text{ao})=\text{FeI}_2(\text{cr})+2\text{Br}^-(\text{ao})$;
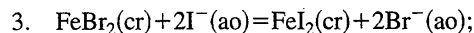
$$\Delta H°=-2.74\pm0.30 \text{ kJ·mol}^{-1} \text{ and } \Delta(\Delta_f H°)$$

$$=126.52\pm0.30 \text{ kJ·mol}^{-1}.^f$$

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

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

The measurements on the $\Delta_{sol}H$ of FeBr$_2$(cr) in 2000H$_2$O(l) [65PAO (No. 174)] and on FeI$_2$(cr) in 4000H$_2$O(l) [65PAO/SAB (No. 201)] may be combined such that:

4. $\text{FeBr}_2(\text{cr})+\text{FeI}_2(4000\text{H}_2\text{O})$

$$=\text{FeI}_2(\text{cr})+\text{FeBr}_2(2000\text{H}_2\text{O})$$;
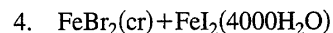
$$\Delta H=-2.93\pm0.56 \text{ kJ·mol}^{-1}.$$

Estimating (AI.b, No. 176)

5. $\text{FeBr}_2(2000\text{H}_2\text{O})=\text{FeBr}_2(4000\text{H}_2\text{O})$;
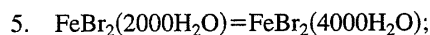
$$\Delta H=-0.20\pm0.20 \text{ kJ·mol}^{-1},$$

and assuming correction to standard conditions is essentially the same for FeBr$_2$(4000H$_2$O) and FeI$_2$, we obtain $\Delta H°(3) =-3.13\pm0.6$ kJ·mol^{-1} and $\Delta(\Delta_f H°)=126.13\pm0.6$ kJ·mol^{-1}.

The $\Delta(\Delta_f H°)$'s are in good agreement, and using $\Delta(\Delta_f H°)=126.5\pm0.3$ kJ·mol^{-1} and our tentative $\Delta_f H°(\text{FeBr}_2,\ \text{cr})=-245.00\pm0.25$ kJ·mol^{-1}, we obtain -118.5 ± 0.4 kJ·mol^{-1} for $\Delta_f H°(\text{FeI}_2,\ \text{cr})$, in agreement with the direct determination -118.08 ± 0.27 kJ·mol^{-1} from 90EFI/EVD and 89EFI/EVD. We tentatively select -118.5 ± 0.4 kJ·mol^{-1}.

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

The enthalpy of solution has been measured by 65PAO/SAB (No. 201) (in 4000H$_2$O) as -81.42 ± 0.25 kJ·mol^{-1}. With an estimate for $\phi_L=1.2\pm0.5$ kJ·mol^{-1}, $\Delta_{sol}H°$ becomes -82.62 ± 0.6 kJ·mol^{-1} and with our "tentative" $\Delta_f H°(\text{FeI}_2,\ \text{cr})=-118.5\pm0.40$ kJ·mol^{-1}, we obtain $\Delta_f H°(\text{FeI}_2,\ \text{ai})=-201.12\pm0.72$ kJ·mol^{-1} and $\Delta_f H°(\text{Fe}^{2+}$, ao) $= - 87.56 \pm 0.8$ kJ·mol^{-1}. (If we use $\Delta_f H°(\text{FeI}_2,\ \text{cr})=-118.08\pm0.27$ with the above $\Delta_{sol}H°$, $\Delta_f H°(\text{Fe}^{2+}$, ao)$=-87.14\pm0.7$ kJ·mol^{-1}.)

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

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^{f}From their $\Delta_f H°(\text{FeBr}_2,\ \text{cr}) - \Delta_f H°(\text{FeCl}_2,\ \text{cr})=96.37\pm0.24$ kJ·mol^{-1} one can obtain $\Delta_f H°(\text{FeI}_2,\ \text{cr})-\Delta_f H°(\text{FeCl}_2,\ \text{cr})=222.97\pm0.31$ kJ·mol^{-1}. This relationship is equally important in the final smoothing process.

2.4. The Sulfate System

2.4.1. $\Delta_f H°(FeSO_4·7H_2O, cr)$

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:

$$Fe(cr)+H_2O_2(3.5H_2O)^g+5H_2O(l)+H_2SO_4(0.3H_2O)^h$$

$$=FeSO_4·7H_2O(cr);$$
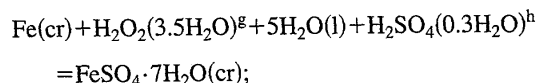
$$\Delta H=-569.96±0.28 \ kJ·mol^{-1}.$$

The resultant $\Delta_f H°$ is $-3013.66±0.5 \ kJ·mol^{-1}$. 63ADA/KEL (No. 211) measured the enthalpy of reaction of Fe(cr) and the $\Delta_{sol}H$ of the heptahydrate in $H_2SO_4·7.068H_2O$ such that

$$Fe(cr)+H_2SO_4·7.068H_2O^h+7H_2O(l)$$
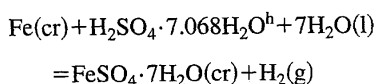
$$=FeSO_4·7H_2O(cr)+H_2(g)$$

$$\Delta H=-137.09±0.40 \ kJ·mol^{-1}.$$

The resultant $\Delta_f H°$ is $-3014.47±0.45 \ kJ·mol^{-1}$. The measurements are in excellent agreement with one another; an average value of $-3014.06±0.40 \ kJ·mol^{-1}$ shall be used for $\Delta_f H°(FeSO_4·7H_2O, cr)$ in the following section.

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

2.4.1.1.1. Enthalpy of solution in H_2O

The process of interest is:

$$FeSO_4·7H_2O(cr)=FeSO_4(ai)+7H_2O(l)$$
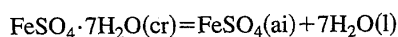
The early measurements of 68LAR/CER (No. 229) and 68LAR are given as $\Delta_r H°=11.80±0.42 \ kJ·mol^{-1}$ (see catalog entry for details). This value includes estimates for ϕ_L, based on $\phi_L(NiSO_4)$. The recent measurements of 83DMI (No. 227) on $\Delta_{sol}H$, as a function of m enable one to obtain ϕ_L in $FeSO_4(aq)$ and to recorrect; although the $\phi_L(FeSO_4)$ values differ from those contained in 68LAR/CER, the average value for $\Delta_{sol}H°$ remains essentially the same. The resultant value for $\Delta_f H°(Fe^{2+}, ao)=-92.11±0.50 \ kJ·mol^{-1}$.

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

The calculated $\Delta_f H°(Fe^{2+}, ao)=-91.01±0.20 \ kJ·mol^{-1}$ using our working value for $\Delta_f H°(FeSO_4·7H_2O, cr)$ $=-3014.06±0.40 \ kJ·mol^1$. However the measurements by 83DMI are meant to be part of a cycle; hence, they may be used directly to obtain $\Delta_f H°(Fe^{2+}, ao)=-90.61±0.20$ $kJ·mol^{-1}$ from $\Delta_f H°(FeSO_4·7H_2O, cr)=-3013.66±0.5$ and $\Delta_{sol}H°=12.90 ±0.10 \ kJ·mol^{-1}$.

2.4.1.1.2. Measurements in $HClO_4$

Measurements were also made of the solution of $FeSO_4·7H_2O(cr)$ in 2, 3, and 4 $mol·dm^{-3}$ $HClO_4$ solutions [83DMI (No. 223), 85VAS/DMI (No. 222)]. In these acidic solutions the reaction is predominantly:

$$FeSO_4·7H_2O(cr)+H^+(ao)=Fe^{2+}(ao)+HSO_4^-(ao)+7H_2O(l).$$
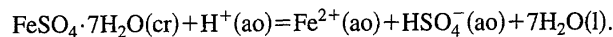
Correction for residual $SO_4^{2-}(ao)$ at each concentration has been made using 89COX/WAG:

$$SO_4^{2-}(ao)+H^+(ao)=HSO_4^-(ao);$$
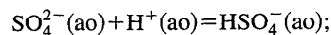
$$\Delta H°=-22.44±1.0 \ kJ·mol^{-1}.$$

The data contained in 83DMI are sufficiently detailed, in giving the varying concentrations of $FeSO_4(aq)$ 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:

$$(\Delta_r H_{(I)}-\Delta H°_{(D-H)})/kJ·mol^{-1}$$

$$=(35.50±0.10)+(2.29±0.02)(I/mol·kg^{-1}),$$

$$(\Delta_r H_{(I)}-\Delta H°_{(D-H)})/kJ·mol^{-1}$$

$$=(35.30±0.55)+(2.42±0.15)(I/mol·kg^{-1}).$$

We accept the first equation. We then obtain with $\Delta_f H°(FeSO_4·7H_2O, cr)=-3014.06±0.40 \ kJ·mol^{-1}$, $\Delta_f H°$ $(Fe^{2+}, ao)=-90.85±0.41 \ kJ·mol^{-1}$. Alternatively, using only 83DMI's value for consistency with his cycle, $\Delta_f H°(Fe^{2+}, ao)=-90.45±0.30 \ kJ·mol^{-1}$. (From the second equation, $\Delta_f H°(Fe^{2+}, ao)= -91.05±0.68$ and -90.65 $±0.62 \ kJ/mol^{-1}$, respectively.)

2.4.2. $\Delta_f H°((NH_4)_2Fe(SO_4)_2·6H_2O, cr)$—Mohr's Salt

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

$$Fe(cr)+H_2O_2(4.95H_2O)+(NH_4)_2SO_4(cr)^i+H_2SO_4(0.2H_2O)^i$$

$$+4H_2O(l)-(NH_4)_2Fe(SO_4)_26H_2O(cr).$$
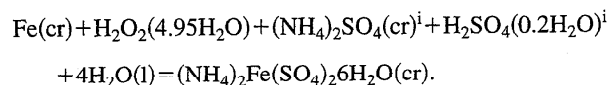
The individual values are:

$^g\Delta_f H°(H_2O_2·3.5H_2O)$ from 82WAG/EVA.

^{h}89PAR calculations provide $\Delta_f H°(H_2SO_4·0.3 \ H_2O)$ and $\Delta_f H°(H_2SO_4·7.068 \ H_2O)=-823.752$ and $-876.568 \ kJ·mol^{-1}$, respectively, as values compatible with CODATA Key Values.

^{i}89PAR calculations provide $\Delta_f H°(H_2SO_4, 0.20H_2O)=-820.668 \ kJ·mol^{-1}$ and $\Delta_f H°((NH_4)_2SO_4, cr)=-1182.30 \ kJ·mol^{-1}$ as values compatible with the CODATA Key Values [89COX/WAG].

$HClO_4$	$\dfrac{\Delta H}{kJ \cdot mol^{-1}}$	
$\overline{mol \cdot dm^{-3}}$	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, $\Delta H = -579.68 \pm 0.44$ kJ·mol^{-1}, excludes the values in 1 mol·dm^{-3} $HClO_4$. The calculated $\Delta_f H° = -3920.00 \pm 1.0$ kJ·mol^{-1}.

2.4.2.1. The standard enthalpy of solution of $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O(cr)$ and $\Delta_f H°(Fe^{2+}, ao)$

2.4.2.1.1. Measurements in $HClO_4$

Measurements were also made by 83DMI (No. 226) on the enthalpy of solution of $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O(cr)$ in 2, 3 and 4 mol·dm^{-3} $HClO_4$. As for the measurements on $FeSO_4 \cdot 7H_2O(cr)$ the process is primarily:

$$(NH_4)_2FeSO_4 \cdot 6H_2O(cr) + 2H^+(ao)$$

$$= 2NH_4^+(ao) + Fe^{2+}(ao) + 2HSO_4^-(ao) + 6H_2O(l).$$
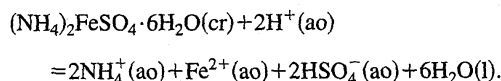
Correction for the residual SO_4^{2-}(ao) at each concentration has been made using CODATA Key Values. 83DMI contains the experimental details that also allow extrapolation of ΔH to $I=0$ in two different ways: (1) extrapolation to $I=0$ depending on total ionic strength on the solution, and (2) a two-stage 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:

$$(\Delta_r H_{(I)} - \Delta_r H°_{(D-H)})/(kJ \cdot mol^{-1})$$

$$= (69.47 \pm 0.18) + (0.31 \pm 0.05)(I/mol \cdot kg^{-1}).$$

The second method gives

$$(\Delta_r H_{(I)} - \Delta_r H°_{(D-H)})/(kJ \cdot mol^{-1})$$

$$= (68.4 \pm 1.1) + (0.2 \pm 0.3)(I/mol \cdot kg^{-1}).$$

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

2.5. The Tentative Selected Parameters

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

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

	$\Delta_f H°(Fe^{2+}, ao)$ kJ·mol^{-1}
Section 2.1.2	
$\Delta_f H°(FeCl_2,cr) = -341.66 \pm 0.25$ kJ·mol^{-1} and $\Delta_{sol} H° = -83.00 \pm 0.10$ kJ·mol^{-1}	−90.50±0.25
Consistent Cycle,	
$\Delta_f H°(FeCl_2,cr) = -341.11 \pm 0.22$ kJ·mol^{-1} and $\Delta_{sol} H° = -83.11 \pm 0.10$ kJ·mol^{-1}	−90.06±0.25
Section 2.2.2	
$\Delta_f H°(FeBr_2,cr) = -245.00 \pm 0.25$ kJ·mol^{-1} and $\Delta_{sol} H° = -86.85 \pm 0.12$ kJ·mol^{-1}	−89.03±0.32
Consistent cycle,	
$\Delta_f H°(FeBr_2,cr) = -244.74 \pm 0.22$ kJ·mol^{-1} and $\Delta_{sol} H° = -86.85 \pm 0.12$ kJ·mol^{-1}	−88.77±0.30
Section 2.3.2	
From $\Delta_f H°(FeI_2,cr) - \Delta_f H°(FeBr_2,cr)$ $= 126.5 \pm 0.30$ kJ·mol^{-1}, the "tentative" $\Delta_f H°(FeBr_2,cr) = -245.00 \pm 0.25$ kJ·mol^{-1}, and $\Delta_{sol} H = -82.62 \pm 0.6$ kJ·mol^{-1}	−87.56±0.72
$\Delta_f H°(FeI_2,cr) = -118.08 \pm 0.27$ kJ·mol^{-1} and $\Delta_{sol} H° = -82.62 \pm 0.6$ kJ·mol^{-1}	−87.14±0.66
Sections 2.4.1.1.1 and 2.4.1.1.2	
$\Delta_f H°(FeSO_4 \cdot 7H_2O,cr) = -3014.06 \pm 0.40$ kJ·mol^{-1} and $\Delta_{sol} H° = +12.90 \pm 0.10$ kJ·mol^{-1} (to $SO4^{2-}$(ao))	−91.01±0.20
or $\Delta_{sol} H° = 35.50 \pm 0.10$ kJ·mol^{-1} (to HSO_4^-(ao))	−90.85±0.41
$\Delta_f H°(FeSO_4 \cdot 7H_2O,cr) = -3013.66 \pm 0.50$ kJ·mol^{-1} and $\Delta_{sol} H° = +12.90 \pm 0.10$ kJ·mol^{-1} (to SO_4^{2-}(ao))	−90.61±0.20
or 35.50 ± 0.10 kJ·mol^{-1} (to HSO_4^-(ao))	−90.45±0.30
Section 2.4.2.1	
$\Delta_f H°((NH4)_2Fe(SO4)_2 \cdot 6H_2O,cr)$ $= 3920.0 \pm 1.0$ kJ·mol^{-1} and $\Delta_{sol} H°$ $= 69.40 \pm 0.20$ kJ·mol^{-1} (to HSO_4^-(ao))	−95.30±1.0
Tentative Selected Value	−90.00±0.5

The tabulated values indicate good agreement from the $FeCl_2(cr)$, $FeBr_2(cr)$, and $FeSO_47H_2O(cr)$ systems for $\Delta_f H°(Fe^{2+}, ao)$. We select $\Delta_f H°(Fe^{2+}, ao) = -90.00 \pm 0.5$ kJ·mol^{-1} as our "tentative" value. As a result of this, some modifications must be made in the previous selections for $\Delta_f H°(FeCl_2, cr)$, $\Delta_f H°(FeBr_2, cr)$, $\Delta_f H°(FeI_2, cr)$, and $\Delta_f H°(FeSO_4 \cdot 7H_2O, cr)$. These changes from the initial se-

lections are given below. With the exception of the $\Delta_f H°(FeSO_4 \cdot 7H_2O$,cr) and its $\Delta_{sol} H°$, these adjusted values will become our final recommended values.

	Initial Selections $\Delta_f H°$	Adjusted Tentative Values $\Delta_f H°$
	$\overline{kJ \cdot mol^{-1}}$	$\overline{kJ \cdot mol^{-1}}$
$\Delta_f H°(Fe^{2+}$, ao)	-90.00 ± 0.5	
$\Delta_{sol} H°(FeCl_2$, cr)	-83.00 ± 0.14 (Sec. 2.1.2)	
$\Delta_f H°(FeCl_2$, cr)	-341.66 ± 0.60 (Sec. 2.1.1.4)	-341.16 ± 0.60
$\Delta_{sol} H°(FeSO_4 \cdot 7H_2O$, cr)	$+12.90 \pm 0.10$ (Sec. 2.4.1.1.1)	$+12.90 \pm 0.10$
$\Delta_f H°(FeSO_4 \cdot 7H_2O$, cr)	-3014.06 ± 0.40 (Sec. 2.4.1)	-3013.05 ± 0.65
$\Delta_f H°(FeBr_2$, cr)	-245.0 ± 0.25 (Sec. 2.2.1)	-245.7 ± 0.7
$\Delta_f H°(FeI_2$, 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 Fe³⁺, $\Delta_f H°(Fe^{3+}$, ao)

The $\Delta_f H°$ (Fe³⁺, ao) is evaluated. We begin with:

(1) the determinations for $\Delta_f H°(FeCl_3$, cr), those independent of other Fe compounds as well as those linked to $FeCl_2$(cr), combined with a selection for $\Delta_{sol} H°(FeCl_3$, cr) which in itself requires a working value.

(2) the direct determination of $\Delta_f H°(Fe^{3+}$, ao) through oxidation of Fe(cr).

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

In Sec. 3.4 we summarize the various possibilities and select a value for $\Delta_f H°(Fe^{3+}$. ao). modify our initial selection for $\Delta_f H°(FeCl_3$, cr), and also select a value for $\Delta_f H°(FeBr_3$, cr). These selections will eventually become our final recommended values.

