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Qualification of Thermodynamic Data for Geochemical Modeling of Mineral-Water Interactions in Dilute Systems

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ACRONYMS AND ABBREVIATIONS

(aq) aqueous

CR Condition Report

(cr) crystalline

CSH calcium silicate hydrate

DIRS Document Input Reference System

DTN data tracking number

(g) gas

NEA Nuclear Energy Agency

OECD Organization for Economic Cooperation and Development

(s) solid

YMP Yucca Mountain Project

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1. PURPOSE

The purpose of this analysis report is to qualify the thermochemical database data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756], qualified by this report) and supporting calculations (DTNs: MO0302SPATHDYN.001 [DIRS 161886], and MO0303SPASPEQ2.000 [DIRS 162278]), which were originally documented in *Data Qualification: Update and Revision of the Geochemical Thermodynamic Database*, *Data0.ymp* (Steinborn et al. 2003 [DIRS 161956]). This original document still serves as the record of development of the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]).

The data0.ymp.R2 thermodynamic database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) was developed for use with software code EQ3/6 (EQ3/6 V8.0, STN: 10813-8.0-00) (BSC 2003 [DIRS 162228]) and software code EQ6 (EQ6 V7.2bLV, STN: 10075-7.2bLV-02) (BSC 2002 [DIRS 159731]) to conduct geochemical modeling of mineral-fluid interactions involving aqueous solutions (ionic strengths of up to one molal; see Section 6.5) and temperatures of up to 300°C along the liquid-vapor saturation curve of pure water. The data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) is an update of the previously qualified predecessor database data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]). The scope of this report is limited to qualification of the updates, as well as identification and evaluation of certain errors and discrepancies as discussed below.

This documents the qualification of data0.ymp.R2 report the database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) and in so doing, also identifies and evaluates between sources and the data0.ymp.R2 discrepancies data database (DTN: MO0302SPATHDYN.000 [DIRS 161756]). These discrepancies are mainly the result of errors in the transcription of thermodynamic parameter data from original sources to calculation spreadsheets used to develop the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]). The potential importance of these discrepancies for downstream applications of the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) is evaluated in this report, and summarized in Section 7. An updated database called data0.ymp.R4 (output DTN: SN0410T0510404.002) is generated as output from this report, to address and correct the This analysis report is developed from Technical Work Plan discrepancies found. for: Near-Field Environment and Transport In-Drift Geochemistry Analyses (BSC 2004 [DIRS 172402]).

The data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) is used in predictive models for waste form and waste package corrosion, modeling of in-package and in-drift chemical conditions, and prediction of dissolved radionuclide concentrations. The data are also used to support criticality assessments and modeling of reactive transport of radionuclides in groundwater. This database is a principal input for geochemical code EQ3/6 and in a modified format, for PHREEQC (PHREEQC Post V1.1, STN: 10723-1.1-00) (BSC 2002 [DIRS 157839]). **Parameters** from the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) have also been used to develop inputs for reactive transport code TOUGHREACT (TOUGHREACT V3.0, STN: 10396-3.0-00) (LBNL 2002 [DIRS 161256]; BSC 2004 [DIRS 170268]).

Use of the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) has promoted consistency for the various types of thermodynamic calculations used to support licensing of the Yucca Mountain repository. The intermediate version data0.ymp.R1 of the database was generated in the course of development, but not used for calculations that support licensing. The version data0.ymp.R3 of the database (DTN: MO0312SPATDMIF.000 [DIRS 167800]) is an update of the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) that only incorporates a correction in the stoichiometry of the Pu phase PuO₂(OH)₂:H₂O. This modification is also incorporated in the data0.ymp.R4 database (output DTN: SN0410T0510404.002).

The development of data0.vmp.R2 updates implemented the database in (DTN: MO0302SPATHDYN.000 [DIRS 161756]) from the predecessor database data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]) are documented Data Qualification: Update and Revision of the Geochemical Thermodynamic Database, Data0.ymp (Steinborn et al. 2003 [DIRS 161956]) and summarized as follows:

- 1. Incorporation of newer data for Np and Pu species, published by the Organization for Economic Cooperation and Development/Nuclear Energy Agency (OECD/NEA) (Lemire 2001 [DIRS 159027]).
- 2. Addition of solid phases, including clays, zeolites, uranium silicate minerals, and cement phases.
- 3. Addition of several uranium silicate minerals.
- 4. Calculation of equilibrium constants (log K) for temperatures above 25°C (to at least 200°C whenever possible; data for many reactions extend to 300°C).
- 5. Change in basis for silicate species using the Rimstidt (1997 [DIRS 101709]) convention.

Additional changes in the corrected data0.ymp.R4 database (output DTN: SN0410T0510404.002) consist mainly of updates and corrections to log K values for dissociation reactions over the appropriate temperature ranges. Other updates and corrections are described in Section 6 and include:

- Log K values for some zeolite phases (Section 6.3.2).
- Log K values for Np and Pu solids (Section 6.3.4.5).
- Log K values for metal-bearing gases and solids (Section 6.3.4.5).
- Identification of large discrepancies in calculated log K values for cement phases, such as Ca-gismondine and Friedl salt (Section 6.3.3.4).

- Correction of the log K values for the HF₂⁻ dissociation reaction (Section 6.4).
- Correction of the Pu phase PuO₂(OH)₂:H₂O stoichiometry using the formula of Lemire (2001 [DIRS 159027]; see Table 4-1 and Section 4.1.1 of this report). This correction is also made in a previous version of the database (data0.ymp.R3; DTN: MO0312SPATDMIF.000 [DIRS 167800]) and is incorporated in the output database file data0.ymp.R4 (output DTN: SN0410T0510404.002).

In addition, three condition reports (CRs) (CR-85, CR-168, and CR-304) directed against the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) are addressed in this report. Details of these CR items are given in *Technical Work Plan for: Near-Field Environment and Transport In-Drift Geochemistry Analyses* (BSC 2004 [DIRS 172402], Appendix 6). For completeness, these are also listed as follows:

- 1. CR-85 captures Deficiency Report BSC(O)-03-D-236 (initiated on August 14, 2003). It states that the data qualification method of technical assessment, as used originally to qualify the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]; Steinborn et al. 2003 [DIRS 161956]) is invalid. Since the Deficiency Report was initiated, technical assessment was eliminated as a method for data qualification, then subsequently reinstated. This CR is now closed.
- 2. CR-168 captures Technical Error Report TER-03-0037, *Data Qualification: Update and Revision of* the *Geochemical Thermodynamic Database*, *Data0.ymp*. This report cited the 20 sources of data listed in Table 1-1 and describes the following deficiency: "The Data Qualification Report did not in all cases provide adequate justification for the qualification of the 20 sources for geochemical data." The error report goes on to say, "Additionally, the subject matter expert for each of the above was not identified in the Data Qualification Report. This condition was noted in BSC(O)-03-D-130."
- 3. CR-304 captures the previous Condition/Issue Identification and Reporting/Resolution System Issue 3867 and describes the condition as "Engineered Systems include database qualification...SA-PAP-2003-017 was conducted as a second management review of Biosphere, Waste Package, and Waste Form Analyses and Model Reports (AMR) preliminary feeds to TSPA-LA [Total System Performance Assessment for the License A major crosscutting issue observed is captured in this CIRS Application]. [Condition/Issue Identification and Reporting/Resolution System] issue. Self-Assessment Attachment 1, page 7, item 2 describes this issue. Several database issues were raised as part of the review. It was noted that the EQ3/6 and Pitzer databases (as well as an industry standard materials database used by THERMO-CALC) needed additional qualification efforts before they could be used in applications. Engineered Systems should review the schedule to ensure adequacy of database qualification and ensure that qualification is complete prior to analyses....This may be accomplished by preparing a punchlist to help monitor the completed documents as they get approved."

