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WATEQ3 Geochemical Model: Thermodynamic Data for Several Additional Solids

**Kenneth M. Krupka
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September 1982

**Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
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PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151

NTIS Price Codes
Microfiche A01

Printed Copy

Pages	Price Codes
001-025	A02
026-050	A03
051-075	A04
076-100	A05
101-125	A06
126-150	A07
151-175	A08
176-200	A09
201-225	A010
226-250	A011
251-275	A012
276-300	A013

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ACKNOWLEDGMENTS

The authors would like to thank A. R. Felmy and D. C. Girvin for their reviews of this document, and W. J. Deutsch and J. M. Zachara for many fruitful discussions on mineralogy. The authors would also like to thank P. R. Partch and B. K. Marshall for their editorial reviews of this document. This research was supported by the Department of Energy under Contract DE-AC06-76RL0 1830. Support in FY1981 was provided by the Waste/Rock Interactions Technology (WRIT) Program, the Office of Nuclear Waste Isolation (ONWI), and the Terrestrial Effects of Oil Shale Program, Office of Health and Environmental Research, and in FY1982 by the Geochemical Modeling and Nuclide/Rock/Groundwater Interactions Studies (GMIS) Program, ONWI.

FOREWORD

At the Pacific Northwest Laboratory, geochemical modeling activities have centered on model development and application studies. These activities are in response to the need for accurate predictions of solubility limitations and retardation by adsorption for water-soluble pollutants in laboratory and natural water/rock systems. Predicting solubility limits and retardation factors for water-soluble pollutants is crucial to technologies such as nuclear energy, oil shale development, seasonal thermal energy storage, and uranium mining, where the isolation of waste materials must be assessed.

In concert with these application efforts, modeling capabilities must be developed to enhance the competency of the geochemical model to deal with the environmental impact of wastes from these technologies. These on-going efforts include: 1) the development of a competent thermodynamic data base, which is the subject of this report; 2) critical reviews of thermodynamic data, which are necessary to generate an internally consistent and accurate data base; and 3) the development of an advanced computer code, which has the capabilities to model aqueous speciation, solubility controls, mass transfer, and adsorption.

Because of the need to model aqueous speciation, solubility controls and adsorption, efforts at the Pacific Northwest Laboratories have focused on developing a new geochemical model. This model, MINTEQ, is a hybridization of the extant geochemical codes WATEQ3 (Ball, Jenne and Cantrel 1981) and MINEQL (Westall, Zachary and Morel 1976). The MINTEQ model drives an efficient code for mass transfer and adsorption modeling from MINEQL, and incorporates the superior thermodynamic data base and user-oriented features of the WATEQ model series, including the revision WATEQ4. All previous and current thermodynamic data base enhancement activities in the WATEQ model series are transmitted to the new model. Thus the data base enhancement described in this report is an integral part of the geochemical modeling capabilities at the Pacific Northwest Laboratory.

John S. Fruchter
GMIS Program Manager

SUMMARY

Geochemical models such as WATEQ3 can be used to model the concentrations of water-soluble pollutants that may result from the disposal of nuclear waste and retorted oil shale. However, for a model to competently deal with these water-soluble pollutants, an adequate thermodynamic data base must be provided that includes elements identified as important in modeling these pollutants. To this end, several minerals and related solid phases were identified that were absent from the thermodynamic data base of WATEQ3.

In this study, the thermodynamic data for the identified solids were compiled and selected from several published tabulations of thermodynamic data. For these solids, an "accepted" Gibbs free energy of formation, $\Delta G_{f,298}^0$, was selected for each solid phase based on the recentness of the tabulated data and on considerations of internal consistency with respect to both the published tabulations and the existing data in WATEQ3. For those solids not included in these published tabulations, Gibbs free energies of formation were calculated from published solubility data (e.g., lepidocrocite), or were estimated (e.g., nontronite) using a free-energy summation method described by Mattigod and Sposito (1978). The "accepted" or estimated free energies were then combined with internally consistent, ancillary thermodynamic data to calculate equilibrium constants for the hydrolysis reactions of these minerals and related solid phases.

Including these values in the WATEQ3 data base increased the competency of this geochemical model in applications associated with the disposal of nuclear waste and retorted oil shale. Additional minerals and related solid phases that need to be added to the solubility submodel will be identified as modeling applications continue in these two programs.

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INTRODUCTION

The thermodynamic data bases for extant geochemical models require major additions to make the models competent to deal with water-soluble pollutants arising from solid and liquid wastes associated with the various energy technologies. These technologies include nuclear waste disposal, retorted oil shale disposal, seasonal thermal energy storage, and uranium mill tailings disposal.

The present effort was committed to increasing the competence of the solubility submodel for evaluating solubility equilibria in basalt aquifers and for water in contact with retorted oil shale. The WATEQ3 solubility data base, although currently limited to temperatures between ambient and 100°C (373 K), is thought to be competent for most anticipated applications in the seasonal thermal energy program. A list of the additional solid phases required to provide competence for basalt aquifers, beyond those already in the model (Truesdell and Jones 1974; Ball, Nordstrom and Jenne 1980; Ball, Jenne and Cantrell 1981), was generated by William Deutsch of Pacific Northwest Laboratory from the extensive mineralogical study of the Columbia Plateau basalts by Lloyd Ames (1980). The authors, with the assistance of John Zachara, Pacific Northwest Laboratory, compiled a list of additional solid phases that might contribute significant amounts of dissolved solids to leachates or might limit the levels of dissolved constituents in waters in contact with retorted oil shales. This list included data from the extensive mineralogical investigations of an oil shale in Israel that retorted naturally since the Eocene epoch (Gross 1977) and recent unpublished, mineralogical data from various investigations of retorted oil shales. Based on the authors' judgement that Mg and Ca oxides probably are present in freshly retorted oil shale, these oxides were also added. The minerals and other solid phases that were added to the data base of WATEQ3 are listed in Table 1. The mineral glossary by Fleischer (1980) was used as a guide for mineralogical nomenclature. Additional minerals and related solid phases that need to be added to the solubility submodel will be identified as modeling applications continue in these two programs.

TABLE 1. Formula and Name of Minerals and Other Solid Phases Added to the Data Bank of WATEQ3.

Formula	Mineral Name
CaO	Lime
Ca(OH) ₂	Portlandite
Fe _{0.947} O	Wüstite
γ-FeO(OH)	Lepidocrocite
MgO	Periclase
FeAl ₂ O ₄	Hercynite
MgAl ₂ O ₄	Spinel
MgFe ₂ O ₄	Magnesio-ferrite
Na ₃ AlF ₆	Cryolite
CaSiO ₃	Wollastonite
CaSiO ₃	Pseudowollastonite
Ca ₂ (SiO ₄)	Ca-Olivine
β-Ca ₂ (SiO ₄)	Larnite
Ca ₃ SiO ₅	(No mineral name)
CaMgSiO ₄	Monticellite
Ca ₂ MgSi ₂ O ₇	Åkermanite
Ca ₃ Mg(SiO ₄) ₂	Merwinite
KAlSiO ₄	Kalsilite (or Kaliophillite)
KAlSi ₂ O ₆	Leucite
KAlSi ₃ O ₈	Microcline
KAlSi ₃ O ₈	High Sanidine
NaAlSiO ₄	Nepheline
Ca ₂ Al ₂ SiO ₇	Gehlenite
Na _{0.33} Fe ₂ (Al _{0.33} Si _{3.67})O ₁₀ (OH) ₂	Na-Nontronite
K _{0.33} Fe ₂ (Al _{0.33} Si _{3.67})O ₁₀ (OH) ₂	K-Nontronite
Ca _{0.17} Fe ₂ (Al _{0.33} Si _{3.67})O ₁₀ (OH) ₂	Ca-Nontronite
Mg _{0.17} Fe ₂ (Al _{0.33} Si _{3.67})O ₁₀ (OH) ₂	Mg-Nontronite

In this study, the thermodynamic data for the identified solids were compiled and selected from several "standard" tabulations of thermodynamic data. An "accepted" Gibbs free energy of formation, $\Delta G_{f,298}^0$, was selected for each solid phase based on the recentness of the tabulated data and on considerations of internal consistency with respect to both the published tabulations and the existing data in WATEQ3. Thermodynamic data for a few of the identified solids, which were not included in these "standard" tabulations, were obtained by other means. The Gibbs free energy of formation for lepidocrocite was calculated from published solubility data. Thermodynamic data for ideal end-member nontronite and for a nontronite typical for altered Columbia Plateau basalts were estimated using the free-energy summation method described by Mattigod and Sposito (1978). The estimation method is briefly described in this report.

The accepted values for the Gibbs free energies for formation for the identified solids were then used to calculate $\log_{10} K_{r,298}^0$ values for the hydrolysis reactions involving these solids. Appendix A shows an example of the calculations necessary to generate internally consistent $\Delta G_{f,298}^0$ and $\log_{10} K_{r,298}^0$ values based on previously selected "best" values for S_{298}^0 and $\Delta H_{f,298}^0$ for the constituent elements, the ancillary components in the reaction, and the solid phase subject of the $\log_{10} K_{r,298}^0$ value. These thermochemical data were added to the data base of WATEQ3 for the evaluation of solubility equilibria in basalt aquifers and for water in contact with retorted oil shale. This set of $\log_{10} K_{r,298}^0$ values was derived primarily from measured heats of formation ($\Delta H_{f,298}^0$) and entropy (S_T^0) data or was estimated by analogy to other solids for which the thermodynamic data are available. It would be desirable to search the available literature for solubility data from which to compute alternate values of $\log_{10} K_{r,298}^0$ for comparison with this set of $\log_{10} K_{r,298}^0$ values.

SOURCES OF TABULATED THERMODYNAMIC DATA

Thermodynamic data for the additional solid phases listed in Table 1 were compiled from several sources (CODATA Task Group 1976; Helgeson et al. 1978; Naumov, Ryzhenko and Khodakovsky 1974; Parker, Wagman and Evans 1971; Robie, Hemingway and Fisher 1978; Sadiq and Lindsay 1979; Stull and Prophet 1971; Wagman et al. 1968, 1969, 1981). Although major differences exist in the approaches and rationales which the authors used while making these tabulations, comparisons of thermodynamic data compilations can be made to check for the most recently published data and for data consistency. In this study, these compilations of thermodynamic data were also evaluated in relation to the needs of the WATEQ3 data base for modeling geochemical systems.

Of primary importance to the WATEQ model, is the U.S. National Bureau of Standards (NBS) Technical Note Series 270 (Parker, Wagman and Evans 1971; Wagman et al. 1968, 1969, 1981). Additions to the data base of WATEQ3, by Ball, Nordstrom and Jenne (1980) and Ball, Jenne and Cantrell (1981) were based primarily on the thermodynamic data for the constituent ions (except for U and Mn^{+3}) given in the NBS Technical Note Series 270 tabulations. These NBS tabulations were also a major source of data for individual ion species in the earlier versions of WATEQ (Truesdell and Jones 1974), WATEQ2 (Ball, Nordstrom and Jenne 1980) and WATEQF (Plummer, Jones and Truesdell 1976). The NBS 270 series of publications are revisions of earlier tables of thermodynamic data by Rossini et al. (1952). The interim NBS report by Parker, Wagman and Garvin (1976) was also used in the present calculations. The values tabulated in the NBS Series 270 reports and Wagman et al. (1976) are consistent with each other because the same ancillary thermodynamic data were used for all of these tables.

An international committee, the CODATA Task Group on Key Values for Thermodynamics, was formed a few years ago to prepare a recommended list of key thermodynamic data. Key values were selected and published for 74 species, which were mostly in the gaseous state, in CODATA (1976). D. D. Wagman and W. H. Evans, two principal contributors to the NBS Series 270, were also, respectively, a member and a consultant to the CODATA Task Group. Due to the nature of this committee and its task, thermodynamic values were accepted for the

present calculations from CODATA, rather than from from the NBS 270 Series, if the values differed significantly between these two sources. Because the values from CODATA (1976) may not be completely compatible with values in the NBS Series 270, Parker, Wagman and Garvin (1976) prepared an extensive list of thermochemical values that are compatible with the CODATA values. This NBS report was prepared for the International Atomic Energy Agency to assist in the evaluation of the thermochemistry of the actinide elements. However, these two CODATA references do not provide extensive data for geologically related species and solid phases.

The summary of thermodynamic data by Robie, Hemingway and Fisher (1978) was the principal source of the data selected for the solid phases added to WATEQ3. The tables in Robie, Hemingway and Fisher (1978), designed for the geoscientist, provide a critical summary of internally consistent, thermodynamic data for minerals and other related solids. Robie, Hemingway and Fisher (1978) also used the key thermodynamic values from CODATA (1976) and made extensive use of the tabulated data in the NBS Series 270 and the JANAF (Stull and Prophet 1971) publications. Their selection of these references thus minimizes incompatibility between the thermochemical tables in Robie, Hemingway and Fisher (1978) and the data bank in all published versions of WATEQ. Moreover, the main source of thermodynamic data used for solids in the original version of the data base of WATEQ (Truesdell and Jones 1974) was Robie and Waldbaum (1968). This latter publication is the parent to the more recent bulletin by Robie, Hemingway and Fisher (1978). Both of these bulletins relied on early tabulations by Kelley (1960) and Kelley and King (1961) for relative enthalpy ($H_T^0 - H_{298}^0$)^(a), entropy (S_T^0), and heat capacity (C_p^0) data for minerals and related substances. Robie and his coworkers have augmented these sources of data with critical literature reviews of publications that contain more recently measured or revised thermodynamic values of heats of formation ($\Delta H_{f,T}^0$), Gibbs free energy of formation ($\Delta G_{f,T}^0$), ($H_T^0 - H_{298}^0$), S_T^0 , and C_p^0 .

(a) The subscript "298" refers to a standard reference temperature of 298.15 K (25.0°C). The superscript "o" accompanying thermodynamic symbols refers to a standard reference pressure of 1.0 atm (1.013 bars).

The JANAF Thermochemical Tables by Stull and Prophet (1971) and their later supplements (Chase et al. 1974, 1975, 1978) were also considered as a source of thermodynamic data for minerals and other solid phases. These tables were compiled as a task in the National Standard Reference Data System and were administered by the U.S. National Bureau of Standards. Because the JANAF tables were also used in the review and compilation of Robie, Hemingway and Fisher (1978), our tabulation of data from the JANAF tables was a somewhat superfluous act with respect to a comparison of thermodynamic values. However, the importance of these tables by Stull and Prophet (1971) and Chase et al. (1974, 1975, 1978) should not be understated; the data and accompanying documentation are informative and valuable.

The "standard" thermodynamic data tabulated in the compilations cited above are primarily based on direct calorimetric, solubility, electrochemical and spectroscopic measurements. However, a different approach was taken in the derivation and tabulation of thermochemical data by Helgeson et al. (1978). These latter authors used thermodynamic relations to combine existing or estimated thermodynamic data with mineral-equilibria relations determined from hydrothermal experiments to derive an internally consistent set of thermodynamic values for minerals. Their criteria for these derivations are that the resulting thermodynamic values be compatible with geologic observations and with studies of phase equilibria between minerals. A further difference in approach is that the values derived by Helgeson et al. (1978) were not necessarily referenced back to thermodynamic data from the NBS Series 270 and CODATA publications, especially with respect to data for the aqueous species. Although thermodynamic values from Helgeson et al. (1978) were not selected for the present additions to the data base in WATEQ3, values from Helgeson et al. (1978) were included in the preliminary compilation and were used as an indication that the accepted thermodynamic data were compatible with observed mineral-stability relations.

Sadiq and Lindsay (1979) also completed a literature review, critique, and tabulation of thermodynamic data for minerals, amorphous phases, and aqueous species relevant to the chemistry of soils. Much of the data in Sadiq and Lindsay (1979) for minerals and related solids are referenced to the

values given in the NBS Series 270 and CODATA tabulations, as well as to publications by R. Robie and B. Hemingway. Thus, the differences between the values given in Sadiq and Lindsay (1979) and Robie, Hemingway and Fisher (1978) should be relatively minor. Based on the values cited in Sadiq and Lindsay (1979), most of the small differences can probably be attributed to their accepted values for the ancillary thermochemical values used to compute the $\Delta G_{f,298}^0$ values for the solids.

Naumov, Ryzhenko and Khodakovsky (1974) was also used as a potential source of thermodynamic data for minerals and related solid phases. Their tabulation was reviewed for potential references in the Soviet literature that may have been missed in the other thermodynamic tabulations; however, no new references were identified. Although some undocumented criticisms exist with respect to internal inconsistencies of the thermodynamic data tabulated in Naumov, Ryzhenko and Khodakovsky (1974), no obvious inconsistencies were found during this review. Moreover, because Naumov, Ryzhenko and Khodakovsky (1974) reference most of their thermodynamic data for silicate minerals to Kelley (1960) and Kelley and King (1961), their data are often identical with those in Robie and Waldbaum (1968) and Robie, Hemingway and Fisher (1978).

THERMODYNAMIC DATA SELECTED FOR MINERALS
AND RELATED SOLID PHASES

Values of $\Delta H_{f,298}^0$ based on the elements and of S_{298}^0 were selected for minerals, related solids, aqueous species, and elements from the references described in the previous section. These values were then used to calculate a set of internally consistent $\Delta G_{f,298}^0$ values for the minerals and solids of interest. Selection of the accepted $\Delta H_{f,298}^0$ and S_{298}^0 values was based on the recentness and creditability of the published compilations of thermodynamic data and on earlier additions of data to the WATEQ models.

The selected thermodynamic values for the minerals, elements, and related solids and aqueous species, which were used to compute the final values of heats of reaction, $\Delta H_{r,298}^0$, and $\log_{10} K_{r,298}^0$, are given in Tables 2, 3, and 4.^(a) These tables contain lists of accepted values of $\Delta G_{f,298}^0$, $\Delta H_{f,298}^0$ (based on the elements), and S_{298}^0 , as well as the sources from which these values were chosen. With four exceptions [data for $\text{Al}(\text{OH})_4^-$, wollastonite, gehlenite, and åkermanite], the sources of data in Tables 2, 3 and 4 are those discussed in the previous section.

Robie, Hemingway and Fisher (1978) was the major source for the accepted data in Tables 2, 3, and 4. The NBS Series 270 and CODATA publications, however, were also used extensively. If the values tabulated in Robie, Hemingway and Fisher (1978) for a particular solid phase or species are identical to the values given in the NBS Series 270 or CODATA tabulations, the selected data are referenced back to these earlier publications. Values taken from Robie, Hemingway and Fisher (1978), as a main source of thermodynamic data, should maintain internal consistency in the data bank because this compilation relies heavily on the thermodynamic data tabulated in the NBS Series 270 publications and Robie and Waldbaum (1968), as did earlier versions of the WATEQ model.

(a) A sufficient number of digits are given for thermodynamic values throughout this report to ensure their traceability to their quoted sources. For conversion, 1 cal = 4.184 Joules absolute was used.

TABLE 2. Accepted Thermodynamic Values for Elements Used for Calculation of Values of $\Delta H_{f,298}^0$ and $\text{Log}_{10} K_{f,298}^0$. [By convention, $\Delta H_{f,298}^0$ and $\Delta G_{f,298}^0$ for the elements are equal to zero. The abbreviations "c" and "g" refer to crystalline and gaseous states, respectively. All entropy values are equal to those in Robie, Hemingway and Fisher (1978), corrected to 1 atm.]

Element	S_{298}^0 (cal mol ⁻¹ K ⁻¹)	Reference
Al (c)	6.776	CODATA (1976)
Ca (c)	9.950	Robie, Hemingway and Fisher (1978)
F ₂ (g)	48.443	CODATA (1976)
Fe (c)	6.520	Wagman et al. (1969)
H ₂ (g)	31.207	CODATA (1976)
K (c)	15.46	CODATA (1976)
Mg (c)	7.811	Robie, Hemingway and Fisher (1978)
Na (c)	12.26	CODATA (1976)
O ₂ (g)	49.006	CODATA (1976)
Si (c)	4.496	CODATA (1976)

Certain thermodynamic values for $\text{Al}(\text{OH})_4^-$, wollastonite (CaSiO_3), åkermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$), and gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) were taken from sources other than those described in the previous section. The revised Gibbs free energy of formation for $\text{Al}(\text{OH})_4^-$ was selected from Hemingway, Robie and Kittrick (1978) because it had been recomputed from the new heat of formation for gibbsite [$\text{Al}(\text{OH})_3$] determined by Hemingway and Robie (1977a) and tabulated in Robie, Hemingway and Fisher (1978). A revised entropy at 298 K, S_{298}^0 , for wollastonite (CaSiO_3) was taken from the recent study of Krupka et al. (1980). The latter authors calculated a revised entropy of wollastonite based on their new low-temperature heat capacity measurements. Revised values of $\Delta H_{f,298}^0$ for

TABLE 3. Accepted Thermodynamic Values for Aqueous Species Used for Calculation of Values of $\Delta H_{f,298}^0$ and $\text{Log}_{10} K_{r,298}^0$. [The standard state for an aqueous species is a molality of 1.0. Unless otherwise noted, $\Delta H_{f,298}^0$ and S_{298}^0 values are from the same reference. Values noted by asterisk are identical to those in Robie, Hemingway and Fisher (1978) corrected to 1 atm.]

Species	$\Delta H_{f,298}^0$ (kcal mol ⁻¹)	$\Delta G_{f,298}^0$ (kcal mol ⁻¹)	S_{298}^0 (cal mol ⁻¹ K ⁻¹)	Reference
Al ⁺³	-126.9	-116.9	-73.61	Robie, Hemingway and Fisher (1978)
Al(OH) ₄ ⁻	--	-311.9	--	Hemingway, Robie and Kittrick (1978)
Ca ⁺²	-129.740*	-132.294	-12.69*	Parker, Wagman and Evans (1971)
CaOH ⁺	--	-171.7	--	Parker, Wagman and Evans (1971)
Ca(OH) ₂ ⁰	-239.68	-207.49	-17.8	Parker, Wagman and Evans (1971)
F ⁻	-80.151*	-67.34	-3.150*	CODATA (1976)
Fe ⁺²	-21.3*	-18.85	-32.9*	Wagman et al. (1969)
Fe ⁺³	-11.6*	-1.10	-75.5*	Wagman et al. (1969)
K ⁺	-60.270*	-67.513	24.149*	CODATA (1976)
Mg ⁺²	-111.58*	-108.7	-33.0*	Parker, Wagman and Evans (1971)
Na ⁺	-57.43*	-62.59	13.96*	CODATA (1976)
OH ⁻	-54.977*	-37.604	-2.560*	CODATA (1976)
H ₄ SiO ₄ ⁰	-348.9*	-312.55	43.021*	ΔH : Robie et al. (1978); S: Wagman et al. (1968)

TABLE 4. Accepted Thermodynamic Values for Several Additional Solids and Water for Calculation of Values of $\Delta H_f^0, 298$ and $\log_{10} K_p$.
 [All values are corrected to a 1 atm pressure; ℓ = liquid. Unless otherwise noted, $\Delta H_f^0, 298$ and S_{298}^0 values are from the same reference. Values noted by asterisk are identical to those in Robie, Hemingway and Fisher (1978) corrected to 1 atm.]

Formula	Mineral or Solid Phase	$\Delta H_f^0, 298$ (kcal mol ⁻¹)	$\Delta G_f^0, 298$ (kcal mol ⁻¹)	S_{298}^0 (cal mol ⁻¹ K ⁻¹)	Reference
CaO	Lime	-151.790	-144.241	9.132	Robie, Hemingway and Fisher (1978)
Ca(OH) ₂	Portlandite	-235.680*	-214.740	19.93*	Parker, Wagman and Evans (1971)
Fe _{0.947} O	Wustite	-63.640*	-58.597	13.764	ΔH : Wagman et al. (1969) S: Robie, Hemingway and Fisher (1978)
H ₂ O (ℓ)	Water	-68.315*	-56.690	16.718*	CODATA (1976)
MgO	Periclase	-143.760	-136.045	6.439	Robie, Hemingway and Fisher (1978)
FeAl ₂ O ₄	Hercynite	-470.000*	-442.366	25.399	ΔH : Wagman et al. (1969) S: Robie, Hemingway and Fisher (1978)
MgAl ₂ O ₄	Spinel	-549.551	-519.705	19.271	ΔH : Robie, Hemingway and Fisher (1978); S: Parker, Wagman and Evans (1971)
MgFe ₂ O ₄	Magnesio-ferrite	-341.401*	-314.788	29.601	ΔH : Parker, Wagman and Evans (1971) S: Robie, Hemingway and Fisher (1978)
Na ₃ AlF ₆	Cryolite	-791.000	-751.676	56.991	Robie, Hemingway and Fisher (1978)
CaSiO ₃	Wollastonite	-390.827	-370.424	19.524	ΔH : Robie, Hemingway and Fisher (1978); S: Krupka, Kerrick and Robie (1980)

TABLE 4. contd

Formula	Mineral or Solid Phase	$\Delta H_f^0, 298$ (kcal mol ⁻¹)	$\Delta G_f^0, 298$ (kcal mol ⁻¹)	S_{298}^0 (cal mol ⁻¹ K ⁻¹)	Reference
CaSiO ₃	Pseudowollastonite	-389.257	-369.265	20.901	Robie, Hemingway and Fisher (1978)
Ca ₂ (SiO ₄)	Ca-Olivine	-553.685	-525.776	28.800	Robie, Hemingway and Fisher (1978)
β -Ca ₂ (SiO ₄)	Larnite	-551.142	-523.740	30.500	Robie, Hemingway and Fisher (1978)
Ca ₃ SiO ₅		-700.1	-665.35	40.3	Parker, Wagman and Evans (1971)
CaMgSiO ₄	Monticellite	-540.799	-512.246	24.500	Robie, Hemingway and Fisher (1978)
Ca ₂ MgSi ₂ O ₇	Akermanite	-924.10	-876.935	50.031	ΔH : Charlú, Newton and Kleppa (1981); S: Robie, Hemingway and Fisher (1978)
Ca ₃ Mg(SiO ₄) ₂	Merwinite	-1091.489	-1037.173	60.500	Robie, Hemingway and Fisher (1978)
KAlSiO ₄	Kalsilite	-507.151	-479.455	31.850	Robie, Hemingway and Fisher (1978)
KAlSi ₂ O ₆	Leucite	-726.255	-687.377	47.849	Robie, Hemingway and Fisher (1978)
KAlSi ₃ O ₈	Microcline	-948.301	-894.469	51.195	Robie, Hemingway and Fisher (1978)
KAlSi ₃ O ₈	High Sanidine	-946.358	-893.859	55.664	Robie, Hemingway and Fisher (1978)
NaAlSiO ₄	Nepheline	-500.026	-472.649	29.720	Robie, Hemingway and Fisher (1978)
Ca ₂ Al ₂ SiO ₇	Gehlenite	-951.00	-903.50	50.143	ΔH : Charlú, Newton and Kleppa (1981); S: Robie, Hemingway and Fisher (1978)

åkermanite and gehlenite were taken from Charlu, Newton and Kleppa (1981). Values of $\Delta H_{f,970}^0$ for these two silicates were determined by Charlu, Newton and Kleppa using high-temperature, molten-oxide solution calorimetry. They then extrapolated these high-temperature values to 298 K and calculated $\Delta H_{f,298}^0$ values based on the elements using heat capacity and $\Delta H_{f,298}^0$ data in Robie, Hemingway and Fisher (1978). Values of $\Delta H_{f,298}^0$ for wollastonite and S_{298}^0 for åkermanite and gehlenite, however, were selected from Robie, Hemingway and Fisher (1978).

Because of the considerable effort required, a total revision of the data bank for WATEQ3 is not immediately feasible. The use of superceded thermodynamic data to compute $\log_{10} K_{r,298}^0$ values simply for the sake of internal consistency is unjustifiable because modeling efforts would then be based on inferior data. Thus, our newly accepted thermodynamic data may be inconsistent with the previously used data for the ancillary species necessary to calculate the $\Delta H_{r,298}^0$ and $\log_{10} K_{r,298}^0$ values for the dissolution reactions of the solid phases. These inconsistencies should be minor, especially when considered in the computation of $\log_{10} K_{r,298}^0$ values, because Robie, Hemingway and Fisher (1978) also reference the NBS Series 270 tabulations. The problem of internal consistency may exist particularly in hydrolysis reactions that contain the aqueous species $\text{Al}(\text{OH})_4^-$. Robie, Hemingway and Fisher (1978) accepted a revised $\Delta G_{f,298}^0$ for $\text{Al}(\text{OH})_4^-$ based on the work of Hemingway, Robie and Kittrick (1978). For example, the $\log_{10} K_{r,298}^0$ values for the association reaction of $\text{Al}(\text{OH})_4^-$ as now exists in the WATEQ2 data base and as calculated from the data in Tables 3 and 4 are, respectively, -23.0 (Ball, Jenne and Nordstrom 1979, Reaction 82) and -23.35. Because many of the $\log_{10} K_{r,298}^0$ values in WATEQ are based on solubility measurements (e.g., gibbsite), the $\log_{10} K_{r,298}^0$ values will depend on the $\Delta G_{f,298}^0$ values for $\text{Al}(\text{OH})_4^-$, as well as on ancillary data for Al^{+3} , H_2O , OH^- , and pertinent solid phases. Therefore, although the inconsistencies are expected to be minor, they must be evaluated on a case-by-case basis as time permits.

Two of the new, improved thermodynamic values that Robie, Hemingway and Fisher (1978) have accepted are particularly significant to the WATEQ data base. One revision includes the changes in the $\Delta H_{f,T}^0$ and $\Delta G_{f,T}^0$ for the

Al^{+3} ion, the aluminum-hydroxide minerals (including gibbsite), and several aluminosilicate minerals. These major revisions are based on a new enthalpy of formation of gibbsite $[\text{Al}(\text{OH})_3]$, and an enthalpy correction for a particle-size effect in the heat of solution for α -quartz (Hemingway and Robie 1977a). As explained in Robie, Hemingway and Fisher (1978, p. 9), the enthalpy of formation of gibbsite is particularly important because gibbsite is commonly used as the aluminum-bearing phase in a reaction scheme for solution calorimetry of aluminosilicate minerals. Possible discrepancies in the published thermodynamic data for gibbsite were recognized more than a decade ago (Kittrick 1966). The enthalpy of formation, therefore, of a phase derived from such a solution-reaction scheme will depend on the currently accepted values for the enthalpies of formation for the reactants (i.e., gibbsite). Thus, when a new heat of formation is determined for a reference reactant, all heats of formation derived with that reactant must be recalculated to account for the difference between the new and old values. Revisions resulting from the new $\Delta H_{f,298}^0$ of gibbsite were made to thermodynamic data for aluminosilicates in Hemingway and Robie (1977a); for aqueous $\text{Al}(\text{OH})_4^-$, diaspore, boehmite and bayerite in Hemingway, Robie and Kittrick (1978); and for the Al^{+3} ion in Hemingway and Robie (1977b).

The second revision of major importance, which was incorporated in the tabulation of Robie, Hemingway and Fisher (1978), was a correction for particle-size effects in the heat of solution of α -quartz. This correction was applied to some $\Delta H_{f,298}^0$ values of silicate minerals that were determined at the Berkeley Thermodynamics Laboratory of the U.S. Bureau of Mines. The heat of solution of α -quartz was determined experimentally by Hemingway and Robie (1977a) to be greater by 300 cal mol^{-1} for quartz particles less than $10 \text{ }\mu\text{m}$, relative to quartz with larger diameters. Hemingway and Robie (1977a) also found that the Berkeley Thermodynamics Laboratory of the U.S. Bureau of Mines utilized α -quartz of less than $10 \text{ }\mu\text{m}$ in several solution calorimetric studies. Because the enthalpy corrections for this particle-size effect were not realized at the time of their investigations, some of the published $\Delta H_{f,298}^0$ values were based on an inappropriate heat of solution for α -quartz.

Hemingway and Robie (1977a) have reviewed the published data from this group at the U.S. Bureau of Mines and have recalculated the $\Delta H_{f,298}^0$ and $\Delta G_{f,298}^0$ values for several silicate minerals originally computed with the incorrect heat of solution of α -quartz.

The reference state for thermodynamic values in Robie, Hemingway and Fisher (1978) is a temperature of 298.15 K and a pressure of 1 bar (0.9867 atm, or 10^5 Pascals). Thus, for consistency with older tabulations (i.e., NBS Series 270) and the data base in WATEQ, the values selected from Robie, Hemingway and Fisher (1978) must be converted from $P = 0.9867$ atm to a $P = 1.0$ atm standard state. This conversion, computed from the gas law, decreases the entropy of gaseous elements by a constant $0.026 \text{ cal mol}^{-1}\text{K}^{-1}$. Values of $\Delta G_{f,298}^0$ from the elements were recomputed for the selected minerals in Tables 2, 3, and 4, based on the entropies of the gaseous elements at 1 atm. The resulting changes to the values of $\Delta G_{f,298}^0$ for these minerals were minor. A factor of $1 \text{ cal} = 4.1840 \text{ Joules}$ absolute was used to convert the data in Robie, Hemingway and Fisher (1978) to units of calories.

The entropy values (S_{298}^0) tabulated in Robie, Hemingway and Fisher (1978) for aluminosilicate minerals have also been corrected for any configurational entropy terms. These configurational entropies result from Al/Si disorder that is frozen in certain aluminosilicate structures at 0.0 K. In this instance, $S_0^{(a)}$ does not equal zero at 0.0 K (i.e., for high sanidine, $S_0^0 = 4.47 \text{ cal mol}^{-1}\text{K}^{-1}$). The tabulation by Ulbrich and Waldbaum (1976) was used by Robie, Hemingway and Fisher (1978) as a guide for assessing these corrections to the entropy terms.

Tables 2, 3, and 4 also contain our selected thermochemical data for the ancillary components (i.e., elements and aqueous species) necessary to compute values of $\Delta H_{r,298}^0$ and $\log_{10} K_{r,298}^0$ for the hydrolysis reactions. For the aqueous species, the standard state of the selected data is the "hypothetical ideal 1 molal solution," in which the solute has some of the partial molar

(a) The use of "0" as a subscript denotes a temperature of zero Kelvin (-273.15°C).

properties of the infinitely dilute solution (Glasstone 1972). The reference state is, in turn, the infinitely dilute solution. Thus, the activity "A" of the solute is defined such that the ratio of this activity to the molality "m" is then unity at a pressure of one atmosphere. This definition (Glasstone 1972) is based on the principle that

$$\frac{A}{m} \rightarrow 1 \quad \text{as} \quad m \rightarrow 0.$$

SELECTION OF $\Delta G_{f,298}^0$ VALUES FOR LEPIDOCROCITE

Lepidocrocite, $\gamma\text{-FeO(OH)}$, is dimorphous with goethite, $\alpha\text{-FeO(OH)}$. Lepidocrocite forms typically from the rapid oxidation of Fe(II) through the intermediate products of green Fe(II) solution complexes or solid green rusts (Murray 1979). Its formation is generally restricted to Fe(II) systems, but it may occasionally form from pure Fe(III) systems. The addition of thermodynamic data for lepidocrocite is therefore necessary to competently model solubility controls in waters that may undergo rapid oxidation from low E^H conditions. In the compilations described earlier, Sadiq and Lindsay (1979) provide the only tabulation of data for lepidocrocite.

Sadiq and Lindsay (1979) calculated $\Delta G_{f,298}^0$ values for lepidocrocite based on $\log_{10} K_{r,298}^0 = -38.7$ (Langmuir 1969) and $\log_{10} K_{r,298}^0 = -40.6$ (Schuylenborgh 1973) for the reaction

Based on the above $\log_{10} K_{r,298}^0$ from Langmuir (1969), Sadiq and Lindsay (1979) computed a $\Delta G_{f,298}^0 = -112.9 \text{ kcal mol}^{-1}$ for lepidocrocite. On the other hand, Langmuir (1969) tabulated $\Delta G_{f,298}^0 \leq -169.614 \text{ kcal mol}^{-1}$ for lepidocrocite and $\Delta G_{f,298}^0 \geq -115.280$ to $-116.375 \text{ kcal mol}^{-1}$ for goethite, which appears to be a discrepancy with the known stability of lepidocrocite relative to goethite. Lepidocrocite, being dimorphous with goethite [$\alpha\text{-FeO(OH)}$], is considered less stable than goethite at 25°C and 1 atm total pressure (Langmuir 1969; Murray 1979). We have attributed this discrepancy to a possible typographical error by Langmuir, or possibly to the fact that Langmuir (1969) tabulated a minimum $\Delta G_{f,298}^0$ for goethite and a maximum $\Delta G_{f,298}^0$ for lepidocrocite. From the data of Schuylenborgh (1973), Sadiq and Lindsay (1979) calculated $\Delta G_{f,298}^0 = -115.50 \text{ kcal mol}^{-1}$ for lepidocrocite.

Gibbs free energies of formation at 298 K of -112.610 and $-110.018 \text{ kcal mol}^{-1}$ (Table 5) were computed, respectively, from the $\log_{10} K_{r,298}^0$ values of -40.6 (Schuylenborgh 1973) and -38.7 (Langmuir

TABLE 5. $\Delta G_{f,298}^0$ for Lepidocrocite and $\log_{10} K_r^0$ for Its Hydrolysis Reaction: $\gamma\text{-FeO(OH)} + 3\text{H}^+ = \text{Fe}^{+3} + 2\text{H}_2\text{O}$.

<u>Data Source</u>	<u>$\Delta G_{f,298}^0$</u> <u>(kcal mol⁻¹)</u>	<u>$\log_{10} K_r^0$</u>
Schuylenborgh (1973)	-112.610	1.371
Langmuir (1969)	-110.018	3.271

1969), using the accepted $\Delta G_{f,298}^0$ values in Tables 2 and 3. These free energy values differ by 2.9 kcal from the corresponding values computed by Sadiq and Lindsay (1979) as a result of the different values used for $\Delta G_{f,298}^0$ of Fe^{+3} .

A $\Delta G_{f,298}^0$ value of $-112.610 \text{ kcal mol}^{-1}$ was accepted as the best free energy value for lepidocrocite. Although somewhat subjective, this decision was based on the following logic: 1) data of Schuylenborgh (1973) were more recent, and 2) this $\Delta G_{f,298}^0$ was in accord with the "best" value recommended by Sadiq and Lindsay (1979). The $\Delta G_{f,298}^0$ value calculated from the data of Langmuir (1969) will be used as a limit for the "maximum" positive $\Delta G_{f,298}^0$ value for lepidocrocite.

ESTIMATION OF $\Delta G_{f,298}^0$ FOR IDEAL END-MEMBER NONTRONITE
AND HANFORD NONTRONITE

Nontronite, an iron-rich clay, is an end member of the montmorillonite group (smectites) of minerals. In the ideal nontronite structure, the octahedral positions contain Fe^{+3} and the tetrahedral positions are filled with Al^{+3} and Si^{+4} at the atomic ratio of 0.33 Al/3.67 Si (Deer, Howie and Zussman 1967). Nontronite is a common alteration product in fractures and vesicles in Columbia River basalts under the Hanford Site in southeast Washington. Thus, to adequately model solubility controls in basalt aquifers, a geochemical model should contain thermodynamic data for nontronite. Because the thermodynamic properties of nontronite have not been determined by calorimetric or solubility measurements, $\Delta G_{f,298}^0$ values for ideal end-member nontronite and a composition that approximates nontronite in the Columbia River basalts were calculated using the estimation method of Mattigod and Sposito (1978).

DESCRIPTION OF ESTIMATION METHODS

Methods for estimating the Gibbs free energy of formation of clay minerals (Slaughter 1966a, 1966b, 1966c; Tardy and Garrels 1974; Chen 1975; Nriagu 1975; and Mattigod and Sposito 1978) differ greatly in complexity, underlying assumptions, and actual success in predicting Gibbs free energies of formation for minerals whose $\Delta G_{f,298}^0$ values were previously determined by experimental methods. A discussion and comparison of all reported methods are beyond the scope of this document. [See Benson, Carnahan and Che (1980) for a brief review of the different methods for estimating $\Delta G_{f,298}^0$ of layer silicates. Their general criticism, which we also support, centers on the empirical nature of these estimation methods.]

In this study, the approach of Mattigod and Sposito (1978) was used because of: 1) its simplicity, 2) its provision of a Gibbs free energy correction for cation bonding on the exchangeable, interlayer sites, and 3) its success in estimating $\Delta G_{f,298}^0$ for montmorillonite compositions for which $\Delta G_{f,298}^0$ has been determined experimentally. The estimation methods of

Mattigod and Sposito (1978) and Tardy and Garrels (1974), another commonly used technique, are briefly described. Benson, Carnahan and Che (1980) have criticized the approach of Mattigod and Sposito because it relies on the estimation technique of Chen (1975)^(a) to derive a relationship to correct $\Delta G_{f,298}^0$ for cation bonding on the exchangeable, interlayer sites.^(b) Calculated $\Delta G_{f,298}^0$ values by Mattigod and Sposito (1978), who used this correction scheme, are in good agreement with data from published solubility studies. However, as pointed out by Benson, Carnahan and Che (1980), the solubility studies for clay minerals may themselves be in error due to kinetic limitations in the experiments. Therefore, the use of Chen's approach does not appear to invalidate the estimation method proposed by Mattigod and Sposito (1978), nor does it decrease the empirical nature of their approach. Based on currently available solubility data for clays, the method of Mattigod and Sposito (1978) appears to give the most reasonable estimates of $\Delta G_{f,298}^0$ for clays.

The estimation method described by Mattigod and Sposito (1978) for smectite clays involves a summation of the Gibbs free energies for hydroxide or oxide and H₂O components based on the stoichiometry of the clay and a correctional, free energy term for cation bonding in the exchangeable, interlayer sites. This method can be described by the equation:

$$\Delta G_{f,298}^0 (\text{clay}) = \sum n_i \Delta G_{f,298}^0 (r_i) - (\sum n_i X_i - 12) \Delta G_{f,298}^0 (\text{H}_2\text{O}) - |\delta|$$

where

n_i = stoichiometric reaction coefficient of the ith hydroxide or oxide;

X_i = charge on the cation in the ith hydroxide or oxide;

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- (a) The $\Delta G_{f,298}^0$ -estimation method of Chen (1975) and its limitations are not discussed in our report. They are briefly discussed in Benson, Carnahan and Che (1980) and will be obvious on reading Chen (1975).
 (b) For the $\Delta G_{f,298}^0$ estimations for nontronite, these corrections varied between 4 and 10 percent of the final $\Delta G_{f,298}^0$ values.

$\Delta G_{f,298}^0(r_i)$ = standard Gibbs free energy of formation for the ith hydroxide or oxide in the reaction;

$\Delta G_{f,298}^0(H_2O)$ = standard Gibbs free energy of formation for liquid H_2O ;

$|\delta|$ = absolute value for Gibbs free energy correction based on the exchange capacity of the clay, and the ionic radius and valence of the cation in the exchangeable, interlayer site.

Mattigod and Sposito (1978) present estimation methods based on hydroxide and also on oxide components. The hydroxide-summation method was chosen for our $\Delta G_{f,298}^0$ estimations because the free energy calculations by Mattigod and Sposito, using hydroxide components, are in closer agreement to experimentally-determined $\Delta G_{f,298}^0$ values for several montmorillonites than their calculations are when using oxide components. The general formula for ideal, end-member nontronite (Deer, Howie and Zussman 1967) is

where A refers to the exchangeable cations Na, K, 0.5Ca, or 0.5Mg. For estimating the free energy of ideal nontronite, the formation reaction from the hydroxides is written as

Because the oxygen and hydrogen do not balance in the above reaction, a free energy term [i.e., $(\sum n_i X_i - 12)\Delta G_{f,298}^0(H_2O)$] is applied to the estimation to balance the hydroxyl units in the formation reaction. The stoichiometry for the formation reaction from the hydroxides will obviously differ from those for clays with intermediate compositions. Moreover, the water component (nH_2O) is not included in this reaction because of its low stability in the clay structure.

The correctional term for the exchangeable cation was calculated by Mattigod and Sposito (1978) from the differences between estimated [using the method of Chen (1975)] and experimentally determined $\Delta G_{f,298}^0$ values as a

function of the exchange capacity of the clay, and of the radius and valence of the exchangeable cation. These observed trends were then fit to equations by multiple regression techniques. For the hydroxide-summation method, their equation for the correction for exchangeable cations is

$$\ln_e |\delta| = 1.9283C + 0.3501X - 0.2819Z + 3.5427$$

where

C = exchange capacity of the clay per formula unit, in equivalents per formula weight;

X = radius of the exchangeable cation, in angstroms (Å) (1 nm = 10 Å);

Z = valence of the exchangeable cation.

The antilog of this value is then subtracted from the free energy summation.

Gibbs free energy of formation values for the Na and Ca end-member compositions of nontronite were also estimated with the method of Tardy and Garrels (1974). This method also involves the summation of ΔG_f^0 values for oxide and hydroxide components whose compositions total to the stoichiometry of the clay or layer silicate. However, the ΔG_f^0 values used in the estimation method (Tardy and Garrels 1974) are not the standard $\Delta G_{f,298}^0$ values normally tabulated for the separate oxide and hydroxide phases, but are free energy values calculated for these components accounting for structural effects of the layer silicate. The basic assumption of this method is that the "silicated" free energies for the oxide and hydroxide components within the silicate structure are independent of the matrix in which they occur; that is, the crystal-structure effects are of little consequence. Therefore, one can calculate the "silicated" free energies for oxide and hydroxide components from complex layer silicates using their known, standard Gibbs free energies of formation. For example, by solving simultaneous equations, Tardy and Garrels (1974) calculated "silicated" free energies, $\Delta G_{f,sil}^0$, for SiO_2 , MgO and Mg(OH)_2 from the following equations:

$$4\Delta G_{f,sil}^0(\text{SiO}_2) + 2\Delta G_{f,sil}^0(\text{MgO}) \\ + \Delta G_{f,sil}^0(\text{Mg(OH)}_2) = \Delta G_{f,298}^0(\text{talc})$$

$$3\Delta G_{f,sil}^0(\text{SiO}_2) + 2\Delta G_{f,sil}^0(\text{Mg(OH)}_2) \\ = \Delta G_{f,298}^0(\text{sepiolite}) \quad .$$

Values of $\Delta G_{f,298}^0$ based on the elements for chrysotile, talc and sepiolite were then taken by Tardy and Garrels from published tabulations. Similar equations were written to derive $\Delta G_{f,sil}^0$ for Na_2O , K_2O , CaO , Al_2O_3 and Al(OH)_3 .

Because accurate $\Delta G_{f,298}^0$ values for layer silicates containing ferric iron are lacking, Tardy and Garrels (1974) had to assign a value to $\Delta G_{f,sil}^0(\text{Fe}_2\text{O}_3)$. The calculated value of $\Delta G_{f,sil}^0(\text{SiO}_2)$ was identical to the standard $\Delta G_{f,298}^0$ of quartz from which Tardy and Garrels concluded that the energy associated with silication of SiO_2 was zero. Because the electronegativity for Fe^{+3} is similar to that for Si^{+4} , Tardy and Garrels assumed that the energy of silication was also zero for the silicated Fe_2O_3 component. Therefore, they equated the $\Delta G_{f,sil}^0(\text{Fe}_2\text{O}_3)$ to the standard $\Delta G_{f,298}^0$ of hematite, Fe_2O_3 .

Tardy and Garrels (1974) also calculated Gibbs free energy values, $\Delta G_{f,ex}^0$, for components in the exchangeable, interlayer sites in the clays. Using published equilibrium constants for exchange reactions, they evaluated the differences between Gibbs free energies for layer silicates as a function of the cations in the interlayer sites. Based on some reaction data for muscovite, Tardy and Garrels then assumed that $\Delta G_{f,ex}^0$ and $\Delta G_{f,sil}^0$ were equal for the K_2O component. Values for $\Delta G_{f,ex}^0$ for the other oxide components in the exchange sites (e.g., Na_2O) were calculated by the addition of these free energy differences to the $\Delta G_{f,sil}^0(\text{K}_2\text{O})$.

Tardy and Garrels (1974) normally assigned the magnesium first to the silicated Mg(OH)_2 instead of the silicated MgO component for cases of hydrated silicates. Although Tardy and Garrels determined values for $\Delta G_{f,sil}^0(\text{H}_2\text{O})$ and $\Delta G_{f,ex}^0(\text{H}_2\text{O})$, the hydroxyl units in the layer silicate

structure are balanced by the addition of sufficient $\text{Mg}(\text{OH})_2$ in the ΔG_f^0 summation. Residual magnesium required to balance the Mg^{+2} content in the clay was added as the silicated MgO component.

To estimate the $\Delta G_{f,298}^0$ of a given clay with the procedure of Tardy and Garrels, the formula for the clay is broken down into the appropriate oxide and hydroxide components in the proper stoichiometric proportions. The sum of $\Delta G_{f,\text{sil}}^0$ and $\Delta G_{f,\text{ex}}^0$ values for these components is then equated to the $\Delta G_{f,298}^0$ for that layer silicate composition.

CALCULATION OF $\Delta G_{f,298}^0$ FOR IDEAL END-MEMBER NONTRONITE

Gibbs free energy of formation from the elements at 298.15 K were estimated with the method of Mattigod and Sposito (1978) for four end-member compositions of nontronite. These end-member compositions, which differ only in the cations present in the exchangeable sites, include:

For comparison, $\Delta G_{f,298}^0$ values were also estimated using the method of Tardy and Garrels (1974) for the end-member compositions of nontronite that have the extreme $\Delta G_{f,298}^0$ values computed by the method of Mattigod and Sposito (1978). Ancillary values of $\Delta G_{f,298}^0$ for $\text{Al}(\text{OH})_3$, $\text{Ca}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, KOH , NaOH , and $\text{Mg}(\text{OH})_2$ were taken from Robie, Hemingway and Fisher (1978) and corrected from the 1 bar to 1 atm standard state. The $\Delta G_{f,298}^0$ of solid $\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ was taken from the NBS Technical Note Series 270-3 (Wagman et al. 1968).

To compute the bond correction, δ , for the free energies of cations in the exchangeable interlayer sites, values of 0.080 and 0.120 eq/100 g were used as extreme values for the exchange capacities of montmorillonite clays (Bohn, McNeal and O'Connor 1979). These values were multiplied by the formula weight of each composition to convert units of equivalents per mole (or per

"formula weight"). Values used for ionic radii, which were taken from Evans (1966), include 0.95, 1.33, 0.99, and 0.65 Å for Na^+ , K^+ , Ca^{+2} , and Mg^{+2} , respectively.

The $\Delta G_{f,298}^0$ values estimated for the four end-member nontronite compositions at the two different exchange capacities are given in Table 6. The estimated free energy values range from -1073.1 kcal/mol for Na-nontronite at the low exchange capacity to -1089.0 kcal/mol for Ca-nontronite at the high exchange capacity. The difference of 15.9 kcal between these extreme values constitutes only 1.5 percent of each $\Delta G_{f,298}^0$ value. The differences between these estimated values are not significant with respect to the estimation scheme when compared to the absolute magnitude of the free energy values, but are significant in the final $\log_{10} K_{r,298}^0$ values. For comparison, $\Delta G_{f,298}^0$ values estimated by Wolery (1978) for these same nontronite compositions are also listed in Table 6. Although Wolery used a different set of thermodynamic data and the estimation procedure of Tardy and Garrels (1974), no significant differences exist between the two sets of estimated $\Delta G_{f,298}^0$ values.

In order to compare estimation methods, Gibbs free energies for the ideal Na- and Ca-nontronites were also estimated using the procedure described by Tardy and Garrels (1974). These nontronite compositions were selected because they possessed the minimum and maximum $\Delta G_{f,298}^0$ values as calculated by the method of Mattigod and Sposito (1978). All standard, tabulated $\Delta G_{f,298}^0$ values were taken from Robie, Hemingway and Fisher (1978). The silicated Gibbs free energy, $\Delta G_{f,sil}^0$, for the SiO_2 and Fe_2O_3 components were set equal to the standard $\Delta G_{f,298}^0$ values of α -quartz and hematite, respectively (Tardy and Garrels 1974). The Gibbs free energies of quartz, kaolinite $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$, and pyrophyllite $[\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2]$ were used to evaluate by simultaneous equations the $\Delta G_{f,sil}^0$ of the Al_2O_3 , H_2O , and $\text{Al}(\text{OH})_3$ components. Similarly, the $\Delta G_{f,298}^0$ of muscovite, $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$, was used to calculate the $\Delta G_{f,sil}^0$ of the K_2O component. With the same assumption made by Tardy and Garrels (1974), the $\Delta G_{f,sil}^0$ of K_2O was equated to $\Delta G_{f,ex}^0$ of K_2O in the interlayer sites of the clay. Then, using the $\Delta G_{f,ex}^0$ of K_2O and the free energy differences tabulated in Tardy and Garrels (1974, Table 3), $\Delta G_{f,ex}^0$ values were calculated for Na_2O and CaO in the interlayer sites. These computed values of $\Delta G_{f,sil}^0$ and $\Delta G_{f,ex}^0$ are given in Table 7. Because there is

TABLE 6. Estimated $\Delta G_{f,298}^0$ Values for Ideal End-Member Nontronite and for a Nontronite Composition Characteristic of Altered Columbia Plateau Basalts at the Hanford Site.

Nontronite Composition	Method of Mattigod and Sposito (1978)		Method of Tardy and Garrels (1974)	Estimations in Wolery (1978)
	Low-Exchange(a) Capacity	High-Exchange(a) Capacity		
	$\Delta G_{f,298}^0$ (kcal mol ⁻¹)			
Na-nontronite ^(b)	-1073.1	-1079.6	-1079.6	-1078.271
K-nontronite	-1075.6	-1083.2		-1080.356
Ca-nontronite	-1084.0	-1089.0	-1080.8	-1079.492
Mg-nontronite	-1080.0	-1084.3		-1075.647
Hanford nontronite ^(c)	-1097.0	-1107.2		

(a) Low- and high-exchange capacities used for estimations were 0.080 and 0.120 eq/100 g, respectively.

(b) Compositions of nontronite given in Table 1.

(c) Composition of Hanford nontronite given in text (p. 35).

TABLE 7. Calculated Values for Silicated Free Energies ($\Delta G_{f,sil}^0$) for Estimation of $\Delta G_{f,298}^0$ of Ideal End-Member Nontronite Using the Method of Tardy and Garrels (1974).

Component	$\Delta G_{f,sil}^0$	$\Delta G_{f,sil,ex}^0$ (a)
	(kcal mol ⁻¹)	
SiO ₂	-204.67	
Fe ₂ O ₃	-177.52	
Al ₂ O ₃	-381.09	
Al(OH) ₃	-278.78	
H ₂ O	-58.82	
K ₂ O	-188.272	
CaO ^(a)		-183.07
Na ₂ O ^{ex(a)}		-175.67

(a) Subscript "ex" refers to component on the exchangeable, interlayer sites in the clay.

no Mg in the "ideal" nontronite, Mg(OH)₂ could not be used to balance hydroxyl units in the nontronite formula (Tardy and Garrels 1974). To balance the hydroxyl units, the $\Delta G_{f,298}^0$ of Na- and Ca-nontronite were estimated with $\Delta G_{f,sil}^0$ of either Al(OH)₃ or H₂O. The resulting $\Delta G_{f,298}^0$ values were identical when the calculations were based on either Al(OH)₃ or H₂O. The $\Delta G_{f,298}^0$ values estimated with the method of Tardy and Garrels (1974) for "ideal" Na- and Ca-nontronite are given in Table 6. They do not differ from the Gibbs free energy values estimated with the procedure of Mattigod and Sposito (1978) and those of Wolery (1978).

ESTIMATION OF COMPOSITION AND $\Delta G_{f,298}^0$ FOR HANFORD NONTRONITE

A composition, based on electron probe data, was estimated for the nontronite that exists in fractures and vesicles in Columbia River basalts under the Hanford Site in southeast Washington. Benson and Teague (1979) published extensive tables of clay compositions determined by electron probe

analyses of minerals in Hanford basalts. Because these were chemical analyses of "spot-locations" in mineral grains or aggregates, Benson and Teague could not complete an X-ray diffraction identification for each analyzed grain. Therefore, some subjective criteria had to be used to select a particular oxide analysis from all the clay analyses reported by Benson and Teague (1979). Ames (1980) has identified nontronite by X-ray diffraction in basalt core samples from the Hanford Reservation. In describing the common occurrence of nontronite throughout Columbia River basalts, Ames (1980, p. 155) reports that the nontronite usually contains 25 to 40 wt% ferric iron and the interlayer sites are dominated by calcium, some sodium, and little potassium. In the ideal nontronite structure, the octahedral positions contain Fe^{+3} and the tetrahedral positions are filled with Al^{+3} and Si^{+4} at the atomic ratio of 0.33 Al/3.67 Si (Deer, Howie and Zussman 1967).

Therefore, the following criteria were used for selecting a clay composition from Benson and Teague (1979) that approximates the composition of a Hanford nontronite:

1. analysis should contain little or no K_2O and MgO ,
2. analysis should contain 25 to 40 wt% ferric iron,
3. analysis should result in an atomic ratio of approximately 0.33 Al/3.67 Si.

Because ferric and ferrous iron cannot be differentiated by an electron probe analysis, Benson and Teague (1979) calculated their total iron contents in the oxide compositions as Fe_2O_3 . For our calculations, we assumed that these Fe_2O_3 values equal the total ferric iron in the clay. Based on these criteria, the analysis labeled Sample DC6 4220, 1286 m, Analysis A, and Number 26-31 was selected from Benson and Teague (1979, p. 62) to represent a nontronite in altered Columbia Plateau basalt. This analysis includes 51.88 ± 1.52 wt% SiO_2 , 3.74 ± 0.08 wt% Al_2O_3 , 32.07 ± 0.81 wt% Fe_2O_3 , 1.74 ± 0.13 wt% MgO , 1.10 ± 0.06 wt% CaO , 1.10 ± 0.42 wt% Na_2O , 0.11 ± 0.03 wt% K_2O , and 8.26 wt% H_2O . This composition is similar to the analyses for nontronite from Garfield and Colfax (Whitman County), Washington, reported in Deer, Howie and Zussman (1967), with the exception of the SiO_2 content,

which is significantly higher in the analysis of Benson and Teague (1979). Using this oxide analysis, the following structural formula was calculated with the procedure described by Ames (1980):

A $\Delta G_{f,298}^0$ value was calculated for this composition of nontronite with the method of Mattigod and Sposito (1978). This estimated $\Delta G_{f,298}^0$, listed in Table 6, is more negative by 1.5 to 3.2% from the $\Delta G_{f,298}^0$ values determined for the ideal end-member nontronites. Because the $\Delta G_{f,298}^0$ of the $\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ component constitutes about 75% of the total estimated $\Delta G_{f,298}^0$, the free energy differences between ideal and "Hanford" nontronite are considered insignificant because of the uncertainty assigned to the SiO_2 analysis.

CALCULATION OF $\Delta H_{r,298}^0$ AND $\log_{10} K_{r,298}^0$ OF THE HYDROLYSIS REACTIONS

The hydrolysis reactions for the newly added minerals were determined in accordance with the same criteria for format and reaction species as described in Ball, Nordstrom and Jenne (1980). Heats of reaction were computed for these reactions based on the relation

$$\Delta H_{r,298}^0 = \Sigma \Delta H_{f,298}^0 (\text{products}) - \Sigma \Delta H_{f,298}^0 (\text{reactants}).$$

Values of $\log_{10} K_{r,298}^0$ (equilibrium constant of reaction at 298.15 K) were calculated from the relation

$$\log_{10} K_{r,298}^0 = -\Delta G_{r,298}^0 / (2.30258 \times R \times T),$$

where

$$\Delta G_{r,298}^0 = \Sigma \Delta G_{f,298}^0 (\text{products}) - \Sigma \Delta G_{f,298}^0 (\text{reactants}),$$

$$T = 298.15 \text{ K},$$

$$R = 1.9872 \text{ cal mol}^{-1}\text{K}^{-1}, \text{ gas constant.}$$

The hydrolysis reactions and the values of $\Delta H_{r,298}^0$ and $\log_{10} K_{r,298}^0$, calculated from the ancillary thermodynamic data in Tables 2, 3, and 4, are given in Table 8, except for lepidocrocite and nontronite (discussed previously).

Computed values of $\Delta H_{r,298}^0$ and $\log_{10} K_{r,298}^0$ for microcline and high sanidine, which are two potassium-feldspar polymorphs, have been added to the WATEQ3 data base. Similar data for the hydrolysis reaction of adularia [reaction 39 in Truesdell and Jones (1974)] have been deleted from the WATEQ3 data base, because there is some question concerning the usage of the term "adularia." With respect to Al/Si order, microcline and high sanidine, respectively, are the most ordered and most disordered forms of potassium feldspars. The term "adularia" is commonly used for a variety of orthoclase (which is also a potassium feldspar polymorph) that has a distinct morphological habit and is commonly found in hydrothermal veins. The Al/Si disorder and thermal

TABLE 8. Hydrolysis Reactions and Computed Values of $\Delta H_{r,298}^0$ and $\log_{10} K_{r,298}^0$.

Solid Phase	Reaction	$\Delta H_{r,298}^0$ (kcal)	$\log_{10} K_{r,298}^0$
CaO, Lime	$\text{CaO} + 2\text{H}^+ = \text{Ca}^{+2} + \text{H}_2\text{O}$	-46.265	+32.797
Ca(OH)_2 , Portlandite	$\text{Ca(OH)}_2 + 2\text{H}^+ = \text{Ca}^{+2} + 2\text{H}_2\text{O}$	-30.690	+22.675
$\text{Fe}_{0.947}\text{O}$, Wüstite	$\text{Fe}_{0.947}\text{O} + 2\text{H}^+ = 0.947\text{Fe}^{+2} + \text{H}_2\text{O}$	-24.846	+11.687
MgO, Periclase	$\text{MgO} + 2\text{H}^+ = \text{Mg}^{+2} + \text{H}_2\text{O}$	-36.135	+21.510
FeAl_2O_4 , Hercynite	$\text{FeAl}_2\text{O}_4 + 4\text{H}_2\text{O} = \text{Fe}^{+2} + 2\text{Al(OH)}_4^-$	--- (a)	-19.407
MgAl_2O_4 , Spinel	$\text{MgAl}_2\text{O}_4 + 4\text{H}_2\text{O} = \text{Mg}^{+2} + 2\text{Al(OH)}_4^-$	--- (a)	-10.236
MgFe_2O_4 , Magnesio-ferrite	$\text{MgFe}_2\text{O}_4 + 8\text{H}^+ = \text{Mg}^{+2} + 2\text{Fe}^{+3} + 4\text{H}_2\text{O}$	-66.639	+16.765
Na_3AlF_6 , Cryolite	$\text{Na}_3\text{AlF}_6 + 4\text{H}_2\text{O} = \text{Al(OH)}_4^- + 3\text{Na}^+ + 6\text{F}^- + 4\text{H}^+$	--- (a)	-54.775

(a) No $\Delta H_{f,298}^0$ value for Al(OH)_4^-

TABLE 8. (contd)

Solid Phase	Reaction	$\Delta H_{r,298}^0$ (kcal)	$\log_{10} K_{r,298}^0$
CaSiO ₃ , Wollastonite	$\text{CaSiO}_3 + \text{H}_2\text{O} + 2\text{H}^+ = \text{H}_4\text{SiO}_4^0 + \text{Ca}^{+2}$	-19.498	+12.996
CaSiO ₃ , Pseudo- wollastonite	$\text{CaSiO}_3 + \text{H}_2\text{O} + 2\text{H}^+ = \text{H}_4\text{SiO}_4^0 + \text{Ca}^{+2}$	-21.068	+13.846
Ca ₂ (SiO ₄), Ca-Olivine	$\text{Ca}_2(\text{SiO}_4) + 4\text{H}^+ = \text{H}_4\text{SiO}_4^0 + 2\text{Ca}^{+2}$	-54.695	+37.649
β-Ca ₂ (SiO ₄), Larnite	$\beta\text{-Ca}_2(\text{SiO}_4) + 4\text{H}^+ = \text{H}_4\text{SiO}_4^0 + 2\text{Ca}^{+2}$	-57.238	+39.141
Ca ₃ SiO ₅	$\text{Ca}_3\text{SiO}_5 + 6\text{H}^+ = \text{H}_4\text{SiO}_4^0 + 3\text{Ca}^{+2} + \text{H}_2\text{O}$	-106.335	+73.867
CaMgSiO ₄ , Monticellite	$\text{CaMgSiO}_4 + 4\text{H}^+ = \text{H}_4\text{SiO}_4^0 + \text{Ca}^{+2} + \text{Mg}^{+2}$	-49.421	+30.272
Ca ₂ MgSi ₂ O ₇ , Akermanite	$\text{Ca}_2\text{MgSi}_2\text{O}_7 + \text{H}_2\text{O} + 6\text{H}^+ = 2\text{H}_4\text{SiO}_4^0 + 2\text{Ca}^{+2} + \text{Mg}^{+2}$	-76.445	+47.472
Ca ₃ Mg(SiO ₄) ₂ , Merwinite	$\text{Ca}_3\text{Mg}(\text{SiO}_4)_2 + 8\text{H}^+ = 2\text{H}_4\text{SiO}_4^0 + \text{Mg}^{+2} + 3\text{Ca}^{+2}$	-107.111	+68.543

TABLE 8. (contd)

Solid Phase	Reaction	$\Delta H_{r,298}^0$ (kcal)	$\log_{10} K_{r,298}^0$
KAlSiO ₄ , Kalsilite	$\text{KAlSiO}_4 + 4\text{H}_2\text{O} = \text{H}_4\text{SiO}_4^0 + \text{Al}(\text{OH})_4^- + \text{K}^+$	-- (a)	-10.447
KAlSi ₂ O ₆ , Leucite	$\text{KAlSi}_2\text{O}_6 + 6\text{H}_2\text{O} = 2\text{H}_4\text{SiO}_4^0 + \text{Al}(\text{OH})_4^- + \text{K}^+$	-- (a)	-16.862
KAlSi ₃ O ₈ , Microcline	$\text{KAlSi}_3\text{O}_8 + 8\text{H}_2\text{O} = 3\text{H}_4\text{SiO}_4^0 + \text{Al}(\text{OH})_4^- + \text{K}^+$	-- (a)	-22.669
KAlSi ₃ O ₈ , High Sanidine	$\text{KAlSi}_3\text{O}_8 + 8\text{H}_2\text{O} = 3\text{H}_4\text{SiO}_4^0 + \text{Al}(\text{OH})_4^- + \text{K}^+$	-- (a)	-22.223
NaAlSiO ₄ , Nepheline	$\text{NaAlSiO}_4 + 4\text{H}_2\text{O} = \text{H}_4\text{SiO}_4^0 + \text{Al}(\text{OH})_4^- + \text{Na}^+$	-- (a)	-9.067
Ca ₂ Al ₂ SiO ₇ , Gehlenite	$\text{Ca}_2\text{Al}_2\text{SiO}_7 + 5\text{H}_2\text{O} + 2\text{H}^+ = \text{H}_4\text{SiO}_4^0 + 2\text{Al}(\text{OH})_4^- + 2\text{Ca}^{+2}$	-- (a)	+10.253

(a) No $\Delta H_{f,298}^0$ value for $\text{Al}(\text{OH})_4^-$

stability of orthoclase are intermediate to those of microcline and high sanidine (Ribbe 1975). However, according to Bambauer and Laves (1960), adularia may in some cases be structurally classified as sanidine, orthoclase or microcline. The thermodynamic values for adularia in the WATEQ data base were originally taken from Robie and Waldbaum (1968) who computed $\Delta H_{f,298}^0$ and $\Delta G_{f,298}^0$ for adularia from data in Garrels and Christ (1965). Data for adularia or orthoclase, however, are absent in the more recent compilation by Robie, Hemingway and Fisher (1978). Moreover, the removal of adularia from the WATEQ3 data base will not limit geochemical modeling efforts because the $\log_{10} K_{r,298}^0$ value added for microcline and high sanidine are almost identical to the deleted value for adularia.

Calculated values of $\log_{10} K_{r,298}^0$ for the hydrolysis reaction of lepidocrocite are given in Table 5. The value calculated from the data of Schuylenborgh (1973) was selected as our "best" value for lepidocrocite. The $\log_{10} K_{r,298}^0$ value calculated from the data for lepidocrocite in Langmuir (1969) and the ancillary thermodynamic data in Table 3 will be placed in the WATEQ data base as a "maximum" value for lepidocrocite. Both $\log_{10} K_{r,298}^0$ values in Table 5 are more positive than the $\log_{10} K_{r,298}^0$ for goethite used in the WATEQ data base, and therefore represent the proper stability order between lepidocrocite and goethite.

The $\Delta G_{f,298}^0$ values in Table 6, estimated by the procedure of Mattigod and Sposito (1978), were used to compute $\log_{10} K_{r,298}^0$ for the hydrolysis reactions of ideal Na-, K-, Ca-, and Mg-nontronites. Ancillary Gibbs free energy data for Ca^{+2} , Fe^{+3} , K^{+} , Mg^{+2} , Na^{+} , H_2O , $\text{Al}(\text{OH})_4^{-}$, and H_4SiO_4^0 were taken from Tables 3 and 4 of our "accepted" thermodynamic data. $\log_{10} K_{r,298}^0$ values were calculated using the equations described in an earlier section of this report.

The hydrolysis reactions and the $\log_{10} K_{r,298}^0$ values for the four nontronite compositions are given in Table 9. $\log_{10} K_{r,298}^0$ values for each nontronite composition were computed with both $\Delta G_{f,298}^0$ values that are based on the two extreme exchange capacities for smectite clays. Both $\log_{10} K_{r,298}^0$ values will be incorporated into the WATEQ data base until

TABLE 9. Hydrolysis Reactions and Computed $\log_{10} K_{r,298}^0$ Values for Ideal End-Member Nontronite. Minimum and Maximum $\log_{10} K_{r,298}^0$ Values Calculated from the Low- and High-Exchange Capacities Used in the Free Energy Estimations.

Na-nontronite	$\text{Na}_{0.33}\text{Fe}_2^{+3}(\text{Al}_{0.33}\text{Si}_{3.67})\text{O}_{10}(\text{OH})_2 + 6\text{H}^+ + 4\text{H}_2\text{O} =$ $2\text{Fe}^{+3} + 0.33\text{Na}^+ + 0.33\text{Al}(\text{OH})_4^- + 3.67\text{H}_4\text{SiO}_4^0$ <p>Minimum $\log_{10} K_{r,298}^0 = -19.806$</p> <p>Maximum $\log_{10} K_{r,298}^0 = -24.570$</p>
K-nontronite	$\text{K}_{0.33}\text{Fe}_2^{+3}(\text{Al}_{0.33}\text{Si}_{3.67})\text{O}_{10}(\text{OH})_2 + 6\text{H}^+ + 4\text{H}_2\text{O} =$ $2\text{Fe}^{+3} + 0.33\text{K}^+ + 0.33\text{Al}(\text{OH})_4^- + 3.67\text{H}_4\text{SiO}_4^0$ <p>Minimum $\log_{10} K_{r,298}^0 = -20.447$</p> <p>Maximum $\log_{10} K_{r,298}^0 = -26.018$</p>
Ca-nontronite	$(1/2\text{Ca}_{0.33}\text{Fe}_2^{+3}(\text{Al}_{0.33}\text{Si}_{3.67})\text{O}_{10}(\text{OH})_2 + 6\text{H}^+ + 4\text{H}_2\text{O} =$ $2\text{Fe}^{+3} + 0.167\text{Ca}^{+2} + 0.33\text{Al}(\text{OH})_4^- + 3.67\text{H}_4\text{SiO}_4^0$ <p>Minimum $\log_{10} K_{r,298}^0 = -26.741$</p> <p>Maximum $\log_{10} K_{r,298}^0 = -30.406$</p>
Mg-nontronite	$(1/2\text{Mg}_{0.33}\text{Fe}_2^{+3}(\text{Al}_{0.33}\text{Si}_{3.67})\text{O}_{10}(\text{OH})_2 + 6\text{H}^+ + 4\text{H}_2\text{O} =$ $2\text{Fe}^{+3} + 0.167\text{Mg}^{+2} + 0.33\text{Al}(\text{OH})_4^- + 3.67\text{H}_4\text{SiO}_4^0$ <p>Minimum $\log_{10} K_{r,298}^0 = -26.697$</p> <p>Maximum $\log_{10} K_{r,298}^0 = -29.849$</p>

a suitable method is identified to select the proper $\Delta G_{f,298}^0$ or to ascertain a limit of uncertainty for each $\Delta G_{f,298}^0$ value. Assignment of an uncertainty to each $\Delta G_{f,298}^0$ will be difficult because each free energy value for nontronite is itself an "estimation." However, because each estimated $\Delta G_{f,298}^0$ value is

computed from thermodynamic data with known uncertainties, to carry these uncertainties into the calculation of $\Delta G_{f,298}^0$ and $\log_{10} K_{r,298}^0$ should be possible. Secondly, the two extreme exchange capacities, which are for the complete spectrum of smectite compositions, may overestimate the proper limits of exchange capacity for nontronite compositions. For example, using the exchange capacities of 0.080 and 0.120 eq/100 g, the exchange bond (δ) corrections of 12.79 and 17.75 kcal mol⁻¹, respectively, were calculated for Ca-nontronite. Therefore, overestimation of the exchange capacity of nontronite will increase the differences in the $\Delta G_{f,298}^0$ and $\log_{10} K_{r,298}^0$ values.

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APPENDIX A

EXAMPLE OF $\log_{10} K_{r,298}^0$ CALCULATIONS

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EXAMPLE OF $\log_{10} K_{r,298}^0$ CALCULATIONS

The development and upgrading of the thermodynamic data bank for a geochemical model must be approached in an arduous fashion to maintain the best possible internal consistency with the previously compiled data. This appendix shows an example of the calculations necessary to generate internally consistent $\Delta G_{f,298}^0$ and $\log_{10} K_{r,298}^0$ values based on previously selected "best" values for S_{298}^0 and $\Delta H_{f,298}^0$ for the constituent elements, the ancillary components in the reaction, and the solid phase subject of the $\log_{10} K_r^0$ value. For the example, the $\log_{10} K_{r,298}^0$ and $\Delta H_{r,298}^0$ values for the hydrolysis reaction for wollastonite (CaSiO_3) are calculated from the ancillary thermodynamic data. The hydrolysis reactions will be written in terms of H^+ and/or H_2O as required by the WATEQ3 code (Ball, Nordstrom and Jenne 1980).

STEP 1

"Best" values should be first accepted for S_{298}^0 and $\Delta H_{f,298}^0$ for the constituent elements, the ancillary components in the reaction, and the subject solid phase. These values should be the same as those previously used to calculate $\Delta H_{r,298}^0$ and $\log_{10} K_{r,298}^0$ for the existing phases in the geochemical model. For these calculations, the NBS Series 270 and CODATA were the primary sources for the S_{298}^0 and $\Delta H_{f,298}^0$ values, because they were used in past data supplements to the WATEQ data base. Obviously, as a data bank evolves over several years, the selection of "best" values may change. The earlier $\Delta H_{r,298}^0$ and $\log_{10} K_{r,298}^0$ values should be revised, as time permits, with respect to the more recent thermodynamic data. The "best" thermodynamic values necessary for this calculation are given in Table A.1; these data were listed earlier in Tables 2, 3, and 4.

STEP 2

Values of $\Delta G_{f,298}^0$ for H_2O , $H_4SiO_4^0$ (aqueous), Ca^{+2} and wollastonite are next calculated from the data in Table A.1. They are computed from the fundamental thermodynamic relationship,

$$\Delta G_{f,298}^0 = \Delta H_{f,298}^0 - 298.15 \Delta S_{f,298}^0$$

where $\Delta S_{f,298}^0$ is the entropy difference between that component and its constituent elements. The calculation of these $\Delta G_{f,298}^0$ values are shown on the following pages, and the resulting values should be compared to those in Tables 3 and 4.

$\Delta G_{f,298}^0$ for H_2O

$$\Delta G_{f,298}^0 (H_2O) = \Delta H_{f,298}^0 (H_2O) - 298.15 [S_{298}^0 (H_2O) - S_{298}^0 (H_2) - 0.5 S_{298}^0 (O_2)]$$

$$\Delta G_{f,298}^0 (H_2O) = -68,315 - 298.15 [16.718 - 31.207 - 0.5(49.006)]$$

$$\Delta G_{f,298}^0 (H_2O) = -56,690 \text{ cal mol}^{-1}$$

$\Delta G_{f,298}^0$ for $H_4SiO_4^0$ (aqueous)

$$\Delta G_{f,298}^0 (H_4SiO_4^0) = \Delta H_{f,298}^0 (H_4SiO_4^0) - 298.15 [S_{298}^0 (H_4SiO_4^0) - 2S_{298}^0 (H_2) - S_{298}^0 (Si) - 2S_{298}^0 (O_2)]$$

$$\Delta G_{f,298}^0 (H_4SiO_4^0) = -348,900 - 298.15 [43.0 - 2(31.207) - 4.496 - 2(49.006)]$$

$$\Delta G_{f,298}^0 (H_4SiO_4^0) = -312,550 \text{ cal mol}^{-1}$$

TABLE A.1. Thermodynamic Values Necessary to Calculate Internally Consistent $\Delta H_{f,298}^0$ and $\log_{10} K_{r,298}^0$ Values for Wollastonite.

Phase or Species	$\Delta H_{f,298}^0$ (kcal mol ⁻¹)	S_{298}^0 (cal mol ⁻¹ K ⁻¹)
Ca	0 ^(a)	9.950
e ⁻ (electron) ^(b)	0	15.6035
H ₂	0	31.207
H ⁺	0	0
O ₂	0	49.006
Si	0	4.496
Ca ⁺²	-129.740	-12.69
H ₂ O	-68.315	16.718
H ₂ SiO ₄ ⁰ (Aqueous)	-348.9	43.0
Wollastonite	-390.827	19.524

(a) The $\Delta H_{f,298}^0$ of the elements in their reference state are zero by convention.

(b) The entropy of the electron (e⁻) is calculated from the formation reaction $0.5 \text{ H}_2 = \text{H}^+ + \text{e}^-$. Therefore, the entropy of the electron is equal to $0.5 S_{298}^0$ of H₂.

$\Delta G_{f,298}^0$ for Ca⁺²

$$\Delta G_{f,298}^0 (\text{Ca}^{+2}) = \Delta H_{f,298}^0 (\text{Ca}^{+2}) - 298.15 [S_{298}^0 (\text{Ca}^{+2}) + 2S_{298}^0 (\text{e}^-) - S_{298}^0 (\text{Ca})]$$

$$\Delta G_{f,298}^0 (\text{Ca}^{+2}) = -129,740 - 298.15 [-12.69 + 2 (15.6035) - 9.950]$$

$$\Delta G_{f,298}^0 (\text{Ca}^{+2}) = -132,294 \text{ cal mol}^{-1}$$

$\Delta G_{f,298}^0$ for Wollastonite (wol), CaSiO_3

$$\Delta G_{f,298}^0 (\text{wol}) = \Delta H_{f,298}^0 (\text{wol}) -$$

$$298.15 [S_{298}^0 (\text{wol}) - S_{298}^0 (\text{Ca}) - S_{298}^0 (\text{Si}) - 1.5 S_{298}^0 (\text{O}_2)]$$

$$\Delta G_{f,298}^0 (\text{wol}) = -390,827 - 298.15 [19.524 - 9.950 - 4.496 - 1.5(49.006)]$$

$$\Delta G_{f,298}^0 (\text{wol}) = -370,424 \text{ cal mol}^{-1}$$

STEP 3

These $\Delta G_{f,298}^0$ values and the $\Delta H_{f,298}^0$ values in Table A.1 are then used to compute the $\Delta G_{r,298}^0$ and $\Delta H_{r,298}^0$, respectively, for the dissolution reaction for wollastonite as listed in Table 8. The $\Delta G_{r,298}^0$ value can then be used to calculate the $\log_{10} K_{r,298}^0$ for the same dissolution reaction.

Wollastonite (Wol)

$$\begin{aligned} \Delta G_{r,298}^0 &= \Delta G_{f,298}^0 (\text{H}_4\text{SiO}_4^0) + \Delta G_{f,298}^0 (\text{Ca}^{+2}) - \Delta G_{f,298}^0 (\text{Wol}) \\ &\quad - \Delta G_{f,298}^0 (\text{H}_2\text{O}) - 2\Delta G_{f,298}^0 (\text{H}^+) \end{aligned}$$

$$\Delta G_{r,298}^0 = (-312,550) + (-132,294) - (-370,424) - (-56,690) - 2(0)$$

$$\Delta G_{r,298}^0 = -17,784 \text{ cal mol}^{-1}$$

$$\log_{10} K_{r,298}^0 = -(-17,730 \text{ cal}^{-1} \text{ mol}) /$$

$$(2.30258 \times 1.9872 \text{ cal mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K})$$

$$\log_{10} K_{r,298}^0 = +12.996$$

By analogy to the calculation of $\Delta G_{f,298}^0$,

$$\Delta H_{r,298}^0 = -19,498 \text{ cal mol}^{-1}$$

These calculated $\log_{10} K_{r,298}^0$ and $\Delta H_{r,298}^0$ values are identical to those listed in Table 8.

The $\log_{10} K_{r,298}^0$ values for the other phases in Table 8 can be similarly computed following the three steps given in this appendix. For example, one must: 1) accept "best" values for $\Delta H_{f,298}^0$ and S_{298}^0 for Mg, Mg^{+2} , and merwinite $[\text{Ca}_3\text{Mg}(\text{SiO}_4)_2]$; 2) compute $\Delta G_{f,298}^0$ for Mg^{+2} and merwinite from these values and those previously selected in Table A.1; and 3) calculate a $\log_{10} K_{r,298}^0$ for the dissolution reaction for merwinite (Table 8) using these $\Delta G_{f,298}^0$ values for Mg^{+2} and merwinite and the previously calculated $\Delta G_{f,298}^0$ values (STEP 2) for Ca^{+2} and H_4SiO_4^0 . This procedure creates a set of thermodynamic data that are internally consistent with the accepted primary $\Delta H_{f,298}^0$ and S_{298}^0 values.

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