3.1. The Chloride System

3.1.1. $\Delta_f H°(FeCl_3$, 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 Fe(cr) with 4.36 $mol \cdot kg^{-1}$ HCl by H_2O_2 (see reaction No. 90 and Sec. 2.1.1) and also the enthalpy of solution of $FeCl_3$(cr) in the same molality of HCl (see catalog entry).

The composite reaction and its $\Delta_r H$ are:
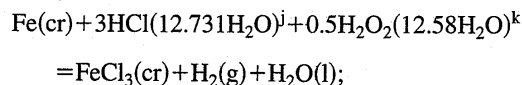
$$Fe(cr) + 3HCl(12.731H_2O)^j + 0.5H_2O_2(12.58H_2O)^k$$
$$= FeCl_3(cr) + H_2(g) + H_2O(l);$$
$$\Delta_r H = -102.59 \pm 0.30 \ kJ \cdot mol^{-1}$$

from which $\Delta_f H°(FeCl_3$, cr$) = -399.24 \pm 0.35 \ kJ \cdot mol^{-1}$.

3.1.1.2. Solution calorimetry with aqueous (KBr, Br₂)
89EVD/EFI (No. 127) have measured the enthalpy of reaction of $FeCl_3$(cr) with aqueous (KBr, Br₂) solutions. Rearranging the reaction listed in AI.b:
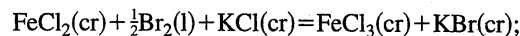
$$FeCl_2(cr) + \tfrac{1}{2}Br_2(l) + KCl(cr) = FeCl_3(cr) + KBr(cr);$$
$$\Delta H° = -11.386 \pm 0.18 \ kJ \cdot mol^{-1}$$

with those cited in Sec. 2.1.1.2, (reactions (1), (3a and 3b), and (4)) we obtain
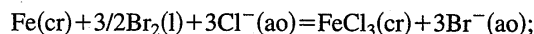
$$Fe(cr) + 3/2Br_2(l) + 3Cl^-(ao) = FeCl_3(cr) + 3Br^-(ao);$$
$$\Delta H° = -258.65 \pm 0.40 \ kJ \cdot mol^{-1}$$

and $\Delta_f H°(FeCl_2$. cr$) = -395.66 \pm 0.40 \ kJ \cdot mol^{-1}$.

3.1.1.3 Bomb combustion
The direct Cl_2(g) bomb combustion enthalpy measurements of 82LAV/TIM (No. 125) led to $\Delta H° = -396.02 \pm 0.14 \ kJ \cdot mol^{-1}$ for:

$$Fe(cr) + 1.5Cl_2(g) = FeCl_3(cr).$$
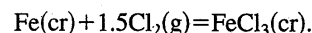
3.1.2. The Relationship Between $\Delta_f H°(FeCl_3$, cr) and $\Delta_f H°(FeCl_2$, cr)

The measurements of 59KOE/COU leading to $\Delta_f H°(FeCl_2$, cr) (No. 90) and $\Delta_f H°(FeCl_3$, cr) (No. 124) may also be rearranged so that:
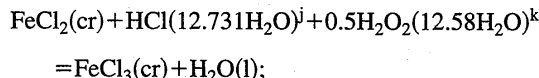
$$FeCl_2(cr) + HCl(12.731H_2O)^j + 0.5H_2O_2(12.58H_2O)^k$$
$$= FeCl_3(cr) + H_2O(l);$$
$$\Delta H = -85.55 \pm 0.21 \ kJ \cdot mol^{-1}$$

resulting in $\Delta_f H°(FeCl_3$, cr$) - \Delta_f H°(FeCl_2$, cr$) = -57.58 \pm 0.25 \ kJ \cdot mol^{-1}$ and $\Delta_f H°(FeCl_3$, cr$) = -399.30 \pm 0.35 \ kJ \cdot mol^{-1}$.

For the reaction given in 3.1.1.2 [89EVD/EFI] and the $\Delta_{sol} H°$'s for KCl(cr) and KBr(cr), cited in 2.1.1.2, we have:
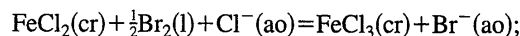
$$FeCl_2(cr) + \tfrac{1}{2}Br_2(l) + Cl^-(ao) = FeCl_3(cr) + Br^-(ao);$$
$$\Delta H° = -8.881 \pm 0.19 \ kJ \cdot mol^{-1}$$

from which we obtain $\Delta_f H°(FeCl_3$, cr$) - \Delta_f H°(FeCl_2$, cr$) = -54.55 \pm 0.20 \ kJ \cdot mol^{-1}$
The high-temperature decomposition measurements (third law) for $FeCl_3$(cr)$ = FeCl_2(cr) + \tfrac{1}{2}Cl_2$(g) are tabulated.

	$\Delta H°$, $kJ \cdot mol^{-1}$
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, $\sim 53.9 \pm 0.70 \ kJ \cdot mol^{-1}$ from the vapor pressure measure-

$^j \phi L$ from 65PAR.

$^k \Delta_f H°$ from 82WAG/EVA.

ments (all in good agreement with one another) disagrees with the calorimetrically determined $\Delta(\Delta_f H^\circ)$ =57.58±0.25 kJ·mol^{-1} from 59KOE/COU but agrees with that derived from 89EVD/EFI, 54.55±0.20 kJ·mol^{-1}. From the $\Delta(\Delta_f H^\circ)$=53.9 kJ·mol^{-1} we obtain $\Delta_f H^\circ$(FeCl$_3$, cr) =−395.16±0.75 kJ·mol^{-1}; from the 89EVD/EFI $\Delta(\Delta_f H^\circ)$=54.55±0.20 kJ·mol^{-1}, $\Delta_f H^\circ$(FeCl$_3$, cr) =−395.71±0.54 kJ·mol^{-1} (−395.66±0.40 kJ·mol^{-1} from 89EVD/EFI's consistent cycle) which supports the direct chlorination enthalpy measured by 82LAV/TIM, 84LAV/ TIM, as −396.02±0.14 kJ·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 FeCl$_3$(cr) and the Derived $\Delta_f H^\circ$(Fe^{3+}, ao)

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

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

The two approaches lead to:

$$\text{FeCl}_3(\text{cr})=\text{FeCl}_3(\text{ai}), \quad \Delta H^\circ=-146.5\pm3.0 \text{ kJ·mol}^{-1}$$

from the measurements in HCl and

$$\text{FeCl}_3(\text{cr})=\text{FeCl}_3(\text{ai}), \quad \Delta H^\circ=-158.99\pm0.84 \text{ kJ·mol}^{-1}$$

from the measurements in H$_2$O. The resultant $\Delta_f H^\circ$(FeCl$_3$, ai) values are −542.52±3.1 and −555.01 ±0.85 kJ·mol^{-1}, respectively and $\Delta_f H^\circ$(Fe^{3+}, ao)=−41.3 ±3.1 kJ·mol^{-1} and −53.79±0.85 kJ·mol^{-1}, respectively. (A different selection for $\Delta_f H^\circ$(FeCl$_3$, cr), e.g. −399.24 kJ from 59KOE/COU would result in $\Delta_f H^\circ$(Fe^{3+}, ao) =−44.55 and −56.01 kJ·mol^{-1}).

The measurements of 90EFI/FUR (Nos. 142–144) on the enthalpy of solution of FeCl$_3$(cr) in HClO4(aq) as a function of concentration of HClO$_4$, extrapolated to I=0 result in $\Delta_{sol}H^\circ$=−156.58±1.2 kJ·mol^{-1} (No. 141) and this results in $\Delta_f H^\circ$(Fe^{3+}, ao)= 51.36±1.2 kJ·mol^{-1}, using our initial tentative selection of −396.02±0.14 kJ·mol^{-1} for $\Delta_f H^\circ$(FeCl$_3$, cr).

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

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

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

$$\text{Fe(cr)}+1.5\text{H}_2\text{O}_2(\text{ao})+3\text{H}^+(\text{ao})=\text{Fe}^{3+}(\text{ao})+3\text{H}_2\text{O(l)}.$$
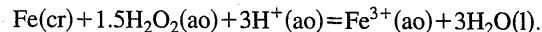
The standard enthalpy effect of this reaction was obtained by two methods: (1) by calculating the dependence of the thermal effects on the total ionic strength of the solutions, and (2) by a two stage approach: extrapolation to infinite dilution against m(Fe^{3+}, aq)$^{1/2}$, and then extrapolation to I=0 of solution.

According to the first method

$$(\Delta_r H_{(I)}-\Delta_r H^\circ_{(D-H)})/\text{kJ·mol}^{-1}$$

$$=(-617.21\pm0.31)-(1.84\pm0.10)(I/\text{mol·kg}^{-1})$$

and to the second method

$$(\Delta_r H_{(I)}-\Delta_r H^\circ_{(D-H)})/\text{kJ·mol}^{-1}$$

$$=(-617.33\pm0.35)-(1.83\pm0.11)(I/\text{mol·kg}^{-1}).$$

Both methods of extrapolation gave the same results and adopting the first mentioned equation $\Delta H^\circ=-617.21\pm0.31$ kJ·mol^{-1} and $\Delta_f H^\circ$(Fe^{3+}, ao)=−46.48±0.32 kJ·mol^{-1}.

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

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

$$\text{Fe}^{2+}(\text{ao})+\tfrac{1}{2}\text{H}_2\text{O}_2(\text{ao})+\text{H}^+(\text{ao})=\text{Fe}^{3+}(\text{ao})+\text{H}_2\text{O(l)}+\text{H}_2(\text{g}).$$
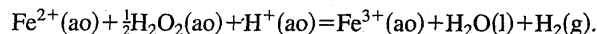
The measurements are all in dilute solutions. The measurements, the $\Delta_r H^\circ$'s and the calculated $\Delta_f H^\circ$(Fe^{3+}, ao)−$\Delta_f H^\circ$(Fe^{2+}, ao) are tabulated (Table 3). Also tabulated are the $\Delta(\Delta_f H^\circ)$'s derived from the c.m.f. measurements as a function of T for

$$\text{Fe}^{2+}(\text{ao})+\text{H}^+(\text{ao})=\text{Fe}^{3+}(\text{ao})+\tfrac{1}{2}\text{H}_2(\text{g})$$
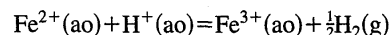
as well as those values derived from the results of 89EVD/ EFI (No. 127), 89EFI/EVD (No. 184) and 90EFI/FUR (Nos. 94, 141, 178, 190) on the calorimetric determinations of $\Delta_f H^\circ$(FeCl$_2$, cr), $\Delta_f H^\circ$(FeCl$_3$, cr), $\Delta_f H^\circ$(FeBr$_2$, cr), $\Delta_f H^\circ$(FeBr$_3$, cr) and their $\Delta_{sol}H^\circ$s, shown as follows.

From Sec. 3.1.2 we have $\Delta_f H^\circ$(FeCl$_3$, cr) −$\Delta_f H^\circ$(FeCl$_2$, cr)=−54.55±0.20 kJ·mol^{-1} from 89EVD/EFI. With the 90EFI/FUR (Nos. 94, 141) measurements of $\Delta_{sol}H^\circ$ for FeCl$_3$(cr) and FeCl$_2$(cr) in HClO$_4$ (−156.58±1.2 and −83.11±0.42 kJ·mol^{-1}, respectively) we obtain

$$\text{Fe}^{2+}(\text{ao})+\tfrac{1}{2}\text{Cl}_2(\text{g})=\text{Fe}^{3+}(\text{ao})+\text{Cl}^-(\text{ao});$$

$$\Delta H^\circ=-128.02\pm1.3 \text{ kJ·mol}^{-1}$$

and

$$\Delta_f H^\circ(\text{Fe}^{3+}, \text{ao})-\Delta_f H^\circ(\text{Fe}^{2+}, \text{ao})=39.06\pm1.3 \text{ kJ·mol}^{-1}.$$
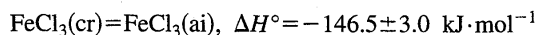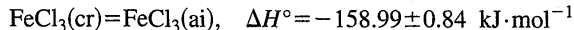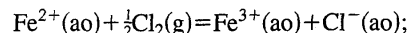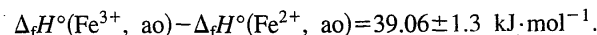
Similarly from the reaction catalog from the measurements by 89EFI/EDV (No. 184) we have $\Delta_f H^\circ$ (FeBr$_3$, cr) − $\Delta_f H^\circ$ (FeBr$_2$, cr) = −17.90 ± 0.14 kJ·mol^{-1}, which we may combine with the $\Delta_{sol}H^\circ$s for FeBr$_3$(cr) and FeBr$_2$(cr) (−150.4±1.3 (No. 178) and −86.85 ±0.12 kJ·mol^{-1} (No. 190), respectively) to obtain

TABLE 3. The enthalpy of oxidation of Fe^{2+}(ao) by H_2O_2(aq) and $\Delta_f H°(Fe^{3+}$, ao$)-\Delta_f H°(Fe^{2+}$, ao$)$

	$\dfrac{\Delta_f H°}{kJ \cdot mol^{-1}}$	$\dfrac{\Delta_f H°(Fe^{3+}, ao)-\Delta_f H°(Fe^{2+}, ao)}{kJ \cdot mol^{-1}}$
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
		42.75 ± 1.5^m
73NIK/ANT (No. 17)		46.7 ± 2.0^m
53MAG/HUI (No. 22)		40.58 ± 0.84
51CON/McV (No. 24)		41.61 ± 1.0
89EVD/EFI and 90EFI/FUR (chloride system) (Nos. 94, 127, 141)		39.06 ± 1.3
89EFI/EVD and 90EFI/FUR (bromide system) (Nos. 178, 184, 190)		39.96 ± 1.32

^{l}72WHI/LAN use 2nd order equation which yields $\Delta H° = 42.67 \pm 1.5$ kJ·mol^{-1}. Linear relationship ($\Delta C_p = 0$) is equally good (88NOR).
^{m}Our calculations using C_p measurements of Fe^{2+}(ao) and Fe^{3+}(ao) by 88HOV.

$$Fe^{2+}(ao)+\tfrac{1}{2}Br_2(l)=Fe^{3+}(ao)+Br^-(ao);$$
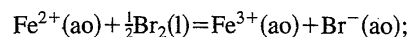
$$\Delta H° = -81.45 \pm 1.31 \text{ kJ} \cdot mol^{-1}$$

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

3.4. The Tentative Selected Parameters

It is quite obvious that $\Delta_f H°(Fe^{3+}$, ao$)$ is ill defined. A tabular summary, Table 4, which includes our rejected values follows.

The agreement is not as good as we would like; however, there is a narrow range with some consistency, from 1) the tentative selection of -90.0 ± 0.5 kJ·mol^{-1} for $\Delta_f H°(Fe^{2+}$, ao$)$ and the $\Delta(\Delta_f H°)$s from $E°$ vs T, the oxidation by the O_2 and from the chloride and bromide systems; 2) the initial selection of $\Delta_f H°(FeCl_3$, cr$) = -396.02 \pm 0.14$ kJ·mol^{-1} and $\Delta_{sol} H° = -156.38 \pm 0.28$ kJ·mol^{-1}; and 3) the direct determination of $\Delta_f H°(Fe^{3+}$, 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 $\Delta(\Delta_f H°) = 41.0 \pm 1.5$ kJ·mol^{-1} and $\Delta_f H°$ (Fe^{3+}, ao$) = -49.0 \pm 1.5$ kJ·mol^{-1} and modify our selection of $\Delta_f H°$ ($FeCl_3$, cr) from -396.02 ± 0.14 kJ·mol^{-1} to -395.66 ± 0.50 kJ·mol^{-1}. The selected values are given below and become our final recommendations.

TABLE 4. The enthalpy of formation of Fe^{3+}(ao) and $\Delta_f H°(Fe^{3+}$, ao$)-\Delta_f H°(Fe^{2+}$, ao$)$

	$\dfrac{\Delta_f H°(Fe^{2+}, ao)}{kJ \cdot mol^{-1}}$	$\dfrac{\Delta(\Delta_f H°)}{kJ \cdot mol^{-1}}$	$\dfrac{\Delta_f H°(Fe^{3+}, ao)}{kJ \cdot mol^{-1}}$
Tentative Selection	-90.0 ± 0.5		
(Rejected Value)	(-95.5)		
$E°$ vs T		38.41 ± 1.5^n	-51.59	(-57.09)
		42.75 ± 1.5^p	-47.25	(-52.75)
		46.7 ± 2.0^p	-43.3	(-48.8)
		40.58 ± 0.84	-49.42	(-54.42)
		41.61 ± 1.0	-48.39	(-53.89)
Calorimetric Oxidation with H_2O_2		44.11 ± 1.0	-45.89	(-51.39)
		41.48 ± 0.10	-48.52	(-54.02)
		40.08 ± 0.5	-49.42	(-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 $\Delta_f H°(FeCl_3$, cr$) = -396.02 \pm 0.14$ kJ·mol^{-1} (-399.24 kJ·mol^{-1}) and $\Delta_{sol} H°(FeCl_3$, cr$) = -146.5 \pm 3.0$ kJ·mol^{-1} (from measurements in HCl)			-41.3 ± 3.1	(-44.55)
or $\Delta_{sol} H°(FeCl_3$, cr$) = -158.99 \pm 0.84$ kJ·mol^{-1} (from measurements in H_2O)			-53.79 ± 0.85	(-57.01)
or $\Delta_{sol} H°(FeCl_3$, cr$) = -156.58 \pm 1.2$ kJ·mol^{-1} (from measurements in $HClO_4$)			-51.36 ± 1.3	(-54.60)
Direct determination (76VAS/RAS)			-46.48 ± 0.32	
(89EVD/EFI and 90EFI/FUR)			-51.00 ± 1.3	

^{n}72WHI/LAN results with $\Delta C_p = 0$.
^{p}72WHI/LAN and 73NIK/ANT results corrected for ΔC_p's using 88HOV.

Compound	$\Delta_f H°$, kJ·mol^{-1}
Fe^{2+}(ao)	-90.0 ± 0.5
Fe^{3+}(ao)	-49.0 ± 1.5
FeCl$_3$(ai)	-550.24 ± 1.5
FeCl$_3$(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, Fe^{2+}, $\Delta_f G°$(Fe^{2+}, ao)

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

1) e.m.f. (Sec. 4.1) and some equilibrium constant measurements (section 4.2.1) that result in values for $\Delta_f G°$ independent of other Fe species.

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

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

4.1. The e.m.f. Measurements

We begin with the measurements that had been selected by 52ROS/WAG.
32RAN/FRA2 (No. 75) measured the E at 298.15 K for the cell:

$$\text{Fe(cr),FeCl}_2(0.1\ \text{mol·kg}^{-1}),\ \text{Hg}_2\text{Cl}_2(\text{cr}),\ \text{Hg(l)}$$
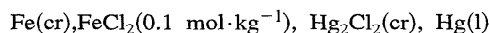
obtaining $E = 0.7996 \pm 0.0010$ V. Then, using $\gamma_\pm$ from 79GOL/NUT, $E° = 0.7027 \pm 0.0010$ V and $\Delta G° = -135.60 \pm 0.20$ kJ·mol^{-1} for

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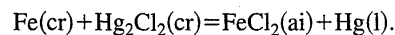
Two different samples of Fe(cr) were used, one electrolytically prepared and deposited on Pt electrodes at 1373 K and the second by the reduction of pure Fe$_2$O$_3$(cr) with H$_2$ at temperatures of 1073 to 1123 K. Oxygen was carefully excluded from both as described by 32RAN/FRA. The cell measurements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

32RAN/FRA2 also reviewed the measurements of 26HAM (No. 73) on the same cell. These measurements were made in various concentrations of FeCl$_2$ (m > 0.1 mol·kg^{-1}) and, corrected to the standard state, result in $E° = 0.710 \pm 0.0014$(2s) V ($\Delta G° = -137.01 \pm 0.30$ 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 FeCl$_2$ reduces the activity of the iron and the measured E approaches their value of $E° = 0.70217$ V.

The 26HAM (No. 72) measurements on

$$\text{Fe(cr)} + 2\text{TlCl(cr)} = \text{FeCl}_2(\text{ai}) + 2\text{Tl(cr)}$$
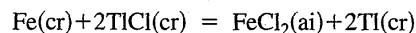
yield $E° = -0.1225$ V ($\Delta G° = 23.65 \pm 1.0$ kJ·mol^{-1}) when approached from the left side of equilibrium and are in better agreement since treatment with TlCl(aq) removes the finer particles of iron.
For the half cell,

$$\text{Fe(cr)} = \text{Fe}^{2+}(\text{ao}) + 2\text{e}^-,$$
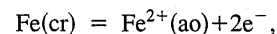
the values from the Hg$_2$Cl$_2$(cr) cell are $E° = 0.4346 \pm 0.0010$ V ($\Delta_f G°$(Fe^{2+}, ao)$=-83.86 \pm 0.20$ kJ·mol^{-1}) from 32RAN/FRA2, and $E° = 0.4418 \pm 0.0015$ V ($\Delta_f G° = -85.26 \pm 0.30$ kJ·mol^{-1}) from 26HAM. From the TlCl(cr) cell, $E° = 0.4340 \pm 0.005$ V ($\Delta_f G° = -83.75 \pm 1.0$ kJ·mol^{-1}).[q]

Much earlier, 06RIC/BEH conducted measurements on the system Fe|FeSO$_4$(0.5 mol·dm^{-3})|KCl(0.1 mol·dm^{-3}) Hg$_2$Cl$_2$−Hg. Although it is not possible to obtain an $E°$ for this cell because of the unknown liquid potential and the high concentration of FeSO$_4$, these experiments showed that iron prepared electrolytically or by reduction of the oxide with hydrogen gave an average potential 0.02–0.03 V higher than vacuum-fused iron. Since the measurements of 26HAM and 32RAN/FRA were both on iron prepared either electrolytically or by the reduction of the oxide with hydrogen and, according to 53PAT/THO, with some oxygen present, 53PAT/THO undertook a reinvestigation of the standard potential of the Fe(cr), Fe^{2+}(ao) half-cell, using hydrogen-free iron prepared by the thermal decomposition of iron pentacarbonyl under vacuum. The powder produced was used directly as the electrode material. Massive iron electrodes prepared by vacuum 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), Hg$_2$SO$_4$(cr) half cell (No. 206):

$$\text{Fe(cr)} + \text{Hg}_2\text{SO}_4(\text{cr}) = \text{FeSO}_4(\text{aq,m}) + 2\text{Hg(l)}$$
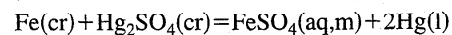
cell	$\dfrac{m}{\text{mol·kg}^{-1}}$	$\dfrac{E}{\text{V}}$	$\gamma_\pm^r$	$\dfrac{E°}{\text{V}}$	$\gamma_\pm$ (72PIT)	$\dfrac{E°}{\text{V}}$
1	.0718	1.1335	.193	1.02361	.186	1.0226
7	.029(air)	1.1485	.281	1.0249	.275	1.0244
4	.0274	1.1488	.290	1.02463	.283	1.02394
5	.0220	1.1522	.330	1.0257	.305	1.0236
				avg. 1.0247		1.0236

[q] $\Delta_f G°$(TlCl, cr)$=-184.93$ kJ·mol^{-1} [82WAG/EVA] and $\Delta_f G° = -184.97 \pm 3.0$ kJ·mol^{-1} [71MED/BER].
[r] $\gamma_\pm$s listed by 53PAT/THO from measurements by 41DEM/HED.

Thus, $E°$ for the cell is 1.0247 ± 0.0003 V ($\Delta G° = -197.74\pm0.06$ kJ$\cdot$mol^{-1}) using $\gamma_\pm s$ given by 53PAT/THO and $E° = 1.0236\pm0.0003$ V using Pitzer's (72PIT) $\gamma_\pm s$ for MgSO$_4$.

The resultant values for $E°$ for the Fe(cr)$-$Fe^{2+}(ao) half cell are 0.4119 ± 0.0003 V ($\Delta_f G°$(Fe^{2+}, ao)$=-79.483$ ±0.60 kJ$\cdot$mol^{-1}) and 0.4180 ± 0.0003 V ($\Delta_f G°$(Fe^{2+}, ao) $=-79.263\pm0.60$ kJ$\cdot$mol^{-1}), respectively.

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

$$Fe(cr)+PbSO_4(cr)=FeSO_4(aq,m)+Pb(cr)$$
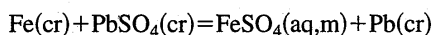
$E=0.1654$ V when m$=.0677$ mol$\cdot$kg^{-1} using massive iron. If $\gamma_\pm = 0.198$ as given by 53PAT/THO, $E°$ $= 0.05461$ V. If $\gamma_\pm = 0.192$ from 72PIT is used, then $E°$ $= .0538$ V.

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

It follows (with 53PAT/THO $\gamma_\pm s$) that $E° = 0.05461$ V (massive iron) and 0.05439 V (iron powder) or (with 72PIT's $\gamma_\pm$) $E° = 0.05380$ and 0.05374 V, respectively. The two different iron electrodes give essentially the same result $E°$ $= 0.05450\pm0.0001$ or 0.05377 ± 0.0001 V ($\Delta G°$ = -10.517 ± 0.020 kJ$\cdot$mol^{-1} or -10.376 ± 0.020 kJ$\cdot$mol^{-1}). The resultant Fe(cr)$-$Fe^{2+}(ao) standard half cell potential is 0.4121 or 0.4113 V ($\Delta_f G° = -79.516$ or -79.375 kJ$\cdot$mol^{-1}).

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

$$Fe(cr)+Hg_2Cl_2(cr)=FeCl_2(ai)+2Hg(l).$$

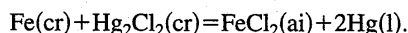The measured E's [m(FeCl$_2$,aq) = 0.0760 and 0.0160 mol$\cdot$kg^{-1}] are 0.7770 (massive iron) and 0.8298 V (iron powder) which lead to $E° = 0.6712$ V ($\Delta G° = -129.522$ kJ$\cdot$mol^{-1}) and $E° = 0.6735$ V ($\Delta G° = -129.966$ kJ$\cdot$mol^{-1}) and for the standard potential of the Fe(cr)$-$Fe^{2+}(ao) half cell $E° = 0.4031$ and 0.4055 V ($\Delta_f G° = -77.777$ and -78.221 kJ$\cdot$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
		TlCl(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 (FeCl$_2$, aq)$=0.0864$ mol$\cdot$kg^{-1} with $\gamma_\pm=0.511$ [79GOL/NUT] for the cell containing air, leading to $E°=0.7041$ V and $E°$ for the Fe(cr)$-$Fe^{2+}(ao) half cell$=0.4361$ V ($\Delta_f G° = -84.15$ kJ$\cdot$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$\cdot$kg^{-1} ($\gamma_\pm = 0.511$) so that $E°$ for the cell is 0.7423 and for the half cell 0.4742 V ($\Delta_f G°$(Fe^{2+}, ao)$=-91.51$ kJ$\cdot$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 $E° = 0.4088$ 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 $\Delta_{sol} G°$ of FeSO$_4\cdot$7H$_2$O(cr) and FeCl$_2\cdot$4H$_2$O(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 $E°$ $= 0.467$ V from extrapolation of forward and reverse kinetic data (in acidic FeCl$_2$ solutions). Since correction to 298 K is negligible and the liquid junction potential should be small, possibly about 0.002 V, this supports the 0.47 V value. His electrodes (see catalog entry) were vacuum annealed for 1 h at about 973 K. However, the impurity level is high ($\sim0.3\%$) and the method of preparation is unknown. The solutions of FeCl$_2$(aq), though, were presaturated with hydrogen in the presence of platinized platinum to reduce any Fe^{3+} present and also stored under hydrogen. This is in line with 53PAT/THO's observation of the hydrogen reduced Fe electrode with solutions completely deoxygenated leading to higher E° values. 78JOH/BAU considered the earlier discordant measurements and measured the cell

$$Fe(cr)|FeCl_2(0.02m)||saturated\ KCl||AgCl(cr)|Ag(cr).$$
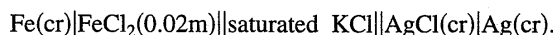
The Fe$-$Fe^{2+} half cell was prepared from coulometrically generated Fe^{2+}(aq) from spectroscopic grade rod Fe (containing less than 10 ppm total spectroscopically detectable impurities under N$_2$ or Ar). About 10 ppm H was also contained in the Fe. Cleaned electrodes were annealed at 993 K for 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 $Fe(cr)/Fe^{2+}(aq)$ is strongly dependent on pH in the acidic region but becomes independent at $pH \geqslant 5.8$ and is 0.415 ± 0.001 V ($\Delta_f G°(Fe^{2+}$, ao)$ = -80.08 \pm 0.20$ kJ·mol^{-1}). If the Fe was not particularly degassed, the potential increased to ~ 0.435 V ($\Delta_f G° = -83.94$ kJ·mol^{-1}) in better agreement with 32RAN/FRA2. This supports the supposition that the difference in E is attributable to differences in H content of the metal. Although they do not recommend either value, they have shown that according to theory the potential is experimentally independent of pH.

We now turn to other paths for obtaining $\Delta_f G°(Fe^{2+}$, ao) and $E°$ of the half cell.

### 4.2. The Equilibrium Constants

4.2.1. The Reaction of Fe(cr) With Aqueous TlClO$_4$ and NaClO$_4$

The measurements of 82GAM/REI (No. 4) are considered. Neutral aqueous solutions of TlClO$_4$ and NaClO$_4$ were reacted with "ultrapure Fe" in sealed ampoules at 323.15 K. The ionic strength of the NaClO$_4$ aqueous solution was 1.0 mol·kg^{-1}. Under these conditions lg K = 1.12 ± 0.06 for

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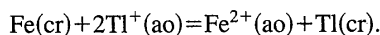
A plot of $\log[Fe^{2+}]$ vs $\log[Tl^+]$ gives a straight line with a slope of 2.0 and $\Delta G° = -6.93 \pm 0.4$ kJ·mol^{-1}. Correction (see catalog entry) to 298.15 K and $I=0$ results in $\Delta G° = -13.51 \pm 1.5$ kJ·mol^{-1} ($E° = 0.0700$ V) and $\Delta_f G°(Fe^{2+}$, ao)$ = -78.28 \pm 1.5$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

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

$$2Tl^+(ao) + H_2(g) + Hg(l) = 2Tl(sat, in Hg) + 2H^+(ao)$$
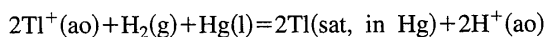
at 323 K under the same conditions and obtained $E° = -0.3865$ V ($I=1.0$). Using $E° = -0.0031$ V from 19RIC/DAN and 22GER for

$$2Tl(sat, in Hg) = 2Tl(cr) + Hg(l)$$
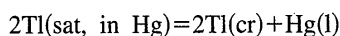
$E° = -0.3896$ V($I=1.0$) at 323.15 K is obtained for

$$2Tl^+(ao) + H_2(g) = 2Tl(cr) + 2H^+(ao)$$
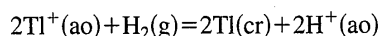
and $E° = -0.3567$ V ($I=0$) at 298.15 K. Then for the Fe(cr)/Fe^{2+}(ao) half cell $E° = 0.4267$ V and $\Delta_f G°(Fe^{2+}$, ao)$ = -82.34$ kJ·mol^{-1}.

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

4.2.2. Solubility Measurements of Fe$_3$O$_4$(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 H$_2$ lead to K$_s$ values at 298 K for the following process:

$$1/3Fe_3O_4(cr) + 2H^+(ao) + 1/3H_2(g)$$

$$= Fe^{2+}(ao) + 4/3H_2O(l). \quad \text{(No. 36 \& No. 41)}.$$
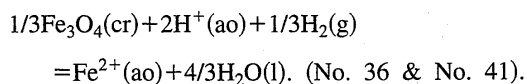
Both sets of solubility measurements were conducted in flow systems with varying pH, redox conditions, and temperature (70SWE/BAE temperature range 323 to 573K, 80TRE/LEB 373 to 573K). The solutions used by 70SWE/BAE ranged from m(KOH) = 4 × 10^{-4} mol·kg^{-1} to m(HCl) = 10^{-4} mol·kg^{-1}. Solution compositions used by 80TRE/LEB included either HCl or NaOH of molalities up to 1 and 40 mmol·kg^{-1}. The results of both investigations were fitted to a scheme of soluble ferrous Fe(OH)$_3^-$ species, $Fe^{2+}(ao)$, 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:

$$(1/3)Fe_3O_4(cr) + (2-b)H^+(ao) + 1/3H_2(g)$$

$$= Fe(OH)_b^{(2-b)+} + (4/3-b)H_2O(l).$$
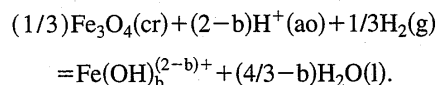
For b=0, the extrapolated values at 298.15 K for $\Delta G°$ are -68.62 ± 3.0 kJ·mol^{-1} from 70SWE/BAE and -64.26 ± 2.0 kJ·mol^{-1} from 80TRE/LEB ($p° = 1$ atm). With the selected value for $\Delta_f G°(Fe_3O_4$, cr) from 88HAA $= -1013.30 \pm 2.15$ kJ·mol^{-1}, $\Delta_f G° = -90.18 \pm 3.1$ and -85.82 ± 2.12 kJ·mol^{-1} respectively. In Table 6 of the 80TRE/LEB paper is given their calculated value for $\Delta_f G°(Fe^{2+}$, ao), obtained from $\Delta_r G°(298.15$ K)$ = -66.7$ kJ·mol^{-1} using $\Delta C_p = 120$ J·K^{-1}mol^{-1}. This $\Delta_r G°$ results in $\Delta_f G° = -88.26$ kJ·mol^{-1}. Comparison of their measured values with the 70SWE/BAE measurements shows the following:

	lg K		
T/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 $\Delta_f G°(Fe^{2+}$, ao) than that of 53PAT/THO or 32RAN/FRA.

4.2.3. Solution of FeSO$_4$·7H$_2$O(cr)

4.2.3.1. Gibbs energy of solution

There have been many measurements of the solubility of FeSO$_4$·7H$_2$O(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 FeSO$_4$, so that m=1.944 mol·kg^{-1}.

Prior to the isopiestic measurements of 74OYK/BAL, the activity coefficients of FeSO$_4$(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 $\Delta_{sol} G° = 14.12 \pm 0.50$ kJ·mol^{-1} for the process

$$FeSO_4·7H_2O(cr) = FeSO_4(ai) + 7H_2O(l).$$
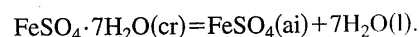
Values from the 72PIT tabulation are in agreement.

The experimental results of 74OYK/BAL require an estimate at $m=0.10$ mol·kg^{-1} for $\gamma_\pm$. With $\gamma_\pm = 0.15$ from 59ROB/STO, $\gamma_\pm$ and a_w at saturation are 0.0423 and 0.925 respectively, leading to $\Delta G° = 13.24$ kJ·mol^{-1} for the above process. (74OYK/BAL use $m=1.964$ mol·kg^{-1} and give $\gamma_\pm = 0.0425$ and $a_w = 0.951$ resulting in $\Delta G° = 13.18$ kJ·mol^{-1}). However 86REA/BEC point out that reanalysis of the data on the 2:2 type electrolytes by 72PIT indicates that a better value for $\gamma_\pm$ for FeSO$_4$ at m=0.10 mol·kg^{-1}, based on 72PIT's value for MgSO$_4$ (0.161) is 0.161 ± 0.01, resulting in $\gamma_\pm = 0.048$ and $a_w = 0.952$ so that $\lg K_s = -2.205$ and $\Delta_{sol}G° = 12.58\pm0.30$ kJ·mol^{-1} (reaction No. 210).

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

The C_p measurements of 49LYO/GIA (No. 208) lead to $S° = 409.2\pm1.2$ J·mol^{-1}·K^{-1} for FeSO$_4$·7H$_2$O(cr) at 298.15 K.

We have, in Sec. 2.3, accepted, for our first iteration, $\Delta_{sol}H° = 12.90\pm0.10$ kJ·mol^{-1}. With $\Delta_{sol}G° = 12.58\pm0.30$ kJ·mol^{-1}, $\Delta_{sol}S° = 1.07\pm1.1$ J·mol^{-1}·K^{-1}. The calculated $S°(Fe^{2+}$, ao$)=-97.88\pm1.4$ J·mol^{-1}·K^{-1} and $\Delta_{fs}S° = 5.37\pm1.55$ J·mol^{-1}·K^{-1} ($S°$(Fe, cr)$=27.319\pm0.002$ J·mol^{-1}·K^{-1}). With our tentative $\Delta_f H°(Fe^{2+}$, ao$)=-90.0\pm0.50$ kJ·mol^{-1} we obtain $\Delta_f G°=-91.60\pm0.85$ kJ·mol^{-1}, ($E°=0.4747\pm0.004$ V), surprisingly more negative than all other values.[s] Using 74OYK/BAL's original values for γ, $\Delta_{sol}G° = 13.24$ kJ·mol^{-1} and $\Delta_{sol}S° = -1.14$ J·mol^{-1}·K^{-1}, so that $S°(Fe^{2+}$, ao$)=-100.09\pm1.14$ J·mol^{-1}·K^{-1} and $\Delta_f G°(Fe^{2+}$, ao$)=-90.94\pm0.85$ kJ·mol^{-1}.

The earlier $\Delta_{sol}G° = 14.12\pm0.50$ kJ·mol^{-1} used in the 69WAG/EVA evaluation (based on an estimated $\gamma_\pm$) with $\Delta_f G°$(FeSO$_4$·7H$_2$O,cr) $= -2509.87$ kJ·mol^{-1} had led to $\Delta_f G°(Fe^{2+}$,ao$) = -91.3$ kJ·mol^{-1} which was rejected because it appeared to be too negative, possibly because the properties of FeSO$_4$(aq) were not sufficiently well established to accept this "very" negative value.

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

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

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

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

4.2.4.1. Vapor pressure measurements

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

---

1. FeCl$_2$·4H$_2$O(cr)$=$FeCl$_2$·2H$_2$O(cr)$+2$H$_2$O(g) (No.119),
    $\Delta H°=108.04\pm4.0$ kJ·mol^{-1},
    $\Delta G°=23.62\pm1.0$ kJ·mol^{-1},
    $\Delta S°=283.1$ J·K^{-1}mol^{-1},

2. FeCl$_2$·2H$_2$O(cr)$=$FeCl$_2$·H$_2$O(cr)$+$H$_2$O(g) (No.120),
    $\Delta H°=63.1\pm5.0$ kJ·mol^{-1},
    $\Delta G°=18.57\pm2.0$ kJ·mol^{-1}.
    $\Delta S°=149.4$ J·K^{-1}mol^{-1},

3. FeCl$_2$·H$_2$O(cr)$=$FeCl$_2$(cr)$+$H$_2$O(g) (No.121),
    $\Delta H°=63.1\pm5.0$ kJ·mol^{-1},
    $\Delta G°=24.93\pm2.0$ kJ·mol^{-1},
    $\Delta S°=128.0$ J·K^{-1}mol^{-1}.

The $\Delta S°$'s for reactions (1) and (2) are reasonable (a usual contribution is $\Delta S°/n = 145\pm10$ J·K^{-1}mol^{-1}) for nH$_2$O(g), indicating that the $\Delta G°$'s and $\Delta H°$'s are acceptable. For reaction (3), the $\Delta S°$ is low, indicating that either the $\Delta G°$, or the $\Delta H°$, or both, are incorrect. We assume that the second law $\Delta H°$ is the more questionable value and accept the $\Delta G°$ for our further use.
We now have

FeCl$_2$·4H$_2$O(cr)$=$FeCl$_2$·H$_2$O(cr)$+3$H$_2$O(g),

$\Delta H°=171.14$ kJ·mol^{-1},

$\Delta G°=42.19$ kJ·mol^{-1},

$\Delta S°=432.5$ J·mol^{-1}·K^{-1},

and

FeCl$_2$·H$_2$O(cr)$=$FeCl$_2$(cr)$+$H$_2$O(g),

$\Delta G°=24.93$ kJ·mol^{-1},

so that

FeCl$_2$·4H$_2$O(cr)$=$FeCl$_2$(cr)$+4$H$_2$O(g),

$\Delta G°=67.12\pm3.0$ kJ·mol^{-1}.

Using 89COX/WAG for

H$_2$O(l)$=$H$_2$O(g); $\Delta G°=8.591\pm0.005$ kJ·mol^{-1},

we obtain

FeCl$_2$·4H$_2$O(cr)$-$FeCl$_2$(cr)$+4$H$_2$O(l);

$\Delta_{dehyd}G°=32.756$ kJ·mol^{-1}.
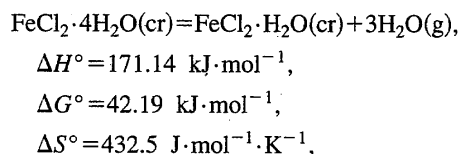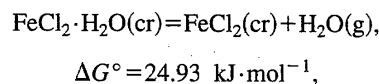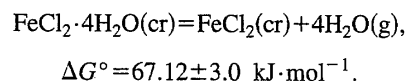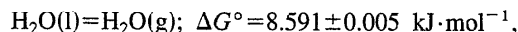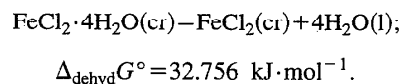
This will be combined with $\Delta_{sol}G°$(FeCl$_2$·4H$_2$O,cr).

4.2.4.2. The Gibbs energy of solution of FeCl$_2$·4H$_2$O(cr)

The solubility of FeCl$_2$·4H$_2$O(cr), the stable phase at 298.15 K, has recently been measured by 85CHO/PHO. The 79GOL/NUT evaluation of a_w, ϕ, and $\gamma_\pm$ of FeCl$_2$(aq) lists recommended values up to $m=2.05$ mol·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 mol·kg^{-1}) but were given no weight in the evaluation. A comparison of the values reveals a 3% difference in ϕ at $m=2.0$ mol·kg^{-1}. Increasing

TABLE 5. The enthalpy of formation of FeOOH(cr, Goethite) from $Fe_2O_3(cr)$ and $H_2O(l)$

		$\Delta_f H°$(FeOOH, cr)/kJ·mol^{-1}	
Investigator	ΔH/kJ·mol^{-1}	$\Delta_f H°$(Fe_2O_3,cr)= -824.9 ± 3.2	$\Delta_f H°$(Fe_2O_3,cr)= -823 ± 6
59SCH (No. 63)	15 ± 10	-562.9 ± 5.2	-561.9
75KOR/FAD (No. 65)	13.70 ± 4.0	-562.2 ± 2.6	-561.3
65BAR (No. 51)	7.87 ± 0.84	-559.3 ± 1.7	-558.4
64FER (No. 64)	4.9 ± 1.2	-557.8 ± 1.8	-556.9

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

$$\Delta G° = -16.85\pm0.5 \text{ kJ·mol}^{-1}$$

for $FeCl_2 \cdot 4H_2O(cr) = FeCl_2(ai) + 4H_2O(l)$.

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

$$FeCl_2(cr) = FeCl_2(ai); \quad \Delta G° = -16.85 - 32.756$$

$$= -49.61\pm3.1 \text{ kJ·mol}^{-1}.$$

In Sec. 2.3 we selected $\Delta_{sol}H°$ for the above process to be -83.00 ± 0.14 kJ·mol^{-1}. The $\Delta_{sol}S°$ then is -112.02 ± 10 J·mol^{-1}·K^{-1} and $S°$(Fe^{2+},ao)= -107.2 ± 10 J·mol^{-1}·K^{-1}, resulting in $\Delta_f G°$(Fe^{2+},ao)= -89.4 ± 3.1 kJ·mol^{-1} and again indicating a far more negative value than all the e.m.f. values, with the exception of 60HUR (No. 6), and the K value from 82GAM/REI (No. 4).

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

The range of values for $\Delta_f G°$(Fe^{2+},ao) indicates that an obvious choice is not apparent. On the basis of the e.m.f. measurements, the most careful work that excluded hydrogen in the preparation of the electrode and from the solution, as well as oxygen, supports the more positive values from 53PAT/THO and 78JOH/BAU. The equilibrium measurements of 82GAM/REI confirm this; however, the values from three other paths (the solubility of $Fe_3O_4(cr)$, and from the entropies of the Fe^{2+}(ao) from the $FeSO_4 \cdot 7H_2O(cr)$ and the $FeCl_2 \cdot 4H_2O(cr) - FeCl_2(cr)$ systems), indicate a much more negative value. It is particularly difficult to ascribe a major error in the $\Delta_{sol}G°$ for $FeSO_4 \cdot 7H_2O(cr)$. 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 Tl$^+$(ao)). We therefore base our initial selection for $\Delta_f G°$(Fe^{2+},ao) on the values from the $Fe_3O_4(cr)$, $FeSO_4 \cdot 7H_2O(cr)$, and $FeCl_2 \cdot 4H_2O(cr) - FeCl_2(cr)$ paths, accepting $\Delta_f G°$(Fe^{2+},ao) = -90.5 ± 1.0 kJ·mol^{-1} ($p°$=1 atm). Table 6 in Sec. 5.2 shows the measurements. (This initial selection for $\Delta_f G°$(Fe^{2+},ao) will become our final recommended value.)

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

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

(1) establishing the thermochemical property values of FeOOH(cr, Goethite) and its $\Delta_{sol}G°$ (section 5.1.3) to obtain a value for $\Delta_f G°$ and

(2) obtaining values for $\Delta_f G°$(Fe^{3+},ao)-$\Delta_f G°$(Fe^{2+},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 $\Delta_f G°$(Fe^{2+},ao) to obtain other values for $\Delta_f G°$(Fe^{3+},ao).

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

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

5.1.1. $\Delta_f H°$(FeOOH, cr, α)

One path to the $\Delta_f G°$(Fe^{3+},ao) is from $\Delta_{sol}G°$(FeOOH, cr, α) and $\Delta_f G°$(FeOOH, cr, α). This involves the $\Delta_f H°$(FeOOH, cr, α). There are four measurements leading to $\Delta_f H°$(FeOOH, cr) from reactions involving $Fe_2O_3(cr)$ and Goethite. The reaction is

$$2FeOOH(cr,\alpha) = Fe_2O_3(cr) + H_2O(l).$$
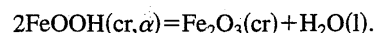
The 59SCH (No. 63) results on the stability regions of Fe_2O_3–FeOOH through pressure and temperature measurements (800, 900, and 970 bar and 411 to 453 K) lead to ΔH=15 ± 10 kJ·mol^{-1} (3rd law). The 75KOR/FAD (No. 65) differential scanning calorimetric measurements (corrected for $\Delta_{vap}H°$(H_2O,l) = 44.004 kJ·mol^{-1}) lead to 13.70 ± 4.0 kJ·mol^{-1} for ΔH.

Calorimetric measurements of the $\Delta_{sol}H$ of FeOOH(cr, α) and $Fe_2O_3(cr)$ in 20.1 wt% aqueous HF at 298.15 K by 65BAR (No. 51) and in 20.1% aqueous HCl (HCl+7.60H_2O) containing 0.18% $FeCl_3$ at 344 K by 64FER (No. 64) give ΔH=7.87 ± 0.84 and 4.9 ± 1.2 kJ·mol^{-1}, respectively. A summary, Table 5, with $\Delta_f H°$(Fe_2O_3,cr)= -824.9 ± 3.2 kJ·mol^{-1} [88HAA] and -823 ± 6 kJ·mol^{-1} [86ARJ/BER] follows.

In our initial assessment, we select $\Delta_f H°$(FeOOH,cr,α) = -559.3 ± 1.7 kJ·mol^{-1} based on 65BAR and $\Delta_f H°$(Fe_2O_3,cr) = -824.9 ± 3.2 kJ·mol^{-1}.

5.1.2. $\Delta_f G°$(FeOOH, cr, α)

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

5.1.3. Gibbs Energy of Solution of FeOOH(cr, α) and $\Delta_f G°$(Fe^{3+},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 Fe^{3+}(aq), e.g. 69LAN, 71LAN, 71LAN/WHI, and 85HSU/MAR.

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

The precipitate in contact with solutions containing Fe^{3+}(ao) depends upon the pH of the solution, temperature, time, the presence of Fe^{2+}(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 $K_s = a$(Fe^{3+})a(OH$^-$)^3 is thus difficult to ascribe accurately to a single, well-defined phase. 85HSU/MAR (No. 28) obtained the activity products, a(Fe^{3+})a(OH$^-$)^3, of Fe(ClO$_4$)$_3$ solutions hydrolyzed and aged at room temperature (298.15 ± 3 K) for 9 to 16 a which contained only well crystallized Goethite as determined by x-ray diffraction. The values determined varied with ionic strength but not with particle size (in contrast to 71LAN/WHI, 71LAN, 74WHI/LAN). The pK_s were 39.80, 40.32, and 40.83 for ionic strengths of about 0.005, 0.04 and 0.2 mol·dm^{-3} and correspond to the reaction,

$$FeOOH(cr,\alpha) + H_2O(l) = Fe^{3+}(ao) + 3OH^-(ao).$$
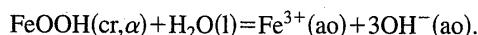
Extrapolation to $I=0$ results in p$K_s = 39.5$ and $\Delta G° = 225.46 \pm 2.0$ kJ·mol^{-1} and $\Delta_f G°$(Fe^{3+},ao) $= -28.52 \pm 2.6$ kJ·mol^{-1}.

Earlier 71LAN/WHI had indicated that the "pK" from precipitation, initially at concentration of Fe^{2+}(ao) or Fe^{3+}(ao) of 10^{-2} mol·dm^{-3} varied from 37.3 to 43.3, beginning as amorphous material and that the pK_s of the aged, macroscopic Goethite would be about 43.3 (this includes a calculated 3.2 pK correction for surface area. In addition from the examination of well waters containing $10^{-3.33}$ to $10^{5.40}$ mol·dm^{-3} Fe^{2+}(ao) and suspended oxyhydroxides, "pK" was 37.1 to 43.5. If we adopt 43.4 ± 0.5 as the pK_s from 71LAN/WHI (No. 27) we obtain $\Delta G° = 247.7 \pm 3.0$ kJ·mol^{-1} and $\Delta_f G° = -6.3 \pm 3.5$ kJ·mol^{-1}.

More recently 89KHO reviewed the oxyhydroxy-H$_2$O system and in a preliminary communiqué indicated that for

$$0.5Fe_2O_3(cr,hematite) + 3H^+(ao) = Fe^{3+}(ao) + 1.5H_2O(l);$$
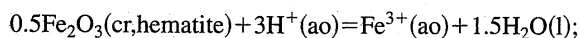
$$\Delta G = 3.0 \pm 2.5 \text{ kJ·mol}^{-1}.$$

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

$$FeOOH(cr,Goethite) + 3H^+(ao) = Fe^{3+}(ao) + 2H_2O(l),$$
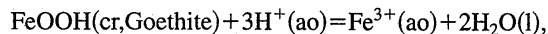
$$\Delta G° = 1.49 \pm 2.6 \text{ kJ·mol}^{-1}.$$

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

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

$$3H_2O(l) = 3H^+(ao) + 3OH^-(ao); \quad \Delta G° = 239.76 \text{ kJ·mol}^{-1}$$
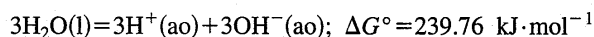
we obtain $\Delta G° = 241.25 \pm 2.6$ and 240.90 ± 2.8 kJ·mol^{-1} for the process

$$FeOOH(cr,\alpha) + H_2O(l) = Fe^{3+}(ao) + 3OH^-(ao),$$
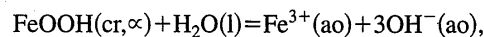
and $\Delta_f G° = -12.75 \pm 2.6$ and -12.45 ± 2.8 kJ·mol^{-1}, respectively.

These values are tabulated.

5.1.4. The Direct Relationship Between $\Delta_f G°$(Fe^{2+}, ao) and $\Delta_f G°$(Fe^{3+}, 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° $= -0.7698 \pm 0.002$ V for

$$Fe^{2+}(ao) + H^+(ao) = Fe^{3+}(ao) + 0.5H_2(g)$$
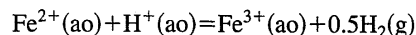
resulting in $\Delta G° = 74.274 \pm 0.20$ kJ·mol^{-1}. 73NIK/ANT (No. 16) also measured the $E°$s (using Tl(Hg), TlCl(cr) reference electrode with saturated KCl solution). At 298.15 K, $E° = -0.770 \pm 0.005$ V and $\Delta G° = 74.30 \pm 0.50$ kJ·mol^{-1}, in excellent agreement with 72WHI/LAN although the values diverge above 298 K resulting in $\Delta H°$(298 K) values that differ by 4 kJ·mol^{-1}. (See Nos. 17 and 15.)

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

5.1.4.2. The equilibrium constants

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

$$Fe^{3+}(ao) + Ag(cr) = Fe^{2+}(ao) + Ag^+(ao)$$
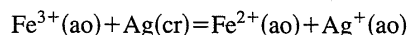
to be K $= 0.363 \pm 0.015$ (measurements of 12NOY/BRA) or $\Delta G° = 2.512 \pm 0.25$ kJ·mol^{-1} and K $= 0.137 \pm 0.010$ for

$$2Fe^{3+}(ao) + 2Hg(l) = 2Fe^{2+}(ao) + Hg_2^{2+}(ao)$$
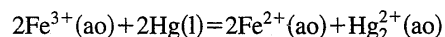
(measurements of 31POP/FLE) or $\Delta G° = 4.927 \pm 0.50$ kJ·mol^{-1} (No. 21).

The resultant ΔGs for

$$Fe^{2+}(ao) + H^+(ao) = Fe^{3+}(ao) + 0.5H_2(g)$$
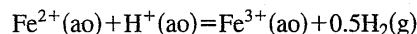
TABLE 6. The Gibbs energies of formation of Fe^{2+}(ao) and Fe^{3+}(ao) and $\Delta(\Delta_f G°)=\Delta_f G°(Fe^{3+},ao)$
$-\Delta_f G°(Fe^{2+},ao)(p°=1$ atm)

Source	$\Delta_f G°(Fe^{2+}, ao)kJ \cdot mol^{-1}$	$\dfrac{\Delta(\Delta_f G°)}{kJ \cdot mol^{-1}}$	$\dfrac{\Delta_f G°(Fe^{3+}, ao)}{kJ \cdot mol^{1}}$
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 Tl^+(ao))	or		
	-82.34 ± 1.5		
34BRA/HER		74.47 ± 0.50	
(Hg, ag reduction)			
Fe_3O_4(cr) solubility[t]			
70SWE/BAE	-90.18 ± 3.1		
80TRE/LEB	-88.26 ± 2.1		
$FeSO_4 \cdot 7H_2O$ (cr), solubility	-91.60 ± 0.85		
$FeCl_2 \cdot 4H_2O$ (cr)	-89.4 ± 3.1		
vapor pressure and solubility			
FeOOH (cr, Goethite), solubility			
84HSU/MAR (pK=39.5)			-28.5 ± 2.6
71LAN/WHI (pK=43.4)			-6.3 ± 4.4
Fe_2O_3 (cr, hermatite), solubility			
89KHO re-analysis of data			-12.6 ± 2.8
(calculated pk_{sp} (Goethite)=42.3)			

[t] $\Delta_f H°$, $\Delta_f G°(p°=1$ atm), $S°$ for Fe_3O_4(cr, magnetite)$=-1116.72\pm2.2$ kJ·mol^{-1}, -1010.30 ± 2.15 kJ·mol^{-1}, and 145.438 ± 0.32 J·K^{-1}mol^{-1}, respectively.

are 74.60 ± 0.50 and 74.34 ± 0.5 kJ·mol^{-1}, respectively ($E° = -0.773\pm0.005$ and -0.7705 ± 0.005 V).

Similarly the measurements of 35SCH/SWE (No. 13) on the reduction of Fe^{3+}(ao) to Fe^{2+}(ao) by Ag(cr) yield $K=0.499$ and $\Delta G° = 1.724\pm0.20$ kJ·mol^{-1}, so that $\Delta G°$ for the Fe^{2+}-Fe^{3+} couple is 75.39 ± 0.2 kJ·mol^{-1} ($E° = -0.781$ V).

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

The e.m.f. measurements and the equilibrium measurements are in good agreement and it would appear that the $\Delta_f G°(Fe^{3+},ao)-\Delta_f G°(Fe^{2+},ao) = 74.27\pm0.20$ kJ·mol^{-1} and $E° = -0.7698\pm0.002$ V.

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

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

It is quite obvious that if we accept $\Delta_f G°(Fe^{2+},ao) = -90.5\pm1.0$ kJ·mol^{-1} and we maintain $\Delta(\Delta_f G°) = 74.27\pm0.20$ kJ·mol^{-1} our value for $\Delta_f G°(Fe^{3+},ao)$ must be -16.2 ± 1.1 kJ·mol^{-1}, in marginal agreement with the 89KHO value obtained from the solubility of Fe_2O_3(cr,hematite). It is also obvious that the more positive

value of -6.3 kJ·mol^{-1} for $\Delta_f G°(Fe^{3+},ao)$ would support the more positive values for $\Delta_f G°(Fe^{2+},ao)$ 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 $\Delta_f G°(Fe^{2+},ao)$, from the solubility of Fe_3O_4(cr,hematite), the solubility of $FeSO_4 \cdot 7H_2O$(cr), and the solubility of $FeCl_2 \cdot 4H_2O$(cr) and the decomposition of the tetrahydrate. Although the uncertainties on the values from Fe_3O_4 and $FeCl_2 \cdot 4H_2O$ are large and some adjustments could be made in the interpretations of the Gibbs energies of reaction, a 6 to 10 kJ·mol^{-1} adjustment is not possible. If we attempt to go the other way, that is, to select a value of -81 kJ·mol^{-1} (or even -84 kJ·mol^{-1}) for $\Delta_f G°(Fe^{+2},ao)$ and use the Gibbs energies of reaction of the three above mentioned paths we would obtain calculated values for the enthalpies of formation of Fe_3O_4(cr), $FeSO_4 \cdot 7H_2O$(cr), and $FeCl_2 \cdot 4H_2O$(cr) and $FeCl_2$(cr) that are incompatible with the selected values for these substances and their $\Delta_{sol}H$'s. (See sections on $\Delta_f H°$($FeSO_4 \cdot 7H_2O$,cr), $\Delta_f H°$($FeCl_2$,cr), and $\Delta_f H°$(Fe^{2+},ao)). We therefore accept:

$$\Delta_f G°(Fe^{3+},ao)=-16.23\pm1.1 \text{ kJ·mol}^{-1}$$

and our previous "tentative" value for $\Delta_f G°(Fe^{2+},ao)$ $=-90.5\pm1.0$ kJ·mol^{-1}.

TABLE 7. Recommended thermodynamic property values ($p° = 1$ atm)

Substance	$\dfrac{\Delta_f H°}{\text{kJ·mol}^{-1}}$	$\dfrac{\Delta_f G°}{\text{kJ·mol}^{-1}}$	$\dfrac{S°}{\text{J·mol}^{-1}\text{·K}^{-1}}$
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
ГcSO$_4$(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 ($p° = 1$ bar)

Substance	$\dfrac{\Delta_f H°}{\text{kJ·mol}^{-1}}$	$\dfrac{\Delta_f G°}{\text{kJ·mol}^{-1}}$	$\dfrac{S°}{\text{J·mol}^{-1}}$
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
ГcSO$_4$(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 ($p° = 1$ atm and $p° = 1$ bar). Predicted (calculated) process values and uncertainties for many of the reactions used in this evaluation are also tabulated ($p° = 1$ bar). In addition, a list of reactions (contained in the reaction 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 Fe^{2+}(ao) $\Delta_f H° = -90.0 \pm 0.5$ kJ·mol^{-1}

$\Delta_f G° = -90.5 \pm 1.0$ kJ·mol^{-1} ($p° = 1$ atm)

$\Delta_f G° = -90.53 \pm 1.0$ kJ·mol^{-1} ($p° = 1$ bar),

$S° = -101.6 \pm 3.7$ J·mol^{-1}·K^{-1}

For Fe^{3+}(ao) $\Delta_f H° = -49.0 \pm 1.5$ kJ·mol^{-1},

$\Delta_f G° = -16.23 \pm 1.1$ kJ·mol^{-1} ($p° = 1$ atm),

$= -16.28 \pm 1.1$ kJ·mol^{-1} ($p° = 1$ bar)

$S° = -278.44 \pm 7.7$ J·mol^{-1}K^{-1}.

This requires a small modification in the values for $\Delta_f H°$ and/or $\Delta_f G°$ for FeSO$_4$·7H$_2$O(cr). We have chosen to adjust $\Delta_{sol}G° = 13.2$ kJ·mol^{-1} by returning to the 74OYK/BAL $\gamma_\pm$ values with $\gamma_\pm = 0.15$ at m=0.1 mol·kg^{-1}. This results in an adjustment in $\Delta_f H°$(FeSO$_4$·7H$_2$O,cr) from the tentative value of $- 3013.05 \pm 0.85$ kJ·mol^{-1} given in Sec. 2.5 to $- 3012.6 \pm 0.9$ kJ·mol^{-1}. The equation for the enthalpy of solution is adjusted for this so that

$$\Delta_r H_{(I)} - \Delta H°_{(D-H)} / \text{kJ·mol}^{-1} = (12.45 \pm 0.12)$$

$$+ (64.16 \pm 2.83)I - (382.5 \pm 57.07)I^2.$$

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 ($p° = 1$ bar)

Substance	$\dfrac{\Delta_r H°}{\text{kJ·mol}^{-1}}$	$\dfrac{\Delta_r G°}{\text{kJ·mol}^{-1}}$	$\dfrac{\Delta_r S°}{\text{J·mol}^{-1}\text{·K}^{-1}}$
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 $FeCl_3(cr)$ and $FeCl_2(cr)$ 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 $FeCl_3(g)$ are contained in 89EFI. The reactions are as follows:

$$FeOCl(cr) + 2HCl(aq) = FeCl_3(cr) + H_2O(l)$$
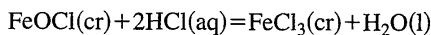
(Appendix AI.b, Nos. 159 and 160),

$$6FeOCl(cr) = 2Fe_2O_3(cr) + Fe_2Cl_6(g)$$

(Appendix AI.b, No. 161)

$$Fe_2O_3(cr) + 6HCl(g) = Fe_2Cl_6(g) + 3H_2O(g)$$
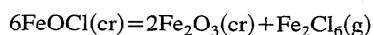
(Appendix AI.b, No. 162),

$$2FeCl_2(cr) + Cl_2(g) = Fe_2Cl_6(g)$$

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

$$2FeCl_3(cr) = Fe_2Cl_6(g) \text{ (Appendix AI.c, Nos. 19–33)},$$

$$Fe_2Cl_6(g) = 2FeCl_3(g),$$

$$Fe_2O_3(cr) + 6HCl(g) = 2FeCl_3(g) + 3H_2O(g),$$

$$2Fe_2O_3(cr) + 6Cl_2(g) = 4FeCl_3(g) + 3O_2(g).$$
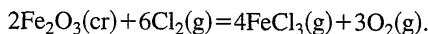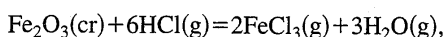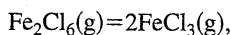
6.3. Effect of values on other networks

The values given here for some iron compounds, particularly for $\Delta_f G°(Fe^{2+},ao)$ and for $\Delta_f H°(FeCl_3,cr)–\Delta_f H°(FeCl_2,cr)$ differ from those given in 82WAG/EVA, 69WAG/EVA, and 71MED/BER, and should not be combined with values from those sources. These new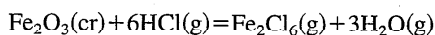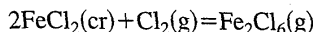 values are not only on the CODATA scale, but indicate that a reanalysis of other key networks are needed. In particular, the thermochemical relationships in the uranium key network [see 83FUG/PAR and 92GRE/FUG] involve the $\Delta_f H°(FeCl_3,cr)–\Delta_f H°(FeCl_2,cr)$ from 82WAG/EVA in the analysis of the $UCl_4(cr)–UO_2Cl_2(cr)$ relationship. The new selections indicate revisions may be necessary not only for $\Delta_f H°(UCl_4,cr)$, $\Delta_f H°(UF_4,cr)$, and $\Delta_f H°(UF_3,cr)$ (see 85O'H and 92FUG), but also for $\Delta_f H°(UO_3,cr,\gamma)$, $\Delta_f H°(UO_2F_2,cr)$, $\Delta_f H°(UO_2Cl_2,cr)$, $\Delta_f H°(U^{4+},ao)$, and $\Delta_f H°(UO_2^{2+},ao)$. The latter two have also been defined by CODATA (see 89COX/WAG) from 83FUG/PAR.

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Appendix I: Reaction Catalogs for Selected Fe Compounds

* Chemical Thermodynamics Data Center
* National Institute of Standards and Technology

* Computer Readable Reaction Catalog
* For Selected Fe Compounds 3/91
* Vivian B. Parker (VBP) with the cooperation of Vadim Medvedev (VM) and M. Efimov (EME) IVTAN, I. Khodakovskii (I.Kh.) and O. Devina (O.D.) VIGAC

AI.a. Descriptive Information

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

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

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

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

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

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

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

*: Private comments and working notes

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

The thermochemical property designation for reactions is:

H for ΔH;   G for ΔG;   S for ΔS;   and S for $S°$

(if the R: entry is for a substance, the formula is preceded by an "=").

The temperature is given in degrees Kelvin or Celsius units. If the temperature is not specified, the measurement is assumed to refer to 298.15 K. The pressure can be assumed to be either one bar or one atmosphere. For 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:

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

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

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

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

K, °C=degrees Kelvin, Celsius temperature.

All values are for the reaction as given.

The recommendations of the Division of Physical Chemistry of the International Union of Pure and Applied Chemistry [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, $m=1$ 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,
$250H_2O$, etc.	=solution of specified composition,
D	=differential (partial molar property).

AI.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; "Cp" is actually "C_p"; "dH" is "ΔH."

1.   Z: 90CTT
       R: =Fe(cr)
       DV: S, 27.319 $ 0.002 J
       C: bcc phase; Cp=25.154 $ 0.065 J/mol.K. At 200 K   H-H(298)=−2.317   kJ,   S=17.9417 J/(mol.K) and Cp=21.6054 J/(mol.K). From 90HAA/CHA. Using H-H(0)=2.192 kJ/mol at 200 K from 85CHA/DAV, H-H(0)=4.509 kJ/mol at 298 K.
       S: 8/89 VBP, 8/90 VBP

2.   Z: 89CTT
       R: =Fe (g)
       DV: S, 180.489 $ 0.030 J
       C: 1 bar, Cp=25.675 $ 0.010 J/(mol.K), H-H(0) =6.850 $ 0.005 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: Fe+2(ao)+2Tl(cr)=Fe(cr)+2Tl+(ao)
       DV: G, +13.51 $ 1.5 kJ
       C: K' at 323K and concentration NaClO4=1.0 mol/ (kg H2O) is 0.07592 $ 0.06. Correction of dG to 298.15 K=(+6.9 kJ) and to I=0 (−0.33kJ). Note: Authors use co-author's half cell value for 2Tl+(ao)+H2(g)=2Tl(cr)+2H +(ao), dG0=68.826 kJ/mol at 298.15 K. NIST and IVTAN evaluations give 64.852 kJ/mol.
       S: VBP Aug. 85, 11-87

5.   Z: 78JOH/BAU
       R: Fe(cr)+2H+(ao)=Fe+2(ao)+H2(g)
       DV: G, −80.08 $0.20 kJ
       C: From cell Fe(cr)|FeCl2(0.02m)||sat'd KCl|| AgCl||Ag(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 ~0.435 V. p=1 atm.
       S: 5/86 VBP

6.   Z: 60HUR
       R: Fe(cr)+2H+(ao)=Fe+2(ao)+H2(g)
       DV: G, −90.11$0.80 kJ
       C: From E0=+0.467 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 2Fe(cr)+OH-(ao)=2Fe+2(ao)+OH-(ao)-4e. Correction to 298 K is negligible. p=1 atm.
       S: 5/86 VBP

7.   Z: 76VAS/RAS
       R: Fe(cr)+3/2 H2O2(ao)+3HClO4(ai) =Fe(C104)3(ai)+3H2O(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, dsolnH0 = −616.89 kJ/mol. From 1.5% H2O, dsolnH0 = −617.81 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.

S: VBP Aug. 85

8. Z: 76VAS/RAS
    R: Fe(cr)+3/2 H2O2(ao)+3HClO4(ai)
       =Fe(ClO4)3(ai)+3H2O(l)
    DV: H, −617.21$0.3 kJ
    C: Reextrapolation to I=0 using Khodakovskii's '86 equation and constants. Individual experimental val-ues are: For m Fe+3(ao)=0.012 mol/(kg H2O) in 1.058, 2.220, 3.501, 4.920 molal HClO4 solns containing 1.0% H2O2, dH =−616.43, −618.27, −621.24 and −623.08 kJ/mol, respectively, in solns containing 1.5% H2O2, dH=−616.51, −618.65, −620.61 and −622.45 kJ/mol respectively. dHD-H corrections for extrapolation are 2.67, 3.08, 3.326, and 3.50 kJ/mol.
    S: O.D., I.Kh. with VBP 5/87

9. Z: 68SOU/CIIA
    R: Fe+2(ao)+1/2 H2O2(ao)+H+(ao)=Fe+3(ao) +H2O(l)
    DV: H, −146.13$1.0 kJ
    C: Oxidation of (NH4)2Fe(SO4)2 soln (0.1 molal) in .05m H2SO4; final concentration Fe+3(ao) is 5E-04 molal with dH=−146.65$0.84 kJ/mol, and oxidation of Fe(ClO4)2 soln (0.2 molal) in 0.1 HClO4 soln); final concentration Fe+3 is 5E-04 molal with dH=−145.60$1.3 kJ/mol
    S: 6/86 VBP

10. Z: 71BER/TUM
    R: Fe+2(ao)+1/2 H2O2(ao)+H+(ao)=Fe+3(ao) +H2O(1)
    DV: H, −148.76$0.10 kJ
    C: Used FeSO4 solutions, m=.003 to .009 mol/ (kg H2O) with about 0.01 m H2SO4.
    S: 6/86 VBP

11. Z: 47FON
    R: Fe+2(ao)+1/2 H2O2(ao)+H+(ao)=Fe+3(ao) +H2O(l)
    DV: H, −150.16$0.50 kJ
    F: TN
    C: In 0.5 mol dm-3 HClO4
    S: 6/86 VBP

12. Z: 47FON
    R: Fe+3(ao)+1/2 H2(g)=Fe+2(ao)+H+(ao)
    DV: H, −40.08$0.50 kJ
    F: TN
    C: in 0.5 mol dm-3 HClO4 solutions
    S: 6/86 VBP

13. Z: 35SCH/SWE
    R: Fe+2(ao)+Ag+(ao)=Fe+3(ao)+Ag(cr)
    DV: G, −1.72$0.2 kJ
    C: K meas. from Fe+3(ao) reduction in HCLO4 aqueous solutions, m=0.9255 to 0.07404= mol/(kg H2O). Ionic strength solution 1.4 to 0.10. Extrapolation to zero using Davies equation for activity coefficients.
    S: 6/86, 10/90 VBP

14. Z: 72WHI/LAN
    R: Fe+2(ao)+H+(ao)=Fe+3(ao)+1/2 H2(g)
    DV: G, +74.274$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. E0 values were corrected for FeOH+2(ao) and Fe2(OH)2+4(ao) complexes. p=1 atm.
S: 6/86 VBP

15. Z: 72WHI/LAN
    R: Fe+2(ao)+H+(ao)=Fe+3(ao)+1/2 H2(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 J/(mol.K); See 73NIK/ANT for use of this dS and 88HOV Cp data.
    S: 8/88 VBP, 3/90 VBP

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

17. Z: 73NIK/ANT
    R: Fe+2(ao)+H+(ao)=Fe+3(ao)+1/2 H2(g)
    DV: H, 46.7 $ 2.0 kJ
    C: E measured in 0.125 to 1.913 mol dm-3 HClO4 (10 concentrations). Fe+2(ao), Fe+3(ao) concentrations are less than 0.01 M. Corrected for ionic strength of solution. Used Tl(Hg), TlCl(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−H298.15) at mean T(319 K)=1.2 kJ/mol, taken from Cp measurements Fe+2(ao) and Fe+3(ao) by 88HOV. Third Law value, using dS=−105.9 J/(mol.K) is 42.27 $ 1.4 kJ/mol. dS over range 298 to 323 K is −57.9 J/(mol.K). Over entire range dS=−72.2 J/(mol.K).
    S: 3/90 VBP

18. Z: 58LAP
    R: Fe+2(ao)+H+(ao)=Fe+3(ao)+1/2H2(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 Fe+3(ao)-Fe+2(ao)-SO4-2(ao) aqueous system. Obtains E0

Fe+2(ao) Fe+3(ao)=0.738 V and log satu-
rated calomel half cell. Concentration of
SO4-2(ao)=0.04 mol dm-3. Corrects for
aFe+3/aFe+2 using Debye-Huckel eqn; no ex-
trapolation 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 HClO74. 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 concen-
    tration 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 (cor-
    rected to unit concentration H+). Ionic strength
    solution=0.55 mol/(kg H2O); corrected to ac-
    tivities using Davies eqn. p=1 atm.

26. S: 6/86 VBP
    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.

27. S: 6/86 VBP
    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.

28. S: 8/87,10/90 VBP
    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.

29. S: 10/90 VBP
    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 complex-
    ing. Uses Davies equation.

30. S: 6/86 VBP
    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

31. S: 8/89 VBP
    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)

32. S: 6/87 VBP
    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).

33. S: 6/87 VBP
    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: Fe+2(ao)+3H2O(l)=Fe(OH)3(cr)+3H +(ao)+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 KsO 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

35. Z: 58LAP

R: 3Fe+2(ao)+4H2O(l)=Fe3O4(cr)+8H +(ao)+2e

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 KsO Fe(OH)3(cr)=−39.43. Refer-ence 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

36. Z: 70SWE/BAE

R: 1/3 Fe3O4(cr)+2H+(ao)+1/3 H2(g)=Fe +2(ao)+4/3 H2O(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

37. Z: 70SWE/BAE

R: 1/3Fe3O4(cr)+H+(ao)+1/3H2(g)=FeOH +(ao)+1/3H2O(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

38. Z: 70SWE/BAE

R: 1/3Fe3O4(cr)+1/3H2(g)+2/3H2O(l) =Fe(OH)2(ao)+H+(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

39. Z: 70SWE/BAE

R: 1/3Fe3O4(cr)+5/3H2(g)+1/3H2O(l)= Fe(OH)3-1(ao)+H+(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

40. Z: 70SWE/BAE

R: Fe+2(ao)+H2O(l)=FeOH+(ao)+H+(ao)

DV: G, +53.1$2.9 kJ

C: Difference in 2 extrapolated K's.

S: 5/86 VBP

41. Z: 80TRE/LEB

R: $1/3Fe_3O_4(cr)+2H+(ao)+1/3H_2(g)=$
    $Fe+2(ao)+4/3H_2O(l)$

DV: H, $-85.44\$4.0$ kJ

DV: G, $-64.26\$$ 2.0 kJ

C: dH (473 K)$=-78.09$ kJ/mol and dS0 (473 K) $=-51.63$ J/(mol.K).Evaluator used dCp=42 J/(mol.K) from 70SWE/BAE

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.

S: 5/86 VBP, 3/88 VBP

42. Z: 80TRE/LEB

R: $1/3Fe_3O_4(cr)+H+(ao)+1/3H_2(g)=$
    $FeOH+(ao)+1/3H_2O(l)$

DV: H, $-58.9\$6.0$ kJ

DV: G, $-9.11\$$ 2.5 kJ

C: Authors established dCp=125 J/(mol.K) used. dH(473 K)$=-36.78$ kJ/mol with dS (475 K)$= -108.96$ J/(mol.K). If use dCp=14 J/mol from 70 SWE/BAE, dH and dG are -39.23 and -4.8 kJ/mol respectively.

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.

S: 5/86 VBP, 3/88 VBP

43. Z: 80TRE/LEB

R: $1/3$ Fe3O4(cr)$+5/3H_2O(l)+1/3H_2(g)=$
    Fe(OH)3-1 (ao)$+H+(ao)$

DV: H, $72.8\$8.0$ kJ

DV: G, $127.7\$3.0$ kJ

C: Authors est'd dCp$=-10.6$ J/(mol.K) used. dH (473 K)$=71.58$ kJ/mol and dS (473 K)$= -188.71$ J/(mol.K).

C: Solubility of carefully characterized 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.

S: 5/86 VBP, 3/88 VBP

44. Z: 80TRE/LEB

R: $1/3Fe_3O_4(cr)+1/3H_2(g)+2/3H_2O(l)$
    $=Fe(OH)2(ao)$

DV: H, $20.8\$4.0$ kJ

DV: G, $55.7\$$ 2.0 kJ

C: Authors established dCp=27 J/(mol.K) used. dH (473 K)$=25.5$ kJ/mol and dS (473 K)$= -102.35$ 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.

S: 5/86 VBP, 3/88 VBP

45. Z: 80TRE/LEB

R: $1/3Fe_3O_4(cr)+5/3H_2O(l)=Fe(OH)3(ao)+1/6H_2(g)$

DV: S, $-72\$8.0$ J

C: Authors dCp$=-10.6$ J/(mol.K) used. dS (473 K)$=75.4$ 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 78JOII/BAU. p=1 atm.

- S: 5/86 VBP, 3/88 VBP
46. Z: 80TRE/LEB
- R: $1/3Fe_3O_4(cr)+8/3H_2O(l)=Fe(OH)4-1(ao)$ $+1/6H_2(g)+H+(ao)$
- 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.
- S: 5/86 VBP
47. Z: 89CTT
- R: $=Fe_2O_3$ (cr)
- DV: S, 87.483 $ 0.06 J
- C: Evaluation of J. Haas
- S: 10/89 VBP
48. Z: 70KIN/WEL
- R: $=FeOOH(cr)$
- DV: S, 60.38$0.63 J
- C: low temp Cp measurements 51 to 298 K.
- S: 6/86 VBP
49. Z: 90CTT
- R: $=FeOOH(cr)$
- DV: S, 60.40 $ 0.6 J
- C: Work of 70KIN/WEL. H-H0=10.820 $ 0.08 kJ, Cp=74.480 $ 0.07 J/(mol.K).
- S: 5/90 VBP
50. Z: 90CTT
- R: $=Fe(OH)2$ (cr)
- DV: S, 93.00 $ 6.0 J
- C: Est'd by IVTAN
- S: 3/90 VBP
51. Z: 65BAR
- R: $2FeOOH(cr)=Fe_2O_3(cr)+H_2O(l)$
- 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.
- S: 5/86 VBP
52. Z: 53LEU/KOL
- R: $Fe(OH)2(cr)=Fe+2(ao)+2OH-(ao)$
- DV: G, 86.17$1.0 kJ

- F: TN
- C: K=8($3)E-16. Used activity coefficients from 37KIE
- S: 5/86 VBP
53. Z: 53LEU/KOL
- R: $Fe(OH)2(cr)=FeOH+(ao)+OH-(ao)$
- 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
54. Z: 80DIB/CHE
- R: $Fe(cr)+Cd(OH)2(cr)=Fe(OH)2(cr)+Cd(cr)$
- DV: H, −10.61$1.0kJ
- C: Electrochem. measurements anodic enthalpy plateau.
- S: 5/86 VBP
55. Z: 43FRI/RIH
- R: $Fe(OH)2(cr)+1/4O_2(g)=0.5 Fe_2O_3(cr)$ $+H_2O(l)$
- DV: H, −125.3$2.5 kJ
- C: dE(296 K)=−124.68 kJ/mol used as dH in IVTAN catalog equation 372
- S: 5/86 VBP
56. Z: 78JOH/BAU
- R: $Fe+2(ao)+H_2O(l)=FeOH+1(ao)+H+(ao)$
- 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.
- S: 5/86 VBP
57. Z: 78JOH/BAU
- R: $Fe(OH)2(am)=Fe+2(ao)+2OH-(ao)$
- DV: H, 19.66$1.7 kJ
- DV: G, 82.14$0.21 kJ
- C: Freshly pptd.
- S: 5/86 VBP
58. Z: 32RAN/FRA
- R: $Fe(cr)+HgO(cr)+H_2O(l)=Hg(l)$ $+Fe(OH)2(cr)$
- 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.
- S: 5/86 VBP
59. Z: 33KRI/AWS
- R: $Fe(OH)2(cr)=Fe+2(ao)+2OH-(ao)$
- DV: G, 82.7$ kJ
- C: Potentiometric
- S: 7/86 VM
60. Z: 50ARD
- R: $Fe(OH)2(cr)=Fe+2(ao)+2OH-(ao)$
- DV: G, 77.7$ kJ
- C: Potentiometric
- S: 7/86 VM
61. Z: 51QUI
- R: $Fe(OH)2(cr)=Fe+2(ao)+2OH-(ao)$
- DV: G, 84.4$ kJ
- C: Potentiometric
- S: 7/86 VM
62. Z: 63BER/KOV
- R: $3Fe(OH)2(cr)=Fe_3O_4(cr)+2H_2O(g)+H_2(g)$

DV: H, 207.9$11
C: Third law value. Second law value=308 kJ/ mol. DTA, 422-465 K. Graph only.
S: 7/86 VM

63. Z: 59SCH
R: 2FeOOH(cr)=Fe2O3(cr)+H2O(l)
DV: H, 14.7 $ 10 kJ
F: TN
C: dG(400 K)=0; 3rd law value. PVT, 411-453 K.
S: VM 7/86, 8/89 VBP

64. Z: 64FER
R: 2FeOOH(cr)=Fe2O3(cr)+H2O(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 kJ/mol); corrected to 298.15 K and H2O(l) using d(H-H298)=1.37 kJ/(mol H2O)
S: VM 7/86, 5/89 VBP

65. Z: 75KOR/FAD
R: 2FeOOH(cr)=Fe2O3(cr)+H2O(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: FeCl2(cr)+H2SO4(200H2O) +2KOH(100H2O)=2HCl(100H2O) +K2SO4(200H2O)+Fe(OH)2(cr)
DV: H, −116.3$3.0 kJ
C: IVTAN 3-85 eq. 369; summation of dsolnH (FeCl2, cr)=−74.89 kJ/mol, dmixH (FeCl2200H2O) with H2SO4(200H2O) =−15.06 kJ/mol and dneutH=−26.53 kJ/mol. dH (292 K)=−116.5 kJ/mol corrected by VBP using dCp=40 J/(mol.K)
S: VM 7/86, 5/87 VBP

67. Z: 1882THO
R: FeSO4(200H2O)+Ba(OH)2(200H2O) =BaSO4(c)+Fe(OH)2(cr)
DV: H, −47.6$5.0 kJ
C: dH meas at 292 K=−50.2 kJ/mol. dCp=440 J/(mol.K) used by VBP. IVTAN 3-85 eq. 370
S: VM 7/86, 6/87 VBP

68. Z: 1882THO
R: Fe(OH)2(cr)+0.25O2(g)=0.5Fe2O3(cr) +H2O(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: FeOOH(cr)=FeOOH(cr2)
DV: H, 21$10.0 kJ
C: FeOOH(cr) is alpha form (Goethite); cr2 is gamma form (lepidocrite). From differences in dH dehydration.
S: 6/87 VBP

70. Z: 37FRI/ZER
R: FeOOH(cr)=FeOOH(cr2)
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.

S: 6/87 VBP
71. Z: 32RAN/FRA
R: Fe(OH)2(cr)+Hg2Cl2(cr)=Hg(l)+HgO(cr) +H2O(l)+FeCl2(ai)
DV: G, +52.16$0.96 kJ
F: TN
C: Combined reaction. Measured Fe(cr)- Fe(OH)2(cr) E0 combined with 32RAN/FRA2 Fe(cr)-FeCl2(ai). E0=−0.270$0.005 V.
S: 5/86 VBP

72. Z: 26HAM
R: Fe(cr)+2TlCl(cr)=FeCl2(ai)+2Tl(cr)
DV: G, +23.65$1.0 kJ
C: From left side of equilibrium. Molality FeCl2 =0.0453 moles/(kg H2O) and TlCl=0.0042 moles/(kg H2O). gamma from 79GOL/NUT. 32RAN/FRA2 say better agreement with their results is because the 26HAM treatment with TlCl(aq) removes the finer particles of iron.
S: 5/86 VBP

73. Z: 26HAM
R: Fe(cr)+Hg2Cl2(cr)=FeCl2(ai)+2Hg(l)
DV: G, −137.0$2.0 kJ
C: Used electrodes prepared from finely divided Fe(cr). Fe2O3(cr) was reduced with H2 which was O2 and H2O free. Mean of 4 meas. with m=0.10, 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 FeCl2 makes activity of the finely divided iron approach those of 32RAN/FRA2.
S: 5/86 VBP

74. Z: 53PAT/THO
R: Fe(cr)+Hg2Cl2(cr)=FeCl2(ai)+2Hg(l)
DV: G, −129.73$0.50 kJ
F: TN
C: E0=0.6723$0.0025 V; mean of measurements: m FeCl2(aq)=0.0760 and 0.0160; gamma =0.5324 and 0.6857 from 79GOL/NUT. H2 free Fe was prepd. by thermal decomposition of Fe(CO)5 under vacuum (powder obtained used directly as electrode material.) Also massive iron electrodes were prepd by vacuum fusion of Fe powder. Also special care to remove all traces of O2 from cells. Authors indicate that varia-tions from their values in E0 for Fe|Fe +2(ao) such as from 32RAN/FRA are due to presence of atomic H in metal. This dE was measured to be ~0.054 V.
S: 5/86 VBP

75. Z: 32RAN/FRA2
R: Fe(cr)+Hg2Cl2(cr)=FeCl2(ai)+2 Hg(l)
DV: G, −135.60$0.20 kJ
F: TN
C: E=0.7996 V for 0.1 m FeCl2 solution; gamma =0.5093 from 79GOL/NUT. E0=0.7027 V. Used two differently prepd samples Fe(cr), electrolytic iron deposited on Pt electrodes and Fe produced by reduction of FeO with H2. O2

76.
- S: 5/86 VBP
- Z: 89CTT
- R: =FeF(g)
- DV: S, 241.536 $ 0.6 J
- C: H−H0=10.574 $ 0.10 kJ/mol, Cp=38.868 $ 0.50 J/(mol.K) One Bar Value. Sent 9/87
- S: 8/89 VBP

77.
- Z: 89CTT
- R: =FeF2(cr)
- DV: S, 87.00 $ 0. J
- C: H−H0=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.
- S: 10/89 VBP

78.
- Z: 89CTT
- R: =FeF2(g)
- DV: S, 268.305 $ 3.0 J
- C: H−H0=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−H0=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−H0=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

carefully excluded from both as described by 32RAN/FRA

C: Summation of 4 reactions at 303 K, corrected using dCp=236 J/(mol.K). dsolnH Fe(cr) and FeCl2(cr) at 303 K=−87.11 $0.17 and= −62.76 $0.09 kJ/mol respectively. Same reaction as IVTAN Eq. 389.

S: 3/86 VBP

91. Z: 88CTT

R: =FeCl2(cr)

DV: S, 118.0 $0.40 J

C: H−H(0)=16.27 kJ/mol, Cp=76.66 J/mol.K

** See updated 89CTT value below.

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

S: 8/88 VBP

92. Z: 89CTT

R: =FeCl2(cr)

DV: S, 118.060 $0.20 J

C: H−H(0)=16.10 kJ/mol, Cp=76.60 J/mol.K

S: 11/89 VBP

93. Z: 82COB/MUR

R: FeCl2(cr)=FeCl2(ai)

DV: H, −82.906 $0.32 kJ

C: Debye Huckel extrap. from measurements in 0.005 molal HClO4. 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: FeCl2(cr)=Fe+2(ao)+2Cl-(ao)

DV: H, −83.11 $0.42 kJ

C: Authors' extrapolation after correction for phiL D-H from measurements in 0.001 m HClO4. Measured values are −82.680, −82.639, −82.502 and −81.925 kJ/mol for m FeCl2(aq) =0.00459, 0.00422, 0.00550 and 0.00849. 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: FeCl2(cr)=FeCl2(0.1315(HClO4+55500H2O))

DV: H, −82.437 $0.45 kJ

C: Average of 4 experimental measurements in 0.001 m HClO4. See above for individual measurements.

S: 5/89 VBP

96. Z: 77CER/HEP

R: FeCl2(cr)=FeCl2(ai)

DV: H, −83.05 $0.42 kJ

C: Measurements on FeCl2.0.0082 H2O(cr), dH =−82.97 kJ/mol and FeCl2. 0.0228(cr), dH =−82.38 kJ/mol, at infinite dilution. These measurements were corrected to anhydrous FeCl2(cr) assuming presence of FeCl2.H2O(cr) or FeCl2.2H2O(cr) in samples with dH=−62.8 kJ/mol and −41.8 kJ/mol respectively. This reaction is also in IVTAN catalog, reaction 390.

S: 3/86, 6/87 VBP

97. Z: 52LI/GRE

R: FeCl2(cr)=FeCl2(8000H2O)

DV: H, −81.84 $0.84 kJ

F: TN

C: Mean of 5 measurements. Molality range 0.00139 to 0.0117 mols/kg H2O. In IVTAN catalog, reaction 386 as dH=−81.5 $0.2 kJ/mol at infinite dilute. If phi(L)=860 J/mol, dH0 =−82.70 kJ/mol.

S: 3/86 VBP

98. Z: 10RIC/BUR

R: Fe(cr)+2HCl(D:6.31H2O)=FeCl2(HCl +6.31H2O:au)+H2(g)

DV: H, −85.78 kJ

C: dH meas at 293 K; Estimated dCp=+40 J/(mol.K)

S: 4/87 VBP

99. Z: 47FON2

R: FeCl2(cr)=FeCl2(72.7HClO4+8000H2O)

DV: H, −79.50 $0.42 kJ

S: 4/87 VBP

100. Z: 62AKH/KOP

R: Fe(cr)+2HCl(D:55.51H2O)=FeCl2(10.6HCl +700H2O)+H2(g)

DV: H, −84.94 $0.10 kJ

F: TN

S: 4/87 VBP

101. Z: 10RIC/ROW

R: Fe(cr)+2HCl(200H2O)=FeCl2(400H2O) +H2(g)

DV: H, −86.28 $2.0 kJ

F: TN

C: Measurement at 293.2 K, in concentrated HCl corrected by authors for HCl diln. to obtain value, dH =−87.03 kJ/mol for product free of excess acid. Estimated dCp=+40 J/(mol.K)

S: 5/87 VBP

102. Z: 87NBS

R: FeCl2(12.54H2O)=FeCl2(1100H2O)

DV: H, −15.55 kJ

C: Extrapolated from 41PER measurements at 285.7 K of dsolnH FeCl2:4H2O(cr) in nH2O from n=12.8 to 1100; dCp corrections using phi Cp from 79BER/MOR.

S: 4/87 VBP

103. Z: 87NBS

R: FeCl2(13H2O)=FeCl2(1100H2O)

DV: H, −15.65 kJ

C: From measurements by 41PER on dsolnH FeCl2:4H2O(cr) in nH2O from n=12.8 to 1100; dCp corrections using phi Cp from 79BER/MOR

S: 4/87 VBP

104. Z: 87NBS

R: FeCl2(15H2O)=FeCl2(1100H2O)

DV: H, −14.20 kJ

C: From measurements by 41PER on dsolnH FeCl2:4H2O(cr) in nH2O from n=12.8 to 1100; dCp corrections using phi Cp from 79BER/MOR

S: 4/87 VBP

105. Z: 87NBS
     R: FeCl2(20H2O)=FeCl2(1100H2O)
     DV: H, −11.00 kJ
     C: From measurements by 41PER on dsolnH
          FeCl2:4H2O(cr) in nH2O from n=12.8 to
          1100; dCp corrections using phi Cp from
          79BER/MOR
     S: 4/87 VBP

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

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

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

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

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

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

112. Z: 87NBS
     R: FeCl2(500H2O)=FeCl2(1100H2O)
     DV: H, −0.40 kJ
     C: From measurements by 41PER on dsolnH
          FeCl2:4H2O(cr) in nH2O from n=12.8 to

          1100; dCp corrections using phi Cp from
          79BER/MOR
     S: 4/87 VBP

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

114. Z: 1882THO
     R: FeCl2:4H2O(cr)=FeCl2(cr)+4H2O(l)
     DV: H, +64.31 $2.0 kJ
     F: TN
     C: dsolnH tetrahydrate=−11.51 $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: FeCl2:4H2O(cr)=FeCl2(400H2O)+4H2O(l)
     DV: H, −11.96 $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 phi Cp for FeCl2 (12.54 H2O)
          to be −37 J/(mol.K) and phi Cp0=−256 $30
          J/K.mol.
     S: 4/87 VBP

116. Z: 1979BER/MOR
     R: FeCl2(12.54H2O)=FeCl2(ai)
     DV: H, −20.558 $0.178 kJ
     DV: H, 288.15 K, −17.938 $0.079 kJ
     DV: H, 308.15 K, −22.353 $0.109 kJ
     C: Also measured phi Cp at 288, 298 and 308 K of
          solution (12.54H2O). Calculates phi Cp0=
          −256 $30 J/(mol.K) at 298.15 K
     S: 4/87 VBP

117. Z: 1889SAB
     R: FeCl2:2H2O(cr)=FeCl2(450H2O)+2H2O(l)
     DV: H, 293 K, −36.4 $2.0 kJ
     DV: H, −37.5 $2.2 kJ
     F: TN
     C: Measurement at 293 K in 300 to 600 H2O; dCp
          estimated=−220 J/(mol.K).
     S: 4/87 VBP

118. Z: 87NBS
     R: FeCl2:4H2O(cr)=FeCl2(ai)+4H2O(l)
     DV: G, −16.85 $0.5 kJ
     C: Saturation m=4.951 from 85CHO/PHA; activ-
          ity coeff=2.46 $0.10 and ln aw=−0.522 $0.10
          from 62KAN/GRO.
     *   Khodakovskii tabulation gives −17.5 $1.0 kJ/
          mol. These values need to be reconciled.
     S: 4/87VBP

119. Z: 1949SCH
     R: FeCl2:4H2O(cr)=FeCl2:2H2O(cr)+2H2O(g)
     DV: H, 108.0 $4.0 kJ
     DV: G, +23.62 $1.0 kJ
     F: TN

C: Vapor pressure measurements 293–338 K. log P atm=7.389−2,820/T. dCp assumed to be=0. Calculated dS=33.8 cal/(molH2O) K is slightly low.

S: 4/87 VBP

120. Z: 1949SCH
R: FeCl2:2H2O(cr)=FeCl2:H2O(cr)+H2O(g)
DV: H, 63.1 $5.0 kJ
DV: G, 18.57 $2.0 kJ
F: TN
C: Vapor pressure measurements 323–383 K; dH =62.9 kJ/mol at mean T=333 K; dCp=−4 J/(mol.K) assumed.; log P atm=7.704 −3,286/T. Calculated dS=35.7 cal/(mol.K) at 298 K. p=1 atm.
S: 4/87 VBP

121. Z: 1949SCH
R: FeCl2:H2O(cr)=FeCl2(cr)+H2O(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 kJ/mol at mean T~413 K; dCp=−4 J/(mol.K) assumed; log P atm=6.619−3,270/T. Calculated dS=30.6 cal/(mol.K) is low. p=1 atm.
S: 4/87 VBP

122. Z: 88CTT
R: =FeCl3(cr)
DV: S, 147.80 $0.3 J
C: From the low temp. Cp measurements (4.7– 307.6K) by 80STU/FER. Cp=96.942 J/(mol.K) and H-Ho=19.440 kJ/mol at 298.15 K. Low temp. results of 51TOD/COU rejected
S: 4/86 VBP, 10/88 VBP

123. Z: 71STU/PRO
R: =FeCl3(cr)
DV: S, 142.335 $2.0 J
F: TN
W: 99
C: From low temp. measurements (51–298 K) by 51TOD/COU who report S0 (51K)=18.828 $1.26 J/(mol.K) and S0 (298.15)−S0 (51K) =115.855 $0.38 J/(mol.K). 71STU/PRO adjusts S0 (51K) to 26.32 J/(mol.K) in order to reconcile 2nd and 3rd law drH for FeCl2(cr) =FeCl3(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: Fe(cr)+3HCl(12.731H2O)+0.5H2O2(12.58 H2O)=FeCl3(cr)+H2(g)+H2O(l)
DV: H, −102.59 $0.30 kJ
F: TN
C: Measured dH(303K)=−100.75 $0.29 kJ/mol; dCp=368 J/(mol.K). Same reaction as IVTAN equation 393 without dCp corrections.
S: 3/86 VBP

125. Z: 82LAV/TIM
R: Fe(cr)+1.5Cl2(g)=FeCl3(cr)
DV: H, −396.02 $0.14 kJ

C: IVTAN 3-85 EQ. 394
Two different samples used; one, NIST electrolytic grade SRM#797-2 and 2nd from Central Res. Instit. of Ferrous Metallurgy, Moscow which had been prepd. by vacuum meeting of Fe(CO)5 and then refined in H2 in presence of ZrH2. Corrected for impurities.
S: VM, VBP 7/87

126. Z: 84LAV/TIM
R: Fe(cr)+1.5Cl2(g)=FeCl3(cr)
DV: H, −396.02 $0.14 kJ
W: 99
C: See 82LAV/TIM
S: VBP 7/87

127. Z: 89EVD/EFI
R: FeCl2(cr)+1/2Br2(l)+KCl(cr)=FeCl3(cr) +KBr(cr)
DV: H, −11.386 $0.18 kJ
C: Calorimetric measurements at 298.15 K of all chloride components in solution of (KBr, 0.43 Br2, 112 HBr, 50.78 H2O) combined with reactions from 89EFI/EVD. dH FeCl3(cr)= −146.523 kJ/mol. Reported earlier as 88EFI/ EVD.
S: 8/88 VBP, 9/91 VBP

128. *Z: 27BAG
*R: 2FeCl3(cr)+H2(g)=2FeCl2(cr)+2HCl(g)
*DV: H, 130.866 $10.00 kJ
*W: 99
*C: IVTAN 3-85 EQ. 98; One pt 564 K, third law: not to be cited.
*S: VM 4/87

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

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

131. Z: 53SCH/OEH
R: 2FeCl3(cr)=2FeCl2(cr)+Cl2(g)
DV: H, 108.54 $1.6 kJ
C: IVTAN 3-85 EQ. 101, readjusted (vbp) in agreement with 86ARI/BER text calculations and returning to S(FeCl2, cr)=118.0 J/(mol.K) at 298.15 K. Transpiration; third law, 19 pts, 435–482 K; second law 112.0 $4.2 kJ/mol
S: VM 4/87 and 10/87, 10/88 VBP

132. Z: 58WIL/GRE
R: 2FeCl3(cr)=2FeCl2(cr)+Cl2(g)
DV: H, 108.75 $1.6 kJ

C: IVTAN 3-85 EQ. 102, readjusted (vbp) in agreement with 86ARI/BER text calculations and returning to S(FeCl2, cr)=118.0 J/(mol.K) at 298.15 K. Transpiration; third law, equation, 433–493 K; second law 109.1 kJ/mol
S: VM 4/87 and 10/87, 8/88 VBP

133. Z: 52LI/GRE
R: FeCl3(cr)=Fe+3(ao)+3Cl-(ao)
DV: H, −158.99 $0.84 kJ
C: IVTAN 3-85 EQ. 392
Molality range .00318 to .000766 moles/kg H2O, 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: FeCl3(cr)=FeCl3(ai)
DV: H, −146.5 $3.0 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: FeCl3(cr)=FeCl3(HCl+111.0 H2O:au)
DV: H, −138.78 $1.0 kJ
C: Smoothed curve from measurements as a function of concentration of HCl of 35KAN/FLU at 293 K and measurements of 76COR/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: FeCl3(cr)=FeCl3(HCl+55.51 H2O:au)
DV: H, −132.85 $1.0 kJ
C: Smoothed curve from measurements as a function of concentration of HCl of 35KAN/FLU at 293 K and measurements of 76COR/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: FeCl3(cr)=FeCl3(HCl+27.75 H2O:au)
DV: H, −123.77 $1.0 kJ
C: Smoothed curve from measurements as a function of concentration of HCl of 35KAN/FLU at 293 K and measurements of 76COR/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: FeCl3(cr)=FeCl3(HCl+18.50 H2O:au)
DV: H, −115.12 $1.0 kJ

C: Smoothed curve from measurements as a function of concentration of HCl of 35KAN/FLU at 293 K and measurements of 76COR/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: FeCl3(cr)=FeCl3(HCl+13.88 H2O:au)
DV: H, −106.62 $1.0 kJ
C: Smoothed curve from measurements as a function of concentration of HCl of 35KAN/FLU at 293 K and measurements of 76COR/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: FeCl3(cr)=FeCl3(HCl+11.10 H2O:au)
DV: H, −98.22 $1.0 kJ
C: Smoothed curve from measurements as a function of concentration of HCl of 35KAN/FLU at 293 K and measurements of 76COR/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: FeCl3(cr)=Fe+3(ao)+3Cl-(ao)
DV: H, −156.78 $1.2 kJ
C: Extrapolation to I=0 from measurements in m HClO4=4.769, 3.61 and 1.085 after correction for phi(L)D-H. See reactions listed separately. Authors' uncertainty of 0.28 kJ/mol increased.
S: 6/89 VBP, 3/90 VBP

142. Z: 90EFI/FUR
R: FeCl3 (cr)=FeCl3(1390(HClO4+11.64H2O))
DV: H, −121.518 $0.5 kJ
C: Mean of two experimental measurements in 3.903 mol dm-3 HClO4(m=4.769) m (FeCl3) =0.0026044 and 0.004279. dH=−121.763 and −121.273 kJ/mol respectively. PhiL 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: FeCl3 (cr)=FeCl3 (105(HClO4+15.376 H2O))
DV: H, −131.806 $0.4 kJ
C: Mean of two experimental measurements in 3.08 mol dm-3 HClO4 (m=3.610) m (FeCl3) =0.004276 and 0.002676. dH=−131.981 and −131.630 kJ/mol, respectively. PhiL D-H correction at I=3.62 is 6.66 kJ/mol.
S: 6/89 VBP

144. Z: 90EFI/FUR
R: FeCl3(cr)=FeCl3(256(HClO4+51.16 H2O))
DV: H, −144.661 $0.5 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 $.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 dCp=−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 dCp=−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, Cp =70.50 J/(mol.K).
S: 7/89 VBP

159. Z: 56SCH/WIT

R: FeCl3 (cr)+H2O (l)=FeOCl (cr)+2 HCl
(3.221 H2O)
DV: H, −24.31 $1.4 kJ
C: dsolnH FeOCl(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: FeCl3(cr)+H2O(l)=FeOCl(cr)
+2HCl(12.731H2O)
DV: H, −50.513 $0.080 kJ
C: dsolnH FeOCl(cr) in excess HCl=−61.296
$.065 kJ/mol.
S: 7/87 VBP

161. Z: 83GRE
R: 6FeOCl (cr)=2Fe2O3 (cr)+Fe2Cl6 (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 ther-
mal functions Fe2O3 (cr).
S: 5/89 and 12/89 EME, 10/89 and 1/90 VBP

162. Z: 49SCH
R: Fe2O3 (cr)+2 HCl (g)=Fe2Cl6 (g)+3 H2O (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. (dH(600 K)=−340 cal, not +340 cal.)
S: 5/89, 12/89 EME, 10/89, 1/90 VBP

163. Z: 50KAN/PET
R: 2FeCl2(cr)+Cl2(g)=Fe2Cl6(g)
DV: H, 23 $12 kJ
C: Static; 606−970 K ; 11 points; third law. Sec-
ond law 54 $16 kJ.
S: 5/89 EME, 11/89 VBP

164. Z: 58WIL/GRE
R: 2FeCl2(cr)+Cl2(g)=Fe2Cl6(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: Fe(cr)+Br2(l)=FeBr2(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). Fe(cr) dH=−395.43 $0.15
kJ/mol; Br2(l), −7.777 $0.089; FeBr2(cr)
−158.47 $0.13. Reported earlier as
88EFI/EVD.
S: 8/88 VBP, 9/91 VBP

166. Z: 89EVD/EFI
R: FeBr2(cr)+2KCl(cr)=FeCl2(cr)+2KBr(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. KBr(cr) dH=18.123 $0.039
kJ/mol, KCl(cr)16.262 $0.079, FeCl2(cr)
−152.16 $0.13. See other 89EFI/EVD and
89EVD/EFI reactions on FeBr2(cr), FeCl3(cr),
FeBr3(cr) and FeI2(cr). Reported earlier as
88EFI/EVD.
S: 8/88 VBP, 9/91 VBP

167. Z: 34HIE/WOE
R: Fe(cr)+Br2(l)=FeBr2(cr)
DV: H, −251.44 kJ
DV: H, 273.15 K, −250.91 kJ
C: Enthalpies of reaction of all components in
Br2(KBr) solutions at 273 K. dCp correction
=−21 J/mol. Enthalpies for components at 273
K are Fe(cr) −408.86, Br2(l) −7.74, and
FeBr2(cr) −165.69 kJ/mol respectively.
S: 6/89 VBP

168. Z: 34HIE/APP
R: FeCl2(cr)+FeBr2(D:HCL+27 H2O)
=FeBr2(cr)+FeCl2(D:HCl+27 H2O)
DV: H, 273.15 K, 4.69 kJ
DV: H, 4.99 kJ
C: Measurements of enthalpies of solution of
FeCl2(cr) (−68.20 kJ/mol) and FeBr2(cr)
(−72.89 kJ/mol) in 2N HCl at 273 K. dCp=12
J/mol
S: 6/89 VBP

169. Z: 89NBS
R: FeCl2(D:HCL+27H2O)+2HBr(ai)
=FeBr2(D:HCl+27 H2O)+2 HCl(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: FeBr2(cr)=FeBr2(1650 H2O)
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: FeBr2(1650 H2O)=FeBr2(ai)
DV: H, −1.44±0.2 kJ
C: Estimated.
S: 7/89 VBP

172. Z: 52LI/GRE
R: FeBr2(cr)=FeBr2(11,500 H2O)
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 re-
spectively.
S: 7/89 VBP

173. Z: 52LI/GRE
R: FeBr2(cr)=FeBr2(ai)

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

174. Z: 65PAO
R: FeBr2(cr)=FeBr2(2000 H2O)
DV: H, −84.35 $0.5 kJ
C: Earlier paper 64PAO/VAC gives concentration and temperature. dH value reported as −26.16 kcal/mol is typographical error. With Table 3 values −20.06 $0.06 kcal/mol (−83.93 kJ) is obtained which is in good agreement with value given in Errata 66PAO, −20.16 kcal.
S: 7/89 VBP

175. Z: 89PAR
R: FeBR2(2000 H2O)=FeBr2(ai)
DV: H, −1.4 $0.2 kJ
C: Estimated; based on phiL D-H=1.21 kJ and phiL m=0.2 kJ/mol.
S: 7/89 VBP

176. Z: 89PAR
R: FeBr2 (2000 H20)=FeBr2 (4000 H2O)
DV: H, −0.20±0.20 kJ
C: Estimated from comparison of divalent bromides
S: 7/89 VBP

177. Z: 67CHR/GRE
R: Fe2O3(cr)+6 HBr(g)=2 FeBr2(cr)+3 H2O(g) +Br2(g)
DV: H, −150.5 $8 kJ
C: Third law; Spectrometric study; T range 468−598 K; second law dH=−150.8 kJ/mol. Used thermal functions for FeBr2(cr) from 85CHA/DAV which gives S (FeBr2, cr)=140.7 $1.3 J at 298.15 K from a private communication (Westrum).
S: 7/89 VBP

178. Z: 90EFI/FUR
R: FeBr2(cr)=Fe+2(ao)+2 Br-(ao)
DV: H, −86.85 $0.12 kJ
C: Author's extrapolation after correction for Phi L D-H from measurements in 0.001 mol dm-3 HClO4. Mea-sured values are −86.803, −86.442, and −86.116 kJ/mol for m =0.004958, 0.004273, and 0.007585 moles/(kg H2O) respectively. PhiL D-H corrections made are 0.665, 0.613, and 0.771 kJ/mol for I=0.01587, 0.01382, and 0.002475. Measure-ments were also made in 1.0257, 0.1026 and 0.0105 mol dm-3 HClO4 solutions. See other reactions.
*** This is really an average of the three measure-ments. A plot of dH vs
*** I or I(1/2) using measurements in 0.01, 0.10, and 1.0 mol dm-3 HClO4 (corrected for phiL D-H) shows high curvature.
S: 5/89 VBP, 11/89 VBP

179. Z: 90EFI/FUR
R: FeBr2(cr)=FeBr2(0.18(HClO4+55,500 H2O))
DV: H, −86.214 $0.20 kJ
C: Average of three measurements in 0.001 mol dm-3 HClO4. See extrapolated value.

S: 5/89 VBP

180. Z: 90EFI/FUR
R: FeBr2(cr)=FeBr2(182(HClO4+51.16 H2O))
DV: H, −82.611 $0.01 kJ
C: Average of two measurements in 1.085 molal HClO4. m FEBr2=0.00567 and 0.00618 mol/(kg H2O). PhiL D-H correction would be 2.674 kJ/mol for extrapolation.
S: 5/89 VBP

181. Z: 90EFI/FUR
R: FeBr2(cr)=FeBr2(28.7(HClO4+512 H2O))
DV: H, −84.322 kJ
C: Experimental measurements in 0.1085 molal HClO4. m FeBr2=0.003777. PhiL D-H correc-tion would be 1.28 kJ/mol for extrapolation.
S: 5/89 VBP

182. Z: 90EFI/FUR
R: FeBr2(cr)=FEBr2(2.13(HClO4+5290 H2O))
DV: H, −85.960 kJ
C: Experimental measurements in 0.0105 m HClO4. m FeBr2=0.004918. PhiL D-H correc-tion would be 0.776 kJ/mol for extrapolation.
S: 5/89 VBP

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

184. Z: 89EFI/EVD
R: FeBr2(cr) I 1/2Br2(l)=FeBr3(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, 50.78H2O). dH FeBr3(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: 2FeBr3(cr)=2FeBr2(cr)+Br2(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 mm=−3,478.6/T+11.327. Corrected us-ing estimated dCp=−6 J/(mol Br2).
S: 7/89 VBP

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

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

188. S: 7/89 VBP
Z: 52LI/GRE
R: FeBr3(cr)=FeBr3(10,000 H2O)
DV: H, −122.3 kJ
C: From smoothed experimental curve. Measurements at 7 concentrations, 0.0074 to 0.00098 mol/(kg H2O). dH varies from −121.3 to −101.7 kJ/mol. See other reactions.

189. S: 7/89 VBP
Z: 52LI/GRE
R: FeBr3(cr)=FeBr3(ai)
DV: H, −146.9 $5.0 kJ
C: Authors correct for formation of FeOH+2(ao) and FeBr+2 (ao).

190. S: 7/89 VBP
Z: 90EFI/FUR
R: FeBr3(cr)=Fe+3(ao)+3Br-(ao)
DV: H, −150.4 $1.3 kJ
C: Extrapolation to I=0 from measurements in m HClO4=4.769, 3.651, and 1.085 mol/(kg H2O) 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: FeBr3(cr)=FeBr3(768(HClO4+11.64 H2O))
DV: H, −119.416 $1.2 kJ
C: Mean of two experimental measurements in 3.903 mol dm-3 HClO4 (m=4.769). m FeBr3 =0.00576 and 0.00629 mol/(kg H2O). dH= −118.813 and −120.018 kJ/mol respectively. PhiL D-H correction at I=4.787 is 6.948 kJ.

192. S: 6/89 VBP
Z: 90EFI/FUR
R: FeBr3(cr)=FeBr3(530(HClO4+15.376 H2O))
DV: H, −128.238 $0.2 kJ
C: Mean of two experimental measurements in 3.11 mol dm-3 HClO4 (m=3.651). m FeBr3 =0.00659 and 0.00719 mol/(kg H2O). dH= −128.230 and −128.246 kJ/mol respectively. PhiL D-H correction at I=3.672 is 6.70 kJ.

193. S: 6/89 VBP
Z: 90EFI/FUR
R: FeBr3(cr)=FeBr3(183(HClO4+51.16 H2O))
DV: H, −139.324 $0.08 kJ
C: Mean of three experimental measurements in 1.0257 mol dm-3 HClO4 (m=1.085). m FeBr3 is 0.00504, 0.00431, and 0.00841 mol/(kg H2O). dH=−139.301, −139.360, and −139.312 kJ, respectively. PhiL D-H at I=1.12 is 5.376 kJ.

194. S: 6/89 VBP
Z: 90EFI/EVD
R: Fe(cr)+I2(cr)=FeI2(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

R: FeBr3(cr)=FeBr3(ai) [illegible]
DV: H, [illegible] $0.19
C: Calorimetric measurements on [illegible] components in solution (KBr [illegible] HBr, 50.78 H2O) dH KI(cr) [illegible] kJ/mol. See other 89EFI/EVD reactions. Reported earlier as 88EFI/EVD

196. S: 8/88 VBP, 9/91 VBP
Z: 66ZAI/GRE
R: FeI2(cr)=Fe(cr)+I2(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/ORA
R: FeI2(cr)=Fe(cr)+I2(g)
DV: H, 193.9 $20 kJ
C: Decomposition FeI2(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: Fe(cr)+I2(cr)=FeI2(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: FeCl2(cr)+FeI2(D: HCl+27 H2O)= FeI2(cr)+FeCl2(D: HCl+27 H2O)
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: FeCl2 (D: HCl+27 H2O)+2HI(ai)= FeI2(D: HCl+27H2O)+2HCl(ai)
DV: H, −4.68 kJ
C: Correction to standard state based on L2's for HCl and HI from 89PAR.
W: −1

201. S: 7/89 VBP
Z: 65PAO/SAB
R: FeI2(cr)=FeI2(4000H2O)
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: Fe(cr)+KI3(au)=FeI2(au)+KI(au)
DV: H, −217.0 $10 kJ

203. S: 7/89 VBP
Z: 97MOS

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

204.   Z: 42MOO/KEL
R: =FeSO4(cr)
DV: S, 25.70 $0.30 cal
F: TN
C: Low temp Cp measurements (53–295 K). S(298.15 K)−S0 (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: =FeSO4(cr)
DV: S, 28.91 $0.30 cal
C: Reanalysis of work of 42MOO/KEL; Magnetic entropy contribution of 3.2 cal/(mol.K) (R ln 5) added to S(298.15)=25.71 cal/(mol.K) helps reconcile second and third law dH's of decomposition.
S: 5/86 VBP

206.   Z: 53PAT/THO
R: Fe(cr)+Hg2SO4(cr)=FeSO4(ai)+2Hg(l)
DV: G, −197.740 $0.060 kJ
C: E0=1.0247 $0.0003 V. See reaction with Hg2Cl2 for comments. Mean of 4 meas. Concentration FeSO4 solution, m−0.022 to 0.0718. Activity coef. used are given by above authors from meas. by 41DEM/FED. Comparison with activity coefficients of CuSO4 by 80MIL/MAR in dilute region indicates values are reasonable.
S: 5/86 VBP

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

208.   Z: 49LYO/GIA
R: =FeSO4:7H2O(cr)
DV: S, 97.8 $0.3 C
F: TN
C: From low temp. Cp measurements (13–307 K and 0.9 and 20 K). Assumed S0(1 K)=0.2 cal/(mol.K); S0(1–10 K)=1.4 $0.07; S(10–20 K)=1.7 $0.08 and S(20–298.15 K)=94.5 $0.15. S associated with magnetic system from integration (Cp total−Cp lattice)=2.8 cal/(mol.K)
S: VBP 5/86

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

210.   Z: 87REA/BEC
R: FeSO4:7H2O(cr)=FeSO4(ai)+7H2O(l)

DV: G, +12.58 $0.30 kJ
C: Reanalysis of isopiestic meas. of 74OYK/BAL activity coefficients; uses gamma at 0.1 m=0.161 and phi=0.556. Uses msat=1.94 $0.02, gamma=0.048, aw=0.952 $0.003.
S: 7/87 VBP

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

212.   Z: 63ADA/KEL
R: Fe(cr)+H2SO4(7.068 H2O)+H2O(l)= FeSO4: H2O(cr)+H2(g)
DV: H, −79.72 $0.40 kJ
F: TN
C: Measurements on FeSO4:1.008 H2O(cr) at 303.15K combined with measurements by 59KOE/COU on Fe(cr); Composite dH= −81.714 $0.29 kJ/mol. corrected to 298.15 K (dCp=−52.7 J/(mol.K)) and to stoichiometric FeSO4:H2O(cr), assuming presence of 0.0013 FeSO4:7H2O(cr) (correction=+1.68 kJ/mol).
S: 3/86 VBP

213.   Z: 64KOH/ZAS
R: FeSO4:4H2O(cr)=FeSO4:H2O(cr)+3H2O(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 H2O) is low. dG at p=1 bar.
S: 3/86 VBP

214.   Z: 64KOH/ZAS
R: FeSO4:7H2O(cr)=FeSO4:4H2O(cr)+3H2O(g)
DV: H, 156.2 $2.0 kJ
F: TN
DV: G, 29.02 $0.5 kJ
F: TN
C: Vapor pressure meas: equations only log P (in mm)=−2719T−1+10.30 (40–54 °C) for dehydration to tetrahydrate. Calculated dS=34.0 cal/(K.mol H2O). dG at p=1 bar.
S: 3/86 VBP

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

216.   Z: 14BIL
R: FeSO4:7H2O(cr)=FeSO4:4H2O(cr)+3H2O(g)
DV: H, 166.4 $6.0 kJ

F: TN
C: Data of 01COH/VIS.
S: 3/86 VBP

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

218. Z: 14FOR
R: FeSO4:7H2O(cr)=FeSO4:H2O(cr)+6H2O(l)
DV: H, 52.18 $1.5 kJ
F: TN
C: dsolnH (286 K) of FeSO4:H2O(cr)=−31.54 kJ/mol combined with dsolnH heptahydrate; dCp for composite=+209 J/(mol.K)
S: 3/86 VBP

219. Z: 14FOR
R: FeSO4:7H2O(cr)=FeSO4:4H2O(cr)+3 H2O(l)
DV: H, +26.18 $1.5 kJ
C: dsolnH (286 K) of FeSO4:4H2O(cr)=−6.69 kJ/mol; dCp for composite=113 J/(mol.K)
S: 3/86 VBP

220. Z: 14FOR
R: FeSO4:7H2O(cr)=FeSO4(cr)+7H2O(l)
DV: H, 83.28 $2.0 kJ
F: TN
C: dsolnH (286 K) of FeSO4(cr)=−62.34 kJ/mol; dCp for composite=392 J/(mol.K).
S: 3/86 VBP 221.

221. Z: 85VAS/DMI2
R: Fe(cr)+H2O2(3.5H2O)+5H2O(l) +H2SO4(0.3H2O)=FeSO4:7H2O(cr)
DV: H, −569.96 $0.28 kJ
C: Measurements of components, H2SO4, FeSO4:7H2O(cr) and H2O2 in 2,3, and 4N HClO4 solutions combined with Fe(cr) measurements from 83DMI and 78VAS/VAS. Authors' calculated value for dfH FeSO4:7H2O(cr) ~−3014.6.
S: Joint, 6/86 VBP and 4/87 O.D and I.Kh.

222. Z: 85VAS/DMI
R: FeSO4:7H2O(cr)+H+(ao)=Fe+2(ao)+HSO4 −(ao)+7H2O(l)
DV: H, +33.58 $0.50 kJ
W: 99
C: Extrapolation of enthalpies of solution of FeSO4:7H2O(cr) in 2N, 3N and 4N HClO4 as a function of m(1/2) to m(Fe+2(ao))=0 and to ionic strength solution=0 using corrections from 78VAS/YAS. See 83DMI.
S: 6/86 VBP

223. Z: 83DMI
R: FeSO4:7H2O(cr)+H+(ao)=Fe+2(ao) +HSO4-(ao)+7H2O(l)
DV: H, +35.50 $0.10 kJ
C: Recalc. to correct for SO4=(ao) in solution. Ionic strength corrections from Khod.
S: 3/87 VBP, I.Kh., O.D.

224. Z: 85VAS/DMI
R: FeSO4:7H2O(cr)=FeSO4(ai)+7H2O(l)
DV: H, +11.99 $0.20 kJ

W: 99
C: 16 measurements, extrapolation; equation only. dsolnH(m)=11.99 ($0.09)+36.33 ($0.48) m(1/ 2). Recalc. gives much higher value. See 83DMI.
S: 6/86 VBP

225. Z: 78VAS/VAS
R: (NH4)2 SO4(cr)+Fe(cr)+H2O2 (4.95H2O) +H2SO4(0.43H2O)+4H2O(l)=(NH4)2 Fe(SO4)2:6H2O(cr)
DV: H, −579.78 $0.87 kJ
W: 99
C: Summation from meas of dsolnH of all components in 4.0, 3.0, 2.0, 1.0 mol dm-3 HClO4 solutions. Assume all solutions formed are equivalent so that no corrections for SO4=are necessary. Meas. in 1.0 mol dm-3 HClO4 not used. Mean of 6 meas. See 83DMI.
S: VBP Aug. 85, 3/87 VBP

226. Z: 83DMI
R: (NH4)2 Fe(SO4)2:6H2O(cr)+2H+(ao)= 2NH4+(ao)+Fe+2(ao)+2HSO4−(ao) +6H2O(l)
DV: H, 69.40 $0.20 kJ
C: Extrap. from dsolnH meas. in 2.0, 3.0, 4.0 mol dm-3 HClO4 aqueous solutions. m salt=0.01 to 0.04. Correct for SO4=in HClO4 soln., and to ionic strength=0 using Khodakhovskii equation with 1986 constants. Supersedes 78VAS/ VAS.
S: VBP Aug. 85, 3/87 VBP

227. Z: 83DMI
R: FeSO4:7H2O(cr)=FeSO4(ai)+7H2O(l)
DV: H, 12.90 $0.10 kJ
C: Experimental points refit to Khodakhovskii equation with extrapolation to m=0. dH(I) −dH0(DH)/kJ/mol=(12.895 $0.096)+(35.572 $2.372) I
S: VBP, O.D., I.Kh 5/87

228. Z: 83DMI
R: Fe(cr)+H2O2(4.95H2O)+(NH4)2SO4(cr) +H2SO4(0.3H2O)+4H2O(l) =(NH4)2Fe(SO4)2:6H2O(cr)
DV: H, −579.68 $0.44 kJ
C: Supersedes 78VAS/VAS. Meas. in 1N HClO4 not used. Concentration H2SO4 is 0.3H2O, rather than 0.43H2O.
S: O.D., I.Kh., VBP 4/87

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

230. Z: 68LAR/CER
R: FeSO4:4H2O(cr)=FeSO4(ai)+4H2O(l)
DV: H, −13.81 $0.42 kJ

C: From meas of dsolnH of hydrated salts with compositions FeSO4:6.92 H2O, FeSO4:6.78 H2O, FeSO4:5.32 H2O, FeSO4:3.98 H2O, and FeSO4:2.46 H2O. Measured concentrations 0.005 to 0.05m. Authors correct to std state using phiL from 56LAN/MIE for NiSO4. More details in 68LAR

S: 8/85 VBP

231. Z: 68LAR/CER
R: FeSO4:H2O(cr)=FeSO4(ai)+H2O(l)
DV: H, −44.35 $0.84 kJ
C: From meas of dsolnH of hydrated salts with compositions FeSO4:6.92 H2O, FeSO4:6.78 H2O, FeSO4:5.32 H2O, FeSO4:3.98 H2O, and FeSO4:2.46 H2O. Measured concentrations 0.005 to 0.05m. Authors correct to std state using phiL from 56LAN/MIE for NiSO4. More details in 68LAR.

S: VBP Aug. 85

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

S: 10/90 VBP

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

S: 10/90 VBP

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

S: 10/90 VBP

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

S: 10/90 VBP

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

S: 10/90 VBP

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

S: 10/90 VBP

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

S: 10/90 VBP

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

S: 10/90 VBP

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

S: 10/90 VBP

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

S: VBP Aug. 85

242. Z: 64KOS/KAL
R: =FeCO3(cr)
DV: S, 96.1 $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. S0(0–70 K)=16.8 J/(mol.K)

S: VBP Aug. 85

243. Z: 35KRU
R: FeCO3(cr)=FeO(cr)+CO2(g)
DV: H, 127 $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: FeCO3(cr)+2H+(ao)=Fe+2(ao) +CO2(g)+H2O
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

Al.c. Reaction Catalog Provided by IVTAN

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

1. Z: 52SCH/KRE
    R: 2HCl(g)+Fe(cr)=FeCl2(g)+H2(g)

DV: H, 41.3 $6.0 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

S: VM 4/87, 10/88 VBP

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

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

10. Z: 75BUR/MIR
    R: FeCl2(cr)=FeCl2(g)
    DV: H, 198.68 $6.00 kJ
    C: IVTAN 3-85 EQ. 242
         Corrected for S0(FeCl2, g)=293.803 (1 atm) and
         FeCl2(cr), S0=118.0 and H-H(0)=16.27
    C: Torsion, third law, 1000–1300 K equation only; second law 185 kJ
    S: VM 4/87, 10/88 VBP

11. Z: 76RAT/NOV
    R: FeCl2(cr)=FeCl2(g)
    DV: H, 199.75 $4.0
    C: IVTAN 3-85 EQ. 243
         Corrected for S0(FeCl2, g)=293.803 (1 atm) and
         FeCl2(cr), S0=118.0 and H-H(0)=16.27
    C: Mass spectroscopy; third law, 668–766 K equation only; second law 204 kJ
    S: VM 4/87, 10/88 VBP

12. Z: 77LAN/ADA
    R: FeCl2(cr)−FeCl2(g)
    DV: H, 193.23 $4.00 kJ
    C: IVTAN 3-85 EQ. 244
         Corrected for S0(FeCl2, g)=293.803 (1 atm) and
         FeCl2(cr), S0=118.0 and H-H(0)=16.27
    C: Torsion, third law, 711–887 K equation only; second law 207 kJ
    S: VM 4/87, 10/88 VBP

13. Z: 77LAN/ADA
    R: FeCl2(cr)=FeCl2(g)
    DV: H, 196.41 $4.0
    C: IVTAN 3-85 EQ. 245
         Corrected for S0(FeCl2, g)=293.803 (1 atm) and
         FeCl2(cr), S0=118.0 and H-H(0)=16.27
    C: Effusion; third law, 624–952 K equation only; second law 215 kJ
    S: VM 4/87, 10/88 VBP

14. Z: 78NOV
    R: FeCl2(cr)=FeCl2(g)
    DV: H, 202.419 $4.14 kJ
    W: 99

C: IVTAN 3-85 EQ. 246
     Corrected for S0(FeCl2, g)=293.803 (1 atm) and
     FeCl2(cr), S0=118.0 and H-H(0)=16.27
S: VM 4/87, 10/88 VBP

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

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

17. Z: 89CTT
    R: =Fe2Cl6(g)
    DV: S, 528.066$
    C: at 1 bar, H-H(0)=37.30 kJ/mol
    S: 10/88 VBP, 10/90 VBP

18. Z: 88CTT
    R: FeCl3(g)
    DV: S, 344.827$
    C: at 1 bar, H-H(0)=17.815 kJ/mol.K
    S: 10/88 VBP

19. Z: 25MAI
    R: 2FeCl3(cr)=Fe2Cl6(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: 2FeCl3(cr)=Fe2Cl6(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: 2FeCl3(cr)=Fe2Cl6(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 FeCl3(cr)=2 FeCl3(g). Measurements were recalculated for Fe2Cl6(g) as a reaction product.
    S: VM 10/87, 10/88 VBP, 12/89 EME and VBP

22. Z: 38SAN2
    R: 2FeCl3(cr)=Fe2Cl6(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: 2FeCl3(cr)=Fe2Cl6(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: 2FeCl3(cr)=Fe2Cl6(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: 2FeCl3(cr)=Fe2Cl6(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: 2FeCl3(cr)=Fe2Cl6(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: 2FeCl3(cr)=Fe2Cl6(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: 2FeCl3(cr)=Fe2Cl6(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: 2FeCl3(cr)=Fe2Cl6(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: 2FeCl3(cr)=Fe2Cl6(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: 2FeCl3(l)=Fe2Cl6(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: 2FeCl3(cr)=Fe2Cl6(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: 2FeCl3(cr)=Fe2Cl6(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: 2FeCl3(cr)=Fe2Cl6(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: 2FeCl3(cr)=Fe2Cl6(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