An additional CR, CR-3574, which was not listed in the Technical Work Plan, identified errors in actinide and zeolite thermodynamic data in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). This report addresses these issues and supports the closure of the CR.

Table 1-1. Data Evaluated in the Data Qualification Report

Description	Source	Qualification Adequate? (CR-168)	Where Discussed in this Report	Comments
Data from data0.ymp.R0	DTN: MO0009THRMODYN. 001 [DIRS 152576]	Y	Throughout	Qualified input to this report.
Handbook data	Binnewies and Milke 1999 [DIRS 158955]	Y	6.1.4.2, 6.3.4.5, 6.4	Qualified input to this report.
Handbook data	Barin and Platzki 1995 [DIRS 157865]	Y	6, 6.1.2, 6.1.4.2, 6.1.5, 6.3.4.5, 6.4	Qualified input to this report.
Np and Pu data	Lemire 2001 [DIRS 159027]	Υ	6, 6.2.1, 6.2.2, 6.3.4.5	Qualified input to this report.
Soddyite log K _{sp}	Moll et al. 1996 [DIRS 106349]	N	6.3.4.1	Corroborated.
Uranophane log K _{sp}	Perez et al. 2000 [DIRS 157910]	N	6.3.4.2	Corroborated.
Na-Weeksite log K _{sp}	Nguyen et al. 1992 [DIRS 100809]	N	6.3.4.3	Corroborated.
Na-Boltwoodite log K _{sp}	Nguyen et al. 1992 [DIRS 100809]	N	6.3.4.3	Corroborated.
Zeolite data	Chipera et al. 1995 [DIRS 100025]	N	6.3.2	Technical assessment.
Zeolite data	Viani and Bruton 1992 [DIRS 101407]	N	6.3.2	Technical assessment.
Calcium silicates, aluminates, and ferrites data	Babushkin et al. 1985 [DIRS 116981], App. I	Y	6.3.3, 6.3.3.2, 6.3.3.4, 6.3.3.5	Qualified, direct input to this report. Note: This source is used for active species in data0.ymp.R2, but also certain inactive species.
Calcium silicate hydrate data	Fujii and Kondo 1983 [DIRS 144876]. Note that Steinborn et al. (2003 [DIRS 161956]) and CR-168 incorrectly cite Fujii and Kondo (1981 [DIRS 158026]) as the data source for CSH:1.7.	N	6.3.3.1	Used in discussion of species CSH:1.7, which is inactive in data0.ymp.R2.
CaCl₂ data	Chase 1998 [DIRS 157874]	Y	6.3.3.4	Qualified, direct input to this report; used in discussion of species Friedl salt, which is an inactive species in data0.ymp.R2.

Table 1-1. Data Evaluated in the Data Qualification Report (Continued)

Description	Source	Qualification Adequate? (CR-168)	Where Discussed in this Report	Comments
Gehlenite Hydrate Hydrotalcite	Gehlenite Hydrate: Atkins et al. 1992 [DIRS 100700] Hydrotalcite: Bennett et al. 1992 [DIRS 116990]	N	Gehlenite hydrate: 6.3.3.5 Hydrotalcite: 6.3.3.6	Gehlenite hydrate is corroborated, and hydrotalcite is qualified by technical assessment.
Monocarboaluminate and Hemicarboaluminate	Damidot et al. 1994 [DIRS 144866]	N	Monocarbo- aluminate: 6.3.3.7 Hemicarbo- aluminate: 6.3.3.8	Qualified as input by technical assessment.
Syngenite	DTN: MO0109THRMODYN. 000 [DIRS 156190]	Y	6.3.3.9	Source shown is not used as input; syngenite properties are redefined in this report using another source.
Gismondine	Atkins et al. 1993 [DIRS 131758], Section 5.2.6	N	6.3.3.3	Qualified by technical assessment.
SUPCRT92 data for organic species ^a	DTN: MO0106MWDTDG01. 035 [DIRS 161791], slop98.dat	Y	N/A	
Organic metal complex data ^a	Morel and Hering 1993 [DIRS 151052]	N	N/A	
Organic data ^a	Krishnamurty and Harris 1961 [DIRS 159026]	N	N/A	
Organic data ^a	Martell and Smith 1982 [DIRS 159196]	N	N/A	
R-constant	Weast and Astle 1979 [DIRS 102865]	Y	Throughout	Qualified input to this report.
Ti-mineral data (Ti-hydroxy (aq) and rutile)	Ti-hydroxy (aq): Knauss et al. 2001 [DIRS 158998] Rutile: Robie et al. 1979 [DIRS 107109]	N	6.2.2	Corroboration and technical assessment.
Am ⁺⁺⁺ data	Silva et al. 1995 [DIRS 102087]	N	6.2.2	Established fact. ^b
β-UO₃ data	Grenthe et al. 1992 [DIRS 101671]	N	4.1.7	Established fact.b
SiO ₂ solubility	Rimstidt 1997 [DIRS 101709]	N	6.3	This report uses ANL-NBS-HS-000043 Rev. 00 (BSC 2004 [DIRS 170268]) as the source of these data.

Table 1-1. Data Evaluated in the Data Qualification Report (Continued)

Description	Source	Qualification Adequate? (CR-168)	Where Discussed in this Report	Comments
Clay mineral data	Wolery 1978 [DIRS 151346]	N	6.3.1	The clay mineral data in data0.ymp.R2 were developed using the method of Wolery (1978 [DIRS 151346]) and the data of Helgeson et al. (1978 [DIRS 101596]).
HF₂⁻ data	Clark 1966 [DIRS 153163]	N	6.4	Established fact.
HF data	Ellis and Mahon 1977 [DIRS 159230]	N	6.4	Corroboration and technical assessment. These data are used to extend data from Clark (1966 [DIRS 153163]), which is used in this report for temperatures up to 200°C.

^a These data for organic species are not included in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) are outside the scope of this report.

Of the items listed in Table 1-1, the four associated with organic data are not addressed in this report because the organic data described in Data Qualification: Update and Revision of the Geochemical Thermodynamic Database, Data0.ymp (Steinborn et al. 2003 [DIRS 161956]) were submitted as a separate database file (total organics.txt: DTN: MO0208THDYNORG.000 [DIRS 172399]) and are not linked to data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). Thus the qualification of the organic data is beyond the scope of this report. Log K data for various cement phases present in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) and the output database data0.ymp.R4 (output DTN: SN0410T0510404.002) are inactive (they are "commented out" in the database and cannot be accessed by the EQ3/6 code), although they are evaluated and qualified in this report. These inactive data remain inactive in both the data0.ymp.R2 and the data0.ymp.R4 databases, but the thermodynamic information in the comments, and the discussion of these data in this report, are available for possible use in future applications.

Several analysis model reports that use data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) as direct input are listed in Table 1-2.

^b The data source(s) shown were used for data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]), which is qualified input to this report, but covers only the temperature range from 0°C to 100°C.

Table 1-2. List of Approved Analysis Model Reports Using the Thermodynamic Database Data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756])

Analysis Model Report Title	Document Number, Revision
Data Qualification for Thermodynamic Data Used to Support THC Calculations	ANL-NBS-HS-000043 Rev. 00
In-Drift Precipitates/Salts Model	ANL-EBS-MD-000045 Rev. 02
Engineered Barrier System: Physical and Chemical Environment	ANL-EBS-MD-000033 Rev. 03
Environment on the Surfaces of the Drip Shield and Waste Package Outer Barrier	ANL-EBS-MD-000001 Rev. 01
Heat Capacity Analysis Report	ANL-NBS-GS-000013 Rev. 01
In-Package Chemistry Abstraction	ANL-EBS-MD-000037 Rev. 03
Dissolved Concentration Limits of Radioactive Elements	ANL-WIS-MD-000010 Rev. 03
Geochemical Interactions in Failed Co-Disposal Waste Packages for Shippingport PWR and TRIGA Spent Fuel and in Dual Canister Packages of Three Mile Island and Fort St. Vrain Spent Fuel	ANL-EBS-PA-000008 Rev. 00
Impacts of Updated Design and Rates on EQ6 Calculations for Chemical Degradation of Fermi and TRIGA Codisposal Waste Packages	CAL-DSD-MD-000001 Rev. 00A
Mass Transfer Model	MDL-EBS-NU-000004 Rev. 01
Drift-Scale THC Seepage Model	MDL-NBS-HS-000001 Rev. 03
Mountain-Scale Coupled Processes (TH/THC/THM)	MDL-NBS-HS-000007 Rev. 02

Qualification of Thermodynamic Data for Geochemical Modeling of Mineral-Water Interactions in Dilute Systems

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2. QUALITY ASSURANCE

The quality assurance program used for the development of this activity and document is discussed in *Technical Work Plan for: Near-Field Environment and Transport In-Drift Geochemistry Analyses* (BSC 2004 [DIRS 172402]). In accordance with this Technical Work Plan, this activity involves the qualification of a thermodynamic database used in the assessment of the chemical evolution and interactions of aqueous systems in the Engineered Barrier System. These interactions include those present inside the emplacement drifts and waste packages, and the exterior of the waste packages and drip shield.

The information provided by this report is used to investigate the performance of the following safety-category barriers as defined in the *Q-List* (BSC 2004 [DIRS 168361], Table A-2) that are important to the demonstration of compliance with the postclosure performance objectives prescribed in 10 CFR 63.113 [DIRS 156605]:

- Drip Shield
- Waste Package
- Waste Form
- Cladding
- Drift Invert (Ballast).

These barriers are classified as Safety Category with regard to importance to waste isolation as defined in AP-2.22Q, *Classification Analyses and Maintenance of the Q-List*. This report contributes to the analyses and modeling data used to support performance assessment; the conclusions do not directly impact the engineered features important to safety as listed above.

The methods used to control the electronic management of data, as required by AP-SV.1Q, Control of the Electronic Management of Information, are identified in Technical Work Plan for: Near-Field Environment and Transport In-Drift Geochemistry Analyses (BSC 2004 [DIRS 172402]). This document was prepared in accordance with AP-SIII.9Q, Scientific Analyses, and AP-SIII.2Q, Qualification of Unqualified Data. Software usage discussed in the next section was conducted in accordance with LP-SI.11Q-BSC, Software Management.

alification of Thermodynam	nic Data for Geochen	nical Modeling of M	ineral-Water Interaction	ons in Dilute Syster

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3. USE OF SOFTWARE

Only exempt software, defined in accordance with LP-SI.11Q-BSC, *Software Management*, were used in this data qualification analysis report. Whereas the following baseline software items are discussed in this report and included in the reference list (Section 8.5), these were either used previously to develop data that are input to this report (i.e., the data0.ymp.R2 database, DTN: MO0302SPATHDYN.000 [DIRS 161756], qualified by this report, and supporting calculations, DTNs: MO0302SPATHDYN.001 [DIRS 161886] and MO0303SPASPEQ2.000 [DIRS 162278]), or they were used in the discussion of the uses of the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) (see Section 1).

- PHREEQC (PHREEQC Post V1.1, STN: 10723-1.1-00) (BSC 2002 [DIRS 157839])
- EQ3/6 (EQ3/6 V8.0, STN: 10813-8.0-00) (BSC 2003 [DIRS 162228])
- EQ6 (EQ6 V7.2bLV, STN: 10075-7.2bLV-02) (BSC 2002 [DIRS 159731])
- SUPCRT92 (SUPCRT92 V1.0, STN: 10058-1.0-00) (LBNL 1999 [DIRS 153218])
- TOUGHREACT (TOUGHREACT V3.0, STN: 10396-3.0-00) (LBNL 2002 [DIRS 161256]).

Microsoft Excel 2000, a commercially available spreadsheet software package, was installed and used on IBM-compatible computers using the Microsoft Windows operating system. This software, exempt in accordance with Section 2.1 of LP-SI.11Q-BSC, was used to tabulate results, visually display results, and perform standard calculations implementing algebraic equations. These algebraic equations are represented in the spreadsheets by thermodynamic formulations described in Section 6.1. The output of these calculations are presented in Section 6.2. The regression tool intrinsic to Microsoft Excel 2000 was used in many cases. No Excel macros were developed for this effort.

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4. INPUTS

Qualified and unqualified data are used as inputs in this analysis. Unqualified data are qualified in accordance with the Data Qualification Plan in Technical Work Plan for: Near-Field Environment and Transport In-Drift Geochemistry Analyses (BSC 2004 [DIRS 172402]). All source data are summarized in Table 4-1 in Section 4.1. These data are contained in a variety of reference materials that include handbook data and international scientific journal articles. They also include the qualified database data0.ymp.R0 (DTN: MO0009THRMODYN.001 and associated SUPCRT92 data [DIRS 152576]) the (DTN: MO0106MWDTDG01.035 [DIRS 161791]), which were qualified in an earlier data qualification report (CRWMS M&O 2000 [DIRS 152575]). Note that thermodynamic data from data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]) are only available up to 100°C, and that log K values up to temperatures of 300°C were developed for the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756], qualified by this report).

The qualification status of each input is documented in the Document Input Reference System (DIRS) and is summarized in Table 4-1. Inputs listed as "unqualified" in Table 4-1 are qualified in this report in accordance with AP-SIII.2Q, *Qualification of Unqualified Data*, using the qualification method(s) indicated in the table. These data are presented in more detail in Section 4.1.

Potential data sources were identified by searching the on-line card catalogs of the University of New Mexico and Sandia National Laboratory technical libraries. Handbooks identified and reviewed as potential data sources began with Barin and Knacke (1973 [DIRS 160926]) and Binnewies and Milke (1999 [DIRS 158955]). The Binnewies and Milke handbook does not contain entropy data on the elements, but Barin and Platzki (1995 [DIRS 157865]) does contain those data, and was used as the source for this parameter. These handbooks also offer a comprehensive compilation of thermodynamic data and are widely accepted by geochemists in the international scientific community. The available handbook sources are reasonably comprehensive and up-to-date, so they were used to the extent possible.

In the original development of the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), thermodynamic data for approximately 500 solid and aqueous species and 53 elements were collected for use in calculations of in-package chemical reactions and reactions involving corrosion of materials and ambient environmental conditions relevant to the project. The species fit the following broad categories:

- A wide variety of species potentially involved in reactions among waste form, engineered components internal to the waste package, and groundwater entering the waste package
- Species potentially involved in reactions among Engineered Barrier System components and drift air and water chemistry—compounds of alloy metals with fluorides, chlorides, nitrates, carbonates, and other anions, and aqueous species.

The thermodynamic properties compiled for the solid and aqueous species include:

 $\begin{array}{lll} log~K & Log~equilibrium~constant~of~chemical~reaction~(dimensionless) \\ \Delta H^{\circ}_{f,298} & Standard~enthalpy~of~formation~at~298.15K~(kJ/mol~or~kcal/mol) \\ \Delta G^{\circ}_{f,298} & Standard~Gibbs~free~energy~of~formation~at~298.15K~(kJ/mol~or~kcal/mol) \\ S^{\circ} & Standard~entropy~at~298.15K~(also~referred~to~as~S^{\circ}_{298})~(J/mol-K~or~cal/mol-K) \\ C_{p}^{\circ} & Standard~heat~capacity~at~constant~pressure,~at~298.15K~(J/mol-K~or~cal/mol-K) \\ a, b, c & Temperature-dependent~C_{p}^{\circ}~coefficients~(see~Eq.~4-1)~for~use~in~extrapolating~the~database~to~elevated~temperatures,~using~the~Maier-Kelly~equation~(Eq.~4-1)~as~defined~by~Johnson~et~al.~(1992~[DIRS~101632],~p.~910)~for~the~standard~heat~capacity~C_{p}^{\circ},~as~explained~in~Section~6.1.1. \\ \end{array}$

$$C_p^{\circ} = a + bT + \frac{c}{T^2}$$
 (Eq. 4-1)

where T is absolute temperature in Kelvin units. In some cases, log K data representing experimental mineral solubility based on infinite dilution solubility or a nearly-equivalent bounding condition were also extracted from the literature. Based on the thermodynamic relations explained in Section 6.1.1, log K data can be used to extract standard thermodynamic data for the species of interest.

 S° was also compiled for the elements. This is occasionally needed to convert between S° for a chemical species and the corresponding standard entropy at 298.15K. Corresponding heat capacity data for the elements are generally unnecessary, due to use of the apparent Gibbs free energy of formation and apparent enthalpy of formation (e.g., described by Helgeson et al. 1978 [DIRS 101596]), unless the corresponding chemical species, such as $O_2(g)$, are of direct interest.

4.1 DIRECT INPUTS

This section presents data collected from literature, handbooks, and other sources that are adopted as direct input and are listed in Table 4-1. These data include the direct inputs used originally to develop the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]). Many of these direct input data required reduction and transformation for use in qualification, and in developing the corrected data0.ymp.R4 database, which is output from this report (output DTN: SN0410T0510404.002). The qualification and reduction processes are discussed in Sections 6.2 through 6.4.

The purpose of this report as stated in Section 1 is to qualify the existing data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) and the original supporting calculations (DTN: MO0302SPATHDYN.001 [DIRS 161886], DTN: MO0303SPASPEQ2.000 and [DIRS 162278]). The qualification process focuses on changes from the previously qualified data0.ymp.R0 database (DTN: MO0009THRMODYN.001 [DIRS 152576]). Qualification frequently involves evaluation of the original sources of the information used to develop the changes. These original sources are considered direct input to this report. Certain discrepancies and errors were discovered in this process, and most of these are corrected in the data0.ymp.R4 DTN: SN0410T0510404.002) (output and supporting calculations database (DTN: SN0410T0510404.001), which are the only output from this report.

It is noted that the SUPCRT92 database file for the original data0.ymp.R0 database (DTN: MO0009THRMODYN.001 [DIRS 152576]), was modified for the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) to include updates in the thermodynamic properties of quartz and $SiO_2(aq)$ (Section 6.1.5). The modified SUPCRT92 database file is included as a direct input to this report (DTN: MO0303SPASPEQ2.000 [DIRS 162278]).

In addition to the sources of direct input data listed in Table 4-1, indirect supporting input data are presented in Section 6 where they are used for corroboration of selected direct input.

Table 4-1. Direct Input Data

Description	Source	Qualification Method ^a	Status	Where Discussed in Section 4.1
Thermodynamic and volume data from data0.ymp.R2	DTN: MO0302SPATHDYN.000 [DIRS 161756]	T, C	Qualified by this Report	All
Supporting calculations for developing data0.ymp.R2	DTN: MO0302SPATHDYN.001 [DIRS 161886]	T, C	Qualified by this Report	All
SUPCRT92 data file speq02.dat	DTN: MO0303SPASPEQ2.000 [DIRS 162278]	T, C	Qualified by this Report	All
Thermodynamic and volume data from data0.ymp.R0	DTN: MO0009THRMODYN.001 [DIRS 152576]	N/A	Qualified Data	All
SUPCRