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PARTIAL COMPILATION AND REVISION OF BASIC DATA IN THE WATEQ PROGRAMS

By D. Kirk Nordstrom, Susan D. Valentine, James W. Ball, L. Neil Plummer and Blair F. Jones

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PARTIAL COMPILATION AND REVISION OF BASIC DATA IN THE WATEQ PROGRAMS

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ABSTRACT

Several portions of the basic data in the WATEQ series of computer programs (WATEQ, WATEQF, WATEQ2, WATEQ3, and PHREEQE) are compiled. The density and dielectric constant of water and their temperature dependence are evaluated for the purpose of updating the Debye-Hückel solvent parameters in the activity coefficient equations. The standard state thermodynamic properties of the Fe^{2+} and Fe^{3+} aqueous ions are refined. The main portion of this report is a comprehensive listing of aluminum hydrolysis constants, aluminum fluoride, aluminum sulfate, calcium chloride, magnesium chloride, potassium sulfate and sodium sulfate stability constants, solubility product constants for gibbsite and amorphous aluminum hydroxide, and the standard electrode potentials for $Fe^{\circ}(s)/Fe^{2+}(aq)$ and $Fe^{2+}(aq)/Fe^{3+}(aq)$.

INTRODUCTION

Several computer programs that calculate multicomponent chemical equilibrium for homogeneous or heterogeneous aqueous systems are presently available (Nordstrom, et al., 1979). One major difficulty in using these programs is the lack of critically evaluated thermodynamic data, specifically equilibrium constants and reaction enthalpies. Stockmayer (1978) has noted that the effort to evaluate fundamental physical and chemical data lags behind the efforts in other areas of research and technological development. Poor quality data can have dire consequences when applied to such important societal problems as energy supply, environmental quality and industrial productivity (Lide, 1981). The lack of reliable aqueous thermodynamic data makes it difficult to interpret water-quality processes and problems which have become increasingly important with the continued development of energy resources and urban and industrial construction.

Before there can be a meaningful evaluation of data, all the relevant literature must be compiled. The main purpose of this report is to provide an update of the basic data compiled from literature references for selected aqueous reactions relevant to water-mineral equilibria. These data are organized in a form that is convenient for anyone using chemical equilibrium computer programs.

This compilation was initially begun to provide a more reliable data base for the WATEQ series of computer programs. The first program, WATEQ, was developed by Truesdell and Jones (1974) and included a complete list of equilibrium constants and reaction enthalpies with reference sources for the program data base. WATEQF (Plummer, et al., 1976), the FORTRAN version of WATEQ, includes equilibrium constants for manganese species as well as some revisions of the earlier compilation. WATEQ2 (Ball, et al., 1979; 1980) was developed from WATEQ and WATEQF but kept the original programing language (PL/1). Several trace elements (Pb, Cu, Zn, Cd, Ni, Ag, As, I) were added to WATEQ2 and some further revisions of the two previous data bases were given. PHREEQE (Parkhurst, et al., 1980) computes chemical equilibria, pH, and pE (or Eh) for heterogeneous systems including reaction progress calculations and mass transfer between solution phase and solid phases (precipitation-dissolution processes). The PHREEQE data base is similar to that of WATEQF, but revised to be compatible with WATEQ2. Finally, WATEQ3, (Ball, et al., 1981) has incorporated uranium species along with a few more changes in the coding and the data base. The increasing number of changes in these programs makes it difficult to keep track of the data base and is further motivation for organizing the data into a form that can be easily documented, updated and reviewed by WATEQ users. This report is not intended as a primary reference of thermodynamic data. It is only intended as an aid to WATEQ users so that they can make more informed decisions regarding water-quality interpretations when employing WATEQ computations.

EVALUATION OF THE DEBYE-HÜCKEL SOLVENT PARAMETERS

The original WATEQ program utilized activity coefficients for the major ions in natural waters which were calculated from the extended Debye-Hückel equation with a linear term:

$$\log \gamma_i = - \frac{Az_i^2\sqrt{I}}{1 + B\mathring{a}\sqrt{I}} + bI$$

in which γ_i is the activity coefficient of the i^{th} ion, z, is the ion charge, I is the ionic strength, A and B are the Debye-Hückel solvent parameters, $\mathring{a}$ is an empirical ion-size parameter, and b is a fitting parameter. This form of the Debye-Hückel equation was first proposed by Hückel (1925) and is nearly identical to the original Bronsted (1922) equation in which the linear term (bI) accounts for specific short-range interactions between ions of opposite charge. The A and B parameters are functions of the solvent density, the dielectric constant and the temperature:

$$A = \left(\frac{2\pi N\rho_\circ}{1000}\right)^{\frac{1}{2}} \left(\frac{1}{\varepsilon kT}\right)^{3/2} e^3$$

$$B = \left(\frac{8\pi Ne^2\rho_\circ}{1000\varepsilon kT}\right)^{\frac{1}{2}}$$

where e is the electronic charge, ε is the dielectric constant of the solvent, k is the Boltzmann constant, T is the absolute temperature, $\rho_\circ$ is the density of pure water, and N is the Avogadro constant. The following physical constants, evaluated and revised by Cohen and Taylor (1973), were used in the calculations:

$N = 6.022045 \times 10^{23}$ mol^{-1}
$e = 4.803242 \times 10^{-10}$ esu
$k = 1.380662 \times 10^{-16}$ erg K^{-1}
$\ell n\ 10 = 2.302585$.

These constants were substituted into the definition of A and B to obtain:

$$\frac{A}{\ell n 10} = \frac{1.824814 \text{x} 10^6 \text{x } \rho_\circ^{\frac{1}{2}}}{(\varepsilon T)^{3/2}} \text{ mole}^{-\frac{1}{2}} (\text{kg}_{H_2O})^{\frac{1}{2}} \text{ and}$$

$$B = \frac{50.29012 \text{x} 10^8 \text{x } \rho_\circ^{\frac{1}{2}}}{(\varepsilon T)^{\frac{1}{2}}} \text{ cm}^{-1} \text{ mole}^{-1} (\text{kg}_{H_2O})$$

These formulae are more precise than those used in Truesdell and Jones (1974) although the difference is only in the fifth significant figure.

The density has a much smaller effect on A and B than the dielectric constant and an extensive compilation and evaluation is not necessary. The investigation of Gildseth, et al. (1972) provides an accuracy of 3 ppm and a mean absolute deviation of 0.7×10^{-6} g/mL over the temperature range 0-80°C for the density of water. The function which best fits their data and additional measurements of comparably high precision is:

$$\rho_o = 1 - \frac{(t-3.9863)^2(t + 288.9414)}{508929.2\ (t + 68.12963)} + 0.011445 \exp(-374.3/t)$$

where t is degrees C. Any inaccuracies in this representation will be far overshadowed by the uncertainties in the dielectric constant of water.

The dielectric constant is fundamental to any electrolyte theory of aqueous solutions; however, it is not known with the accuracy required for many types of applications, including Debye-Hückel calculations. Truesdell and Jones (1974) used the data of Malmberg and Maryott (1956) in WATEQ. Since then, there have been several additional measurements and three major evaluations of the data. The earliest evaluation is that of Helgeson and Kirkham (1974) who fit a single equation to measurements for the pressure and temperature range of 1-5000 bars and 0-600°C. Bradley and Pitzer (1979) developed a single equation for the dielectric constant up to 350°C and 1000 bars. The most comprehensive evaluation in which the measurements were weighted according to precision and according to temperature range during fitting is that of Uematsu and Franck (1980). In Figure 1 the deviations of each of these three fitted equations are compared to the data of Malmberg and Maryott (1956). It is very clear from this comparison that these three evaluations agree very well with each other, but differ markedly from the data of Malmberg and Maryott (1956) for 0-100°C. The Uematsu and Franck (1980) evaluation has been chosed for the temperature dependence of the dielectric constant of water. Since the WATEQ series data base is only considered to be reliable for the temperature range 0-100°C, we have reduced the lengthy equation of Uematsu and Franck (1980) to:

$$\varepsilon = 2727.586 + 0.6224107T - 466.9151 \ln T - 52000.87/T.$$

This equation fits to within 0.01 of the dielectric constant (about 0.013%) given by Uematsu and Franck's equation at any temperature in the range of 0-100°C. In Table 1 the Debye-Hückel A parameter is recalculated at 10° intervals from 0-100°C and compared with the original WATEQ values, the values of Helgeson and Kirkham (1974) and those of Bradley and Pitzer (1979). The differences between our A values and those from the recent literature are negligible. The change in the temperature dependence of the A parameter reflects the change in the dielectric constant data. These changes will improve the temperature dependence of the activity coefficients.

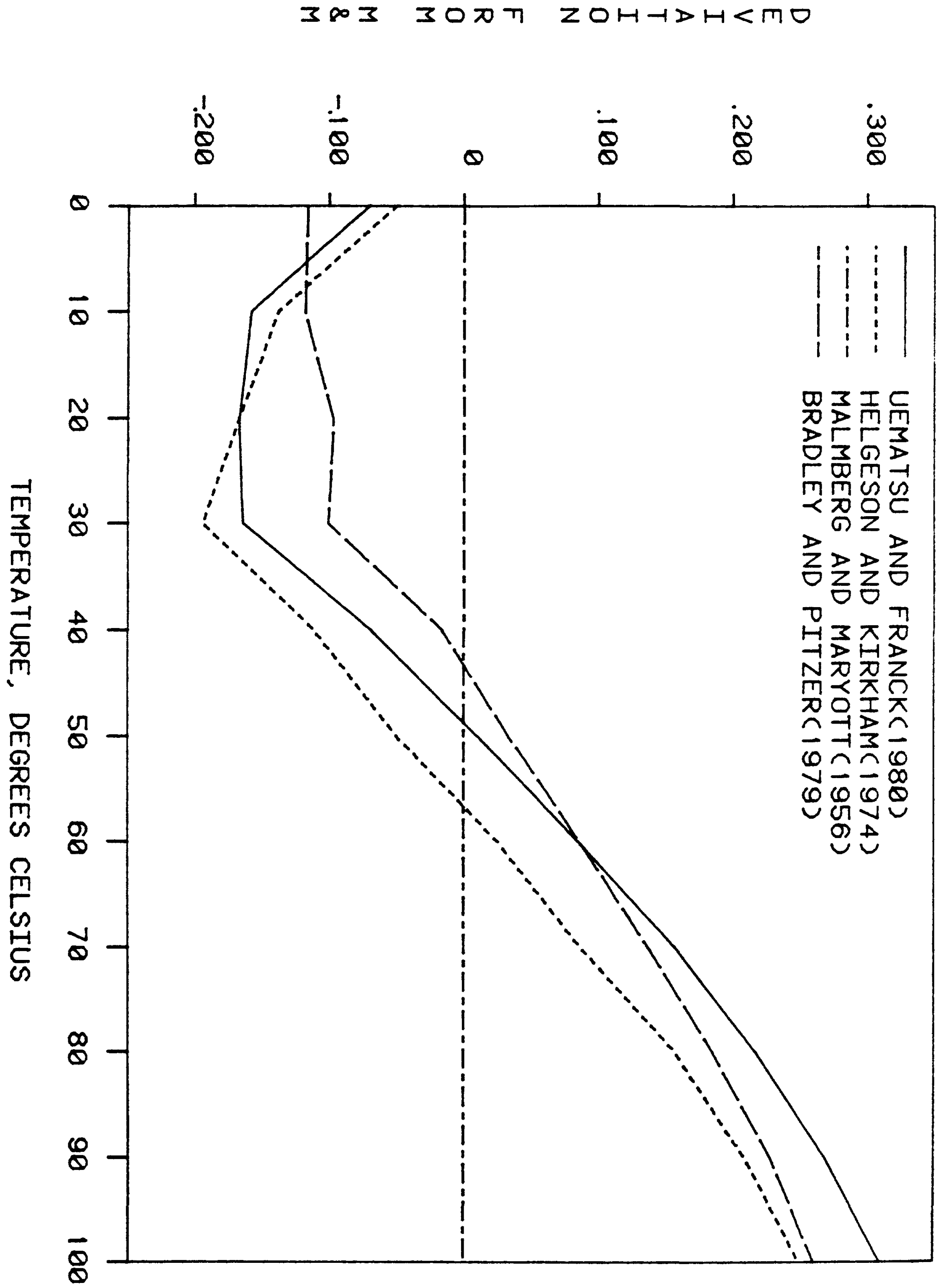

FIGURE 1.--Deviation of three evaluations for the temperature dependence of the dielectric constant relative to Malmberg and Maryott's data.

TABLE 1. - Debye-Hückel "A" parameters as a function of temperature

t, °C	WATEQ	Helgeson & Kirkham, 1974	Bradley & Pitzer, 1974	This report
0	0.4917	0.4913	0.4912	0.4912
10	0.4987	0.4976	0.4977	0.4976
20	0.5062	0.5050	0.5055	0.5052
30	0.5141	0.5135	0.5146	0.5139
40	0.5225	0.5231	0.5238	0.5235
50	0.5314	0.5336	0.5342	0.5342
60	0.5408	0.5450	0.5459	0.5459
70	0.5507	0.5574	0.5576	0.5584
80	0.5613	0.5706	0.5707	0.5718
90	0.5725	0.5848	0.5850	0.5859
100	0.5845	0.5998	0.6006	0.6007

COMPILATION OF DATA

Sources of Data

Primary references containing thermodynamic measurements were compiled from the list of references in Table 2. In addition to these references, several journals including "Geochimica et Cosmochimica Acta," "Marine Chemistry," "Journal of Solution Chemistry," and "Journal of Chemical Thermodynamics" were searched for references cited in articles already known to the authors. A computer search in "Chemical Abstracts" for reactions involving aluminum hydrolysis was carried out for the years 1967-1980. The result (Table 6) is a comprehensive listing of equilibrium constants and reaction enthalpies. Data were checked against the original primary reference if possible or against the abstract in "Chemical Abstracts" to see that the citation and the values were accurately and fully recorded. To narrow the search, only values reported for 25°C (with a few exceptions) were selected. No analytical equations of equilibrium constants as a function of temperature were used in this report.

TABLE 2. - List of compilations searched

Author(s)	Bibliographic information
Baes, C. F., Jr. and Mesmer, R. E.	1976, The Hydrolysis of Cations, John Wiley and Sons, New York, 489 p.
Bond, A. M., and Hefter, G. T.	1980, Critical Survey of Stability Constants and Related Thermodynamic Data of Fluoride Complexes in Aqueous Solution, IUPAC Chem. Data Ser. No. 27, Permagon Press, Oxford, 71 p.
[periodical]	Bulletin of Chemical Thermodynamics, Thermochemistry, Inc., Stillwater, Oklahoma.
Christensen, J. J., Eatough, D. J., and Izatt, R. M.	1975, Handbook of Metal Ligand Heats and Related Thermodynamic Quantities, Marcel Dekker, New York, 495 p.
Charlot, G., Collumeau, A., and Marchon, M. J. C.	1971, Selected Constants: Oxidation-Reduction Potentials of Inorganic Substances in Aqueous Solution, Butterworths, London, 73 p.
Naumov, G. B., Ryzhenko, B. N. and Khodakovskii, I. L.	1971, Handbook of Thermodynamic Data, Atomizdat, Moscow, 240 p. (Eng. trans. by G. Soleimani, ed., I. Barnes and V. Speltz, N.T.I.S. PB-226-722).
Perrin, D. D.	1969, Dissociation constants of inorganic acids and bases in aqueous solution, Pure Appl. Chem., 20, 133-326.
Robie, R. A., Hemingway, B. S., and Fisher, J. R.	1977, Thermodynamic Properties of Minerals and Related Substances at 298.15K and One Atmosphere Pressure and a High Temperatures, U.S. Geol. Survey Bull. 1259, 456 p.
Sadiq, M., and Lindsay, W. L.	1979, Selection of Standard Free Energies of Formation for Use in Soil Chemistry, Colo. State Univ. Tech. Bull. 134, 1069 p.

TABLE 2. - List of compilations searched--Continued

Authors	Bibliographic information
Sillen, L. G., and Martell, A. E.	1964, Stability Constants of Metal-Ion Complexes, Spec. Publ. No. 17, The Chemical Society, London (Metcalfe and Cooper) 754 p.
Sillen, L. G., and Martell, A. E.	1971, Stability Constants of Metal-Ion Complexes, Spec. Publ. No. 25, The Chemical Society, London (Alen and Mowbray), 865 p.
Smith, R. M., and Martell, A. E.	1976, Critical Stability Constants. Vol. 4: Inorganic Complexes, Plenum Press, New York, 257 p.
Yatsimirskii, K. B. and Vasil'ev, V. P.	1960, Instability Constants of Complex Compounds, Van Nostrand, Princeton (Engl. transl.), 214 p.

The Data Base Listing

In Table 6 we have compiled the reported equilibrium constant and enthalpy measurements for (1) aluminum hydrolysis, (2) aqueous ion associations for aluminum fluorides, aluminum sulfates, calcium chloride, magnesium chloride, potassium sulfate and sodium sulfate, (3) the solubility product constants for gibbsite and amorphous aluminum hydroxide, (4) the oxidation-reduction potentials for the Fe°/Fe^{2+} and Fe^{2+}/Fe^{3+} couples, (5) the standard state thermodynamic values of the following aqueous ions: Al^{3+}, Ca^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, K^{+}, and Na^{+}, and (6) the standard state thermodynamic properties of solid gibbsite. These substances are listed in alphabetical order by element, and for any one reaction the listing of measurements is in chronological order. The values which were given in the WATEQ, WATEQF, and WATEQ2 publications are also provided for comparison. The standard state for aqueous species is the hypothetical ideal solution of unit activity at unit molality, 298.15 K and 1 bar. The standard state for gibbsite is the pure crystalline solid of composition $Al(OH)_3$ at 298.15 K and 1 bar. The calorie, rather than the joule, was used as the unit of energy because most of the published data are reported in calories, and the integrity of the original data is preserved by avoiding any additional conversions. The most obvious reason for using the calorie is that the WATEQ data base has always been in calories and keeping the same energy unit would be more convenient for WATEQ users. Anyone else who wants to use this data base for other purposes can easily make the conversion to joules. Furthermore, Adamson (1978) presents valid criticisms for not using SI units.

All equilibrium constants involving hydrolysis have been written in terms of H^+ and H_2O rather than OH^-. This uniformity required conversion of some of the reported values. The notation for equilibrium constants follows the symbols used by Sillen and Martell (1964): $^*K_1$ is the first acid dissociation constant, $^*K_2$ is the second dissociation constant, etc. K_1 represents the addition of hydroxide ion to a metal cation. A subscript "s" refers to the solubility product for a solid phase. For example $^*K_{S4}$ for gibbsite refers to the reaction:

$$Al(OH)_3(solid) + H_2O = Al(OH)_4^- + H^+$$

and the product K_1K_2 refers to:

$$Al^3 + 2OH^- = Al(OH)_2^- \ .$$

There has been considerable discussion in the literature concerning the existence of polynuclear species (e.g. Aveston, 1965; Baes and Mesmer, 1976). We feel that these species occur under non-equilibrium conditions that do not merit evaluation of an equilibrium constant value. However we have included a compilation of the equilibrium constants for the dimer because of the consistency of the values and the direct spectroscopic evidence for its existence (Akitt, *et al.*, 1969). Unfortunately, the dimer was not fitted with the other recommended values for the aluminum hydrolysis constants and the gibbsite solubility product constants (May, *et al.*, 1979). For this reason we do not recommend that the dimer be used in *WATEQ* computations until such time that its importance can be evaluated. Preliminary testing indicates that it has a negligible effect on the other equilibrium constants (Howard May, oral commun.).

Occasionally a reported value is clearly of higher quality than the others, based on the experimental approach and the reported precision. These values have been identified in the REMARKS column of Table 6 by the word RECOMMENDED. Several reactions have not been "recommended" because they can not be adequately evaluated at this time.

Uncertainties reported by the original authors are given in parentheses following the reported value. These numbers usually represent one standard deviation. The original articles should be consulted for further information regarding errors.

Please note that equilibrium constants which can be calculated from standard state free energies are not included. Free energies of substances and reactions are usually not measured directly. Free energies are commonly derived from measurements of enthalpies, heat capacities and equilibrium constants. An exception is the measurement of the Fe°/Fe^{2+} electrode potential which is directly proportional to the free energy of the aqueous ferrous ion if the experiment is carried out under carefully controlled conditions. If an attempt is made to rebuild equilibrium constants from tabulated free energies through the equation, $\Delta G^\circ = - RT\ln K$, then large uncertainties can result unless exactly the same path is used as that from which the free energies were originally calculated. Because free energies are usually taken from different sources, a calculated equilibrium constant can be seriously in error and inconsistent with other data. The solubility product constant for siderite provides a typical example of this problem. Although it is listed in many standard compilations, there has been no direct measurement of the free energy of siderite. If we use the free energy data listed in N.B.S. Technical Note Series 270-3 and 270-4 for $FeCO_3$ (c), Fe^{2+} (aq) and CO_3^{2-} (aq), then the log K = -10.94. The source for $\Delta G_f^\circ(FeCO_3)$ is a solubility product measurement of siderite which is log K = -10.68 (Kelly and Anderson, 1935), noticeably different from the value back-calculated from free energies. The reason for this discrepancy is relatively simple. Different values for ΔG_f° (Fe^{2+}) and $\Delta G_f^\circ(CO_3^{2-})$ were used by Kelly and Anderson (1935) to calculate ΔG_f° $(FeCO_3)$ than are listed in N.B.S. Tech. Notes 270-3 and 270-4. The biggest change has been in the $\Delta G_f^\circ(Fe^{2+})$. Although this example is a fairly typical one, there are some equilibrium constants which are inconsistent by an order of magnitude or more because of the cumulative errors in adding free energies from different sources. For this reason, we have only listed equilibrium constant and reaction enthalpy measurements. No equilibrium constant data are based on free energy calculations. Such calculations can be used to check consistency when enough data are available, but for listing equilibrium constants only primary data are used.

Refinement of the Standard State Thermodynamic Properties of Fe^{2+} and Fe^{3+} Aqueous Ions

Free energies of formation from the elements for aqueous Fe^{2+} and Fe^{3+} ions are reported anywhere in the range of -18.85 to -22.1 kcal/mole and -1.1 to -4.27 kcal/mole, respectively. Enthalpies and entropies are discrepant by similar amounts. Recent measurements (1968-1980) of heats of solution, heats of oxidation and an electrode potential measurement can be used to narrow the range of uncertainty to a more acceptable set of values.

Thermodynamic Data For Aqueous Fe^{2+}

$\Delta G_f^\circ(Fe^{2+})$ can be obtained by three independent pathways. The first pathway is by combining the values for $\Delta H_f^\circ(Fe^{2+})$ with $\Delta S_f^\circ(Fe^{2+})$ using the equation:

$$\Delta G_f^\circ = \Delta H_f^\circ - T\Delta S_f^\circ \ .$$

where ΔH_f°, ΔS_f°, and ΔG_f° are the standard state enthalpies, entropies, and Gibbs free energy of formation from the elements. In the second pathway, ΔG_f° is obtained from the standard electrode potential, E°, for the $Fe^\circ(s)/Fe^{2+}$ redox couple using the equation:

$$\Delta G_f^\circ = -nFE^\circ \ .$$

The third pathway involves calculating $\Delta G_f^\circ(Fe^{2+})$ from measurements of ΔG_f° and the solubility product constant, K, of $Fe(OH)_2(c)$ from the relationship:

$$\Delta G_R^\circ = -RT\ell nK \ .$$

The value for $\Delta H_f^\circ(Fe^{2+})$ can be obtained from heat of solution measurements of $FeCl_2(c)$ and the enthalpies of formation of $FeCl_2(c)$ and $Cl^-(aq)$,

$$\Delta H_f^\circ(Fe^{2+}, aq) = \Delta H_s^\circ(FeCl_2) - 2\Delta H_f^\circ(Cl^-, aq) + \Delta H_f^\circ(FeCl_2)$$

where $\Delta H_s^\circ(FeCl_2)$ is the standard heat of solution of $FeCl_2$. The $\Delta H_s^\circ(FeCl_2)$ has been measured by Li and Gregory (1952), Cerutti and Hepler (1977) and Cobble (1978). All three measurements are in close agreement (Table 3). The $\Delta H_f^\circ(Cl^-, aq)$ is known with a high degree of reliability (e.g. CODATA, 1977) and the only known value for $\Delta H_f^\circ(FeCl_2)$ is that from Koehler and Coughlin (1959). Combining these data, the resultant $\Delta H_f^\circ(Fe^{2+}, aq) = -21.61$ kcal/mol. The $\Delta S_f^\circ(Fe^{2+})$ can be calculated from the third-law entropy, $S^\circ(Fe^{2+})$ reported by Larson, _et al_. (1968) and the entropies of the elements from Robie, _et al_. (1978). The resultant $\Delta G_f^\circ(Fe^{2+}) = -21.34$ kcal/mol. This pathway is shown as set I in Table 4.

Electrode potential measurements for the $Fe^\circ(s)/Fe^{2+}$ couple can be reliable if (1) the iron is pure and free from defects, (2) no oxygen is present in the system, (3) the potential is independent of pH and (4) no hydrogen evolution takes place. No investigation has shown beyond doubt that all of these conditions have been met; however, the most reliable attempt is Johnson and Bauman (1978). Using their value of $E^\circ = 0.415$ V we calculate $\Delta G_f^\circ(Fe^{2+}) = -19.15$ kcal/mol. This pathway is the basis for set II in Table 4. The range of measured values is shown in Table 6. The difference between this number and the number derived from enthalpies and entropies is 2.2 kcal/mol, hardly an acceptable inconsistency.

TABLE 3. - Heat of solution of $FeCl_2$ (solid)

ΔH_s° (kcal/mol)	Reference
-19.5($\pm$0.2)	Li and Gregory (1952)
-19.7($\pm$0.2)	Li and Gregory (1952) corrected by Cerutti and Hepler (1977)
-19.815	Cobble (1978)
-19.82	Cerutti and Hepler (1977)

Careful measurements of the log Ksp (-15.1) for $Fe(OH)_2(c)$ have been made by Leussing and Kolthoff (1953). Two values have been calculated for ΔH°_f of $Fe(OH)_2(c)$ based on heat measurements (see JANAF Tables, Stull and Prophet, 1971). The more commonly accepted value of $\Delta H^\circ_f = -135.8$ kcal/mol was not considered by JANAF to be as accurate as $\Delta H^\circ_f = -137.2$ kcal/mol. JANAF used the latter value and an estimate of $S^\circ = 21.0$ cal/deg•mol to obtain ΔG°_f for $Fe(OH)_2(c) = -117.6$ kcal/mol. We prefer the former enthalpy value which has additional support from the electrochemical measurements of Dibrov, et al. (1980). If the S° value of 21 cal/deg•mol is considered to be the best available estimate then the $\Delta G^\circ_f = -116.2$ kcal/mol. Combining this value with the Ksp we obtain $\Delta G^\circ_f(Fe^{2+}) = -20.40$ kcal/mol. These values form the basis for set III in Table 4.

Thermodynamic Data for Aqueous Fe^{3+}

The thermodynamic properties of Fe^{3+} are usually obtained indirectly from data on Fe^{2+} and the Fe^{2+}/Fe^{3+} electrode potential. One direct value is available on $\Delta H^\circ_f(Fe^{3+}) = -10.89$ ($\pm$.17) kcal/mol from measurements on the heat of oxidation of solid iron to Fe^{3+} by H_2O_2 (Vasil'ev, et al., 1976). Since this value is dependent on the ΔH°_f for H_2O_2, we rechecked the calculation by using the peroxide enthalpy given in Wagman, et al. (1968). The difference is only 50 cal/mol, thus we have accepted the original value reported by Vasil'ev, et al. (1976). We now have an independent check on $\Delta H^\circ_f(Fe^{2+})$ through the Fe^{2+}/Fe^{3+} enthalpy. Unfortunately, the Fe^{2+}/Fe^{3+} enthalpy is not precisely known (see Table 6). Values range from 9.2 to 10.2 kcal/mol. In addition, two measurements have been reported for the heat of reaction, based on hydrogen peroxide oxidation of Fe^{2+}. Sousa-Alonso, et al. (1968) reported -69.8($\pm$0.4) kcal/mol and Bernardelli and Tumanova (1971) reported -71.11 ($\pm$0.03) kcal/mol for the heat of this reaction. From these data the Fe^{2+}/Fe^{3+} reaction enthalpy is 9.26 and 10.57 kcal/mol, respectively. Thus the reaction enthalpy must lie in the range of 9.2 to 10.6 kcal/mol and from the frequency of reported values and the average, a reasonable estimate would be 10.0 kcal/mol. Using this number and the $\Delta H^\circ_f(Fe^{3+})$ from Vasil'ev, et al. (1976) we obtain $\Delta H^\circ_f(Fe^{2+}) = -20.89$ kcal/mol. These enthalpies are used in both sets II and III of Table 4.

The standard electrode potential (-.7702 volts) and thus the ΔG°_f (17.76 kcal/mol) is known very precisely and very accurately (see Table 6) for the Fe^{2+}/Fe^{3+} couple. For this reason, the same recommended value is used in every set of Table 4. Since only one measurement for the enthalpy and entropy of goethite have been reported in the literature (Barany, 1965; King and Weller, 1970), these values are also the same in each set.

TABLE 4. - Three sets of internally consistent, standard state (298.15 K) thermodynamic data for $Fe^{2+}(aq)$, $Fe^{3+}(aq)$, $Fe(OH)_2(c)$, and goethite

Species*	Set I	Set II	Set III
$\Delta G_f^\circ(Fe^{2+})$	-21.34	-19.15	-20.40
$\Delta H_f^\circ(Fe^{2+})$	-21.61	-20.89	-20.89
$S^\circ(Fe^{2+})$	-25.6	-30.4	-26.3
$\Delta G_f^\circ(Fe^{3+})$	-3.78	-1.39	-2.64
$\Delta H_f^\circ(Fe^{3+})$	-11.04	-10.89	-10.89
$S^\circ(Fe^{3+})$	-65.3	-71.9	-69.4
$\Delta G_R^\circ(Fe^{2+}/Fe^{3+})$	17.76	17.76	17.76
$\Delta H_R^\circ(Fe^{2+}/Fe^{3+})$	10.57	10.0	10.0
$\Delta S_R^\circ(Fe^{2+}/Fe^{3+})$	-24.1	-26.0	-26.0
$\Delta G_f^\circ(Fe(OH)_2)$	-117.6	-115.0	-116.2
$\Delta H_f^\circ(Fe(OH)_2)$	-137.2	-135.0	-135.8
$S^\circ(Fe(OH)_2)$	21.0	19.3	21.0
log Ksp	-15.3	-15.1	-15.1
ΔG_f°(goethite)	-116.8	-116.8	-116.8
ΔH_f°(goethite)	-133.7	-133.7	-133.7
S°(goethite)	14.4	14.4	14.4
log Ksp	-41.7	-43.5	-42.7
$\Delta H_f^\circ(FeCl_2$, solid)	-81.69	-80.97	-80.97

*Free energies and enthalpies have units of kcal/mol and entropies have units of cal/deg•mol.

Internal Consistency

Based on the previous discussion, it is possible to derive three sets of data relating to the thermodynamic properties of aqueous Fe^{2+} and Fe^{3+} as shown in Table 4. Each set is internally consistent but not entirely consistent with each other set. Each set assumes certain selected data to be the most reliable, and the remaining data are calculated from these selected values by the standard thermodynamic relationships.

Set I is based on (1) Cerutti and Hepler's (1977) arguments and data for heat of solution measurements of $FeCl_2(c)$ which provides ΔH_f° for Fe^{2+}, and an estimated S° for Fe^{2+} from Larson, et al. (1968) from which ΔG_f° for Fe^{2+} is calculated, (2) the recommended value for E° of Fe^{2+}/Fe^{3+} and Bernardelli and Tumanova's (1971) value for ΔH_f° of Fe^{2+}/Fe^{3+} from which ΔG_f°, ΔH_f° and S° for Fe^{3+} and the log Ksp for goethite are calculated and (3) the JANAF values for $Fe(OH)_2$ from which the log Ksp of $Fe(OH)_2$ is calculated. This set then becomes inconsistent with the E° for $Fe^\circ(s)/Fe^{2+}$ of Johnson and Bauman (1978), the data on $Fe(OH)_2$ by Dibrov, et al. (1980) and Leussing and Kolthoff (1953), and the best estimated enthalpy for Fe^{2+}/Fe^{3+}. A further check on inconsistencies can be made by comparing the Ksp for goethite calculated from free energy data with the ion activity product (IAP) measured by Langmuir and Whittemore (1971). The ΔG_f° for goethite can be obtained from the ΔH_f° of Barany (1965) and the S° data of King and Weller (1970). Combining these data with the ΔG_f° of Fe^{3+} from set I gives a log Ksp = -41.7 which does not compare favorably with the range of log IAP = -43.3 to -43.5 for laboratory solutions containing crystalline goethite and groundwaters from aquifers containing iron minerals.

Set II is based on (1) Johnson and Bauman (1978) for ΔG_f° of Fe^{2+} and the recommended value of ΔG° for Fe^{2+}/Fe^{3+} from which ΔG_f° of Fe^{3+} is calculated, (2) Vasilev, et al. (1976) for ΔH_f° of Fe^{3+} and the best estimated ΔH° of Fe^{2+}/Fe^{3+} from which ΔH_f° of Fe^{2+} is calculated and (3) the log Ksp for $Fe(OH)_2$ from Leussing and Kolthoff (1953) and S° for $Fe(OH)_2$ from Dibrov, et al. (1980) from which ΔG_f° and ΔH_f° of $Fe(OH)_2$ is calculated. This set, of course, is inconsistent with nearly all of the data in set I including primary data such as ΔH_f° and S° for Fe^{2+} and ΔH_f° for $Fe(OH)_2$.

Set III appears to be the best compromise in that it is most consistent with all the primary data. Set III is based on (1) the JANAF estimate for S° of $Fe(OH)_2$ and the ΔH_f° of $Fe(OH)_2$ from Dibrov, et al. (1980) from which ΔG_f° of $Fe(OH)_2$ is calculated, (2) the log Ksp of $Fe(OH)_2$ from Leussing and Kolthoff (1953) and ΔG_f° of $Fe(OH)_2$ from the previous calculation from which ΔG_f° of Fe^{2+} is calculated, (3) the best estimated ΔH° of Fe^{2+}/Fe^{3+} and the ΔH_f° of Fe^{3+} from Vasil'ev, et al. (1976) from which ΔH_f° of Fe^{2+} is calculated. Everything else is calculated from these values. Although set III shows greater consistency with more of the data than any other set, there really is no optimal choice because of the inherently large uncertainties in some of the data. More accurate and more precise measurements of ΔH° for Fe^{2+}/Fe^{3+}, ΔG_f° for Fe^{2+} and Fe^{3+} would help to resolve these inconsistencies. It would also be highly desirable to make additional measurements of ΔH_f° and S° for goethite in order to reduce the uncertainty and inconsistencies related to the log Ksp for goethite.

Reference Source Codes

The symbols for the source column in Table 5 are abbreviated reference citations coded in a similar manner to those in Sillen and Martell (1964). Each reference abbreviation contains the year of publication followed by the first letter of the first author's last name. When more than one article could have the same designation, they are distinguished by a lower case letter starting with "a", e.g. 77Ha, 77Hb.

Additional information is provided by a slash (/), an equality symbol (=), or a comma (,); the symbols are explained in Table 5.

TABLE 5. - Symbols used for "source" code

Symbols	Interpretation
60F=62F=63F	Data from 60F, 62F, and 63F are identical
68S/72P	Data from 68S has been modified by 72P
43B, 53L	Data from 43B and 53L have been combined or averaged

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TABLE 6

TABLE 6. Partial compilation of thermodynamic data for the WATEQ programs

ALUMINUM

Al^{3+} aqueous ion G_f^o=-116.97(.33) kcal/mol H_f^o=-126.9(1) kcal/mol S^o=-73.6(3.6) cal/deg.mol Reference: 77H

……

$Al^{3+} + H_2O = AlOH^{2+} + H^+$

log K	Source	H_r^o	Source	REMARKS
-4.85	07B			
-4.96	42H			
-5.10	53I			
-4.98	54S			
-4.96	55Ka=55Kb			
-4.3	55T			
-5.86	56I			
-5.03	56K			
-4.97(.02)	56K=76B			
-5.02	60F=62F=63F			
-5.05	63R			
-4.9	65N			
-4.7(.3)	67H			
-4.49	68H			
-5.16	68S			10^{-5} M aluminum perchlorate, values at 10^{-4} and 10^{-3} also given
-4.61	69G	11.0	69G	T = 30°C
-4.89	69N			0.1 M sodium perchlorate
-4.99	71V			

-5.01(.04)	72P			
-5.55(.09)	74H			I = 0.15
-5.00	74T	15.64	74T	WATEQ
-4.97	76P	14.775	76P	WATEQF
-5.35	78H			I = 0.4
-4.987(.08)	79M=80B	11.9(0.5)	76B=80B	WATEQ2; RECOMMENDED; H_r^o and S^o (=17.2(1.7) cal/deg.mol) values from 76B are consistent with 79M

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$Al^{3+} + 2H_2O = Al(OH)_2^+ + 2H^+$

log K	Source	H_r^o	Source	REMARKS
-8.56	55T			
-8.63(0.1)	58G			

TABLE 6. Partial compilation of thermodynamic data for the WATEQ programs(continued):

-9.7	63R			
-10.60	68S			10^{-4} M aluminum perchlorate, value at 10^{-5} M unreliable
-10.28(.3)	68S/72P			mean for results at 10^{-3} and 10^{-4} perchlorate
-9.9	69N			0.1 M sodium perchlorate
-9.3	69N/76B			corrected to I = 0
-8.69(0.1)	72P=78H			calculated from K_1K_2 using log K_w = -13.997 (76B)
-9.761	74T	0.0		WATEQ
-10.5	76B			estimate based on a linear increase in hydrolysis constants
-9.30	76P	0.0		WATEQF
-10.13(.08)	79M=80B	22.0	76B	WATEQ2 for log K; RECOMMENDED; H_r^o was obtained by a correlation.

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80B Ball,J.W.,Nordstrom,D.K., and Jenne,E.A.(1980) U.S. Geol. Survey W.R.I. 78-116, 109 pp.

$Al^{3+} + 3H_2O = Al(OH)_3^o + 3H^+$

log K	Source	H_r^o	Source	REMARKS
-15.03	59A			
-15.2	68S			10^{-4} M aluminum perchlorate, value at 10^{-5} unreliable

-15.6	69N			0.1 M sodium perchlorate
-15.0	69N/76B			corrected to I = 0
-15.19(.1)	72P			
-16.5	76B			estimate based on linear increase in hydrolysis constants
-16.76(.09)	79M	33.0		RECOMMENDED; H_r^o obtained by assuming a linear increase

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$Al^{3+} + 4H_2O = Al(OH)_4^- + 4H^+$

log K	Source	H_r^o	Source	REMARKS
-22.47	08W/11S			Footnote (1)
-21.81	20H			Footnote (1)
-23.25	20H			Footnote (2)
-27.98	34M			calculated from reported $\log{}^*K_4 = -11.22$ and $\log{}^*K_1K_2K_3 = -16.76$
-22.21	380			derived from reported $\log{}^*K_{s4} = -11.92$ and reported $\log K_{s0} = -31.7$
-23.26	55R/72P=78H			Footnote (1)
-24.24	55T			derived from reported $\log K_{s4} = -0.68$ and reported $\log K_{s0} = -32.43$
-23.57	58G			derived from reported $\log K_{s4} = -0.53$ and reported $\log K_{s0} = -32.96$
-27.69	60A			
-21.94	60G			Footnote (3)
-24.19	64P			
-23.3(.05)	66K=72P			
-23.3(.1)	66K=78H			
-22.05	67H			
-23.29	68S			10^{-4} M aluminum perchlorate, value at 10^{-5} unreliable

TABLE 6. Partial compilation of thermodynamic data for the WATEQ programs(continued):

-23.37	70B			
-22.07	73H			
-22.71	74H			
-22.054	74T=80B	44.06	74T=80B	WATEQ
-23.0(.3)	76B=80B			WATEQ2
-22.992	76P	42.22	76P	WATEQF
-22.16(.03)	79M			

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80B Ball,J.W.,Nordstrom,D.K., and Jenne,E.A.(1980) U.S. Geol. Survey W.R.I. 78-116, 109 pp.

$2Al^{3+} + 2H_2O = [Al_2(OH)_2]^{4+} + 2H^+$

log K	Source	H_r^o	Source	REMARKS
-8.06	48F=54F			0.12 M barium nitrate
-8.24	48F=54F			0.6 M barium nitrate
-7.55	55Ka=55Kb			I = 0.03 - 0.048
-6.27	56K			0.0001 - 0.03 sodium perchlorate
-7.07(.06)	65A=72P			2 M sodium perchlorate
-7.7	71M=76B			1 M potassium chloride
-6.95(.05)	75T			
-7.1	78H			I = 0.4

References:
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$Al^{3+} + F^- = AlF^{2+}$

log K	Source	H_r^o	Source	REMARKS
6.13	42B=43B =57C			0.53 M potassium nitrate
7.00	42B/55P			corrected to I = 0
6.16	43B/59K			0.53 M potassium nitrate
		1.15	53L	I = 0.06 - 0.2
		1.17	53L/59S	
6.61	59K			I = 0.06 - 0.02
7.01	59K/68H			corrected to I = 0

TABLE 6. Partial compilation of thermodynamic data for the WATEQ programs(continued):

6.08	64B			assumed T = 25°C, I = variable
6.98(.08)	69B	1.06	43B,53L/ 59K=69B	RECOMMENDED; enthalpy value is for I = 0.07
6.69(.02)	71A			
6.114(.08)	71W	0.74	71W	1 M sodium perchlorate
		0.64(.05)	75V	
7.01	74T=76P =80B	0.0	74T=76P =80B	WATEQ = WATEQF = WATEQ2

References:
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43B Brosset,C. and Orring,J.(1943) Sven. Kem. Tidskr. 55, 101-106.
53L Latimer,W.M. and Jolly,W.L.(1953) J. Am. Chem. Soc. 75, 1548-1550.
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59K King,E.L. and Gallagher,P.K.(1959) J. Phys. Chem. 63, 1073-1076.
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75V Vasil'ev,V.P. and Kozlovskii,E.V.(1975) Zh. Neorg. Khim. 20, 1196-1199.
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80B Ball,J.W.,Nordstrom,D.K., and Jenne,E.A.(1980) U.S. Geol. Survey W.R.I. 78-116, 109 pp.

$Al^{3+} + 2F^{-} = AlF_2^{+}$

log K	Source	H_r^o	Source	REMARKS
11.15	42B=43B =57C			
11.21	43B/59K			0.53 M potassium nitrate
		1.93	53L	I = 0.06 - 0.2

		1.97	53L/59S	
9.06	57T			I = variable
11.97	59K			I = 0.07
12.75	59K/68H			corrected to I = 0
11.10	64B			assumed T = 25°C, I = variable
12.60(.10)	69B	1.98	43B,53L/ 59K=69B	RECOMMENDED; enthalpy value is for I = 0.07
12.04	71A			
		1.80(.11)	75V	
12.75	74T=76P =80B	20.0	74T=76P =80B	WATEQ = WATEQF = WATEQ2

References:
42B Brosset,C.(1942) Ph.D. Thesis, Univ. Lund, Lund, 123 pp.
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76P Plummer,L.N.,Jones,B.F., and Truesdell,A.H.(1976) U.S. Geol. Survey W.R.I. 76-13, 61 pp.
80B Ball,J.W.,Nordstrom,D.K., and Jenne,E.A.(1980) U.S. Geol. Survey W.R.I. 78-116, 109 pp.

$Al^{3+} + 3F^- = AlF_3^o$

log K	Source	H_r^o	Source	REMARKS
15.00	42B=43B =57C			0.53 M potassium nitrate
15.12	43B/59K			0.53 M potassium nitrate
		2.12	53L	I = 0.06 - 0.2
		2.18	53L/59S	
16.03	59K			I = 0.07

TABLE 6. Partial compilation of thermodynamic data for the WATEQ programs(continued):

17.02	59K/68H			corrected to I = 0
16.65(.15)	69B	2.16	43B,53L/ 59K=69B	RECOMMENDED; enthalpy value is for I = 0.07
15.72	71A			
17.02	74T=76P =80B	2.50	74T=76P =80B	WATEQ = WATEQF = WATEQ2
		3.07(.3)	75V	

References:
42B Brosset,C.(1942) Ph.D. Thesis, Univ. Lund, Lund, 123 pp.
43B Brosset,C. and Orring,J.(1943) Sven. Kem. Tidskr. 55, 101-106.
53L Latimer,W.M. and Jolly,W.L.(1953) J. Am. Chem. Soc. 75, 1548-1550.
57C Connick,R.E. and Poulson,R.E.(1957) J. Am. Chem. Soc. 79, 5153-5156.
59K King,E.L. and Gallagher,P.K.(1959) J. Phys. Chem. 63, 1073-1076.
59S Scott,P.C.(1959) Ph.D. Thesis, Univ. Minnesota, Minneapolis, 101 pp.
68H Hem,J.D.(1968) U.S. Geol. Survey Water-Supply Paper 1827-B, 33 pp.
69B Bauman,E.W.(1969) J. Inorg. Nucl. Chem. 31, 3155-3162.
71A Agarwal,R.P. and Moreno,E.C.(1971) Talanta 18, 873-880.
74T Truesdell,A.H. and Jones,B.F.(1974) J. Res. U.S. Geol. Survey 2, 233-248.
75V Vasil'ev,V.P. and Kozlovskii,E.V.(1975) Zh. Neorg. Khim. 20, 1196-1199.
76P Plummer,L.N.,Jones,B.F., and Truesdell,A.H.(1976) U.S. Geol. SurveyW.R.I. 76-13, 61 pp.
80B Ball,J.W.,Nordstrom,D.K., and Jenne,E.A.(1980) U.S. Geol. Survey W.R.I. 78-116, 109 pp.

$Al^{3+} + 4F^{-} = AlF_4^{-}$

log K	Source	H_r^o	Source	REMARKS
17.74	42B=43B =57C			0.53 M potassium nitrate
17.83	43B/59K			0.53 M potassium nitrate
		2.40	53L	I = 0.06 - 0.2
		2.14	53L/59S	
18.71	59K			I = 0.07
19.72	59K/68H			corrected to I = 0

19.03(.15)	69B	2.20	43B,53L/ 59K=69B	RECOMMENDED; enthalpy value is for I = 0.07
18.47	71A			
19.72	74T=76P =80B	0.0	74T=76P =80B	WATEQ = WATEQF = WATEQ2

References:
42B Brosset,C.(1942) Ph.D. Thesis, Univ. Lund, Lund, 123 pp.
43B Brosset,C. and Orring,J.(1943) Sven. Kem. Tidskr. 55, 101-106.
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59K King,E.L. and Gallagher,P.K.(1959) J. Phys. Chem. 63, 1073-1076.
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68H Hem,J.D.(1968) U.S. Geol. Survey Water-Supply Paper 1827-B, 33 pp.
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80B Ball,J.W.,Nordstrom,D.K., and Jenne,E.A.(1980) U.S. Geol. Survey W.R.I. 78-116, 109 pp.

$Al^{3+} + 5F^{-} = AlF_5^{2-}$

log K	Source	H_r^o	Source	REMARKS
19.37	42B=43B			0.53 M potassium nitrate
19.29	43B/59K			0.53 M potassium nitrate
		1.65	53L	I = 0.06 - 0.2
		2.27	53L/59S	
20.04	59K			I = 0.07
20.91	59K/68H	1.84	43B,53L/ 59K	RECOMMENDED; enthalpy value is for I = 0.07

References:
42B Brosset,C.(1942) Ph.D. Thesis, Univ. Lund, Lund, 123 pp.
43B Brosset,C. and Orring,J.(1943) Sven. Kem. Tidskr. 55, 101-106.
53L Latimer,W.M. and Jolly,W.L.(1953) J. Am. Chem. Soc. 75, 1548-1550.
59K King,E.L. and Gallagher,P.K.(1959) J. Phys. Chem. 63, 1073-1076.
59S Scott,P.C.(1959) Ph.D. Thesis, Univ. Minnesota, Minneapolis, 101 pp.
68H Hem,J.D.(1968) U.S. Geol. Survey Water-Supply Paper 1827-B, 33 pp.

TABLE 6. Partial compilation of thermodynamic data for the WATEQ programs(continued):

$Al^{3+} + 6F^{-} = AlF_6^{3-}$

log K	Source	H_r^o	Source	REMARKS
19.84	42B=43B			0.53 M potassium nitrate
		-1.24	53L/59S	
20.86	59K/68H	0.10	53L	RECOMMENDED; enthalpy value is for I = 0.06 - 0.2

References:
42B Brosset,C.(1942) Ph.D. Thesis, Univ. Lund, Lund, 123 pp..
43B Brosset,C. and Orring,J.(1943) Sven. Kem. Tidskr. 55, 101-106.
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$Al^{3+} + SO_4^{2-} = AlSO_4^{+}$

log K	Source	H_r^o	Source	REMARKS
3.20	62B=74T =76P	2.29(.08)	69I=74T =76P	WATEQ = WATEQF
3.73	65N			
3.01(.08)	69I=77N =80B			WATEQ2
3.57	69S			
3.2	70R			
		2.15	77N=80B	based on Fuoss equation(Siebert and Christ, unpublished data)

References:
62B Behr,B. and Wendt,H.(1962) Z. Elektrochem. 66, 223-228.
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$Al^{3+} + 2SO_4^{2-} = Al(SO_4)_2^-$

log K	Source	H_r^o	Source	REMARKS
5.10	62B=74T =76P	3.07(.2)	69I=74T =76P	WATEQ = WATEQF
4.90(.1)	69I=77N =80B	2.84	77N=80B	WATEQ2; enthalpy based on Fuoss equation(Siebert and Christ, unpublished data)

References:
62B Behr,B. and Wendt,H.(1962) Z. Elektrochem. 66, 223-228.
69I Izatt,R.M.,Eatough,D.,Christensen,J.J., and Bartholomew,C.H.(1969) J. Chem. Soc. A, 47-53.
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$Al(OH)_3$ solid:Gibbsite G_f^o=-276.03(.30) kcal/mol H_f^o=-309.06(.30) kcal/mol S^o=16.36(.03) cal/deg.mol
Cp=21.92 cal/deg.mol References: 77Ha,77Hb

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$Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O$

log K	Source	H_r^o	Source	REMARKS
9.02	20H	-28.0	20H	aged for several weeks
10.3	380			
9.57	55T			
8.55	57M			
9.04	58G			

TABLE 6. Partial compilation of thermodynamic data for the WATEQ programs(continued):

8.49(.1)	60F=62F =76B			came to equilibrium in 1-3 months from supersaturation, 2-6 micrometer particle size
10.8	63F			amorphous
7.97(.05)	66K			well-crystallized gibbsite, aging time about 4 yrs., no difference in particles .05-50 micrometers in size
9.35(.3)	67H			microcrystalline gibbsite, aged 2-20 wks
11.40	71D			aged 24 hrs at 20^{o}C
8.22	72S			aged for about 2 yrs.
10.4	74H			amorphous, aged for 24 hrs.
10.05	74H			microcrystalline, aged 3 months
8.04(.03)	74S	-21.04(.2)	74S=76S	aged 1.5-2.5 yrs.
9.23	74T=76P	-25.57	74T=76P	WATEQ = WATEQF
		-22.8(1)	78Ha=80B	WATEQ2; heat of solution measured on same material from 66K
9.30	78Hb			
8.11(.02)	79M			synthetic crystalline gibbsite, 2-5 micrometers in size, equilibrium was reversed and reached in a month or less
8.75(.05)	79M=80B			WATEQ2; natural gibbsite from Minas Gerais, same experimental details as 79M above

RECOMMENDATION: 1. For crystalline gibbsite the log K results of 66K,72S,76S and 79M are all in excellent agreement. The value reported by 79M is recommended.

2. The upper solubility limit is not well-defined, but it probably lies in the range of log K=9.35-10.8 for a microcrystalline to an amorphous precipitate, respectively.

References:
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79M May,H.M.,Helmke,P.A., and Jackson,M.L.(1979) Geochim. Cosmochim. Acta 43, 861-868.
80B Ball,J.W.,Nordstrom,D.K., and Jenne,E.A.(1980) U.S. Geol. Survey W.R.I. 78-116, 109 pp.

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……CALCIUM……

Ca^{2+} aqueous ion G_f^o=-132.125(.20) kcal/mol H_f^o=-129.80(.20) kcal/mol S^o=-13.5(.1) cal/deg.mol
Reference: 77CO

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$Ca^{2+} + Cl^- = CaCl^+$

log K	Source	H_r^o	Source	REMARKS
none	30R			T = 18°C
small	43H			
0.68	62C			
0.60	71N			.075 - 1.00 M sodium chloride
0.079	75E			I = 0.7
0.36	75K			theoretical calculation
-0.11	75S			1 M $NaNO_3$, by ion-selective electrode

TABLE 6. Partial compilation of thermodynamic data for the WATEQ programs(continued):

-0.12	75S	1 M $NaNO_3$, by silver chloride electrode
0.35	78J	I = 0.6
-0.30	79E	I = 0.7

References:
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78J Johnson,K.S. and Pytkowicz,R.M.(1978) Am. J. Sci. 278, 1428-1447.
79E Elgquist,B. and Wedborg,M.(1979) Mar. Chem. 7, 273-280.

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……IRON……

Fe^{2+} aqueous ion G_f^o=-19.15(.08) kcal/mole H_f^o=-20.82(.7) kcal/mole S^o=-30.3(2.5) cal/deg.mole
Cp=-0.5(7.2) cal/deg.mol References: 78J,79B and calculations in this report

Fe^{3+} aqueous ion G_f^o=-1.39(.08) kcal/mol H_f^o=-10.84(.2) kcal/mol S^o=-72.0(.7) cal/deg.mol
References: see calculations in this report

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$Fe = Fe^{2+} + 2e^-$

E^o(volts)	G_r^o(kcal/mol)	Source	REMARKS
0.4413	-20.35	26H	
0.4402	-20.30	32R	

0.4090(.00075)	-18.85	53P	
0.442	-20.39	58H	
0.467	-21.54	60H	T = 20°C
0.4153(.0013)	-19.15	78J	RECOMMENDED

References:
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$Fe^{2+} = Fe^{3+} + e^-$

E^o(volts)	G^o_r(kcal/mol)	Source	H^o_r(kcal/mol)	Source	REMARKS
-0.7477(.0005)	17.24	29P			uncorrected for complexing
-0.772(.001)	17.80	29P/34B			corrected for complexing
-0.7701(.0002)	17.76	37S			
			-9.53(.04)	50F	0.5 M perchloric acid
-0.7394	17.05	51C	-9.95(.05)	51C	0.5 M perchloric acid
-0.7375(.001)	17.00	53M	-9.7(.2)	53M	I = 1, sodium perchlorate and perchloric acid
-0.749	17.27	58S			0.25 M nitric acid
-0.746	17.20	58S			1 M nitric acid
-0.767	17.69	58S			1 M perchloric acid
-0.674	15.54	58S			0.5 M sulfuric acid
-0.732	16.88	58S			1 M hydrochloric acid
-0.738	17.02	58L			uncorrected for complexing
-0.771(.004)	17.78	58L/60M			corrected for complexing
-0.7375(.0001)	17.01	62Z			I = 2, sodium perchlorate and perchloric acid
-0.770(.002)	17.76	72W	-10.2(.4)	72W	

TABLE 6. Partial compilation of thermodynamic data for the WATEQ programs(continued):

-0.7695(.0008)	17.75	72W/79N	-9.18	72W/79N	data refit to linear equation
-0.7702(.0001)	17.76	34B,37S 60M,72W	-10.0(.5)		RECOMMENDED; weighted average from four different investigations; for enthalpy value see text

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79N Nordstrom,D.K.(1979) unpublished calculations

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....MAGNESIUM...

Mg^{2+} aqueous ion G_r^o=-109 kcal/mol H_r^o=-112 kcal/mol S^o=-33 cal/deg.mol   References: 71W,77CO,79C

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$Mg^{2+} + Cl^- = MgCl^+$

log K	Source	H_r^o	Source	REMARKS
none	30R			T = 18°C, cited by 75S
small	43H			cited by 75S
none	45S			cited by 75S
-0.9801	73H			

-0.32	75E	I = 0.7
-0.08	75S	1 M $NaNO_3$, by ion-selective electrode
-0.11	75S	1 M $NaNO_3$, by silver chloride electrode
-0.18	77F	
-0.47	78E	I = 0.7
0.28	78J	I = 0.6

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79C Coffy,G. and Olofsson,G.(1979) J. Chem. Thermodyn. 11, 141-144.

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POTASSIUM

K^+ aqueous ion G^o_r=-67.52(.03) kcal/mol H^o_r=-60.27(.03) kcal/mol S^o=24.14(.06) cal/deg.mol
Cp=5.3 cal/deg.mol References: 77G,77CO,81W

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$K^+ + SO_4^{2-} = KSO_4^-$

log K	Source	H^o_r	Source	REMARKS
0.82	30R			
0.96	50J			
0.847	68T=74T=76P	3.082	68T=74T=76P	WATEQ = WATEQF
0.75	69I	1.01	69I	
0.83	72T			

TABLE 6. Partial compilation of thermodynamic data for the WATEQ programs(continued):

0.85(.05)	77N=80B	2.25(1.0)	77N=80B	WATEQ2
1.02	77F			

References:

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50J Jenkins,I.L. and Monk,C.B.(1950) J. Am. Chem. Soc. 72, 2695-2698.

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80B Ball,J.W.,Nordstrom,D.K., and Jenne,E.A.(1980) U.S. Geol. Survey W.R.I. 78-116, 109 pp.

81W Wagman,D.D.,Evans,W.H.,Parker,V.B.,Schumm,R.H., and Nuttall,R.L.(1981) Nat. Bur. Stand. Tech. Note 270-8, 134 pp.

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....SODIUM..

Na^+ aqueous ion G_r^o=-62.60(.02) kcal/mol H_r^o=-57.43(.016) kcal/mol S^o=13.96 cal/deg.mol
Cp=11.1 cal/deg.mol References: 77CO,81W

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$Na^+ + SO_4^{2-} = NaSO_4^-$

log K	Source	H_r^o	Source	REMARKS
0.70	30R			
0.72	50J=76P	1.10	76P	WATEQF
0.90	66M			
0.65	69I	-0.49	69I	

0.305(.007)	69P			I = 0.687
0.226	71L=74T	2.229	71L=74T	WATEQ
0.686	74M			T = 20°C
1.14	53K/75Fa			recalculated sound absorption measurements
1.17	69P/75Fa			corrected to I = 0
1.11	50J/75Fb			refitted conductance measurements to new equation
1.10	75Fb			
0.82(.05)	75R			
0.73	75S			
1.03	77F			
0.70(.05)	77N=80B	1.12(.80)	62A=77N=80B	WATEQ2
1.00	78F	0	80J	I = 0.75
0.73(.01)	79E			I = 0.12
0.60(.02)	79E			I = 0.17
0.57(.03)	79E			I = 0.21

References:

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TABLE 6. Partial compilation of thermodynamic data for the WATEQ programs(continued):

81W Wagman,D.D.,Evans,W.H.,Parker,V.B.,Schumm,R.H., and Nuttall,R.L.(1981) Nat. Bur. Stand. Tech. Note 270-8, 134 pp.

Footnotes:

(1) log K_{s0} = -34.0 (66K,79M) for well-crystallized gibbsite and log K_w = -13.997 (76B) were used to calculate $*K_1K_2K_3K_4$ from K_{s4} or $*K_{s4}$.

(2) log K_{s0} = -31.2 from 63F (in gibbsite section) for amorphous $Al(OH)_3$ was used to calculate $*K_1K_2K_3K_4$.

(3) log K_{s0} = -32.65 from 67H for microcrystalline gibbsite was used to calculate $*K_1K_2K_3K_4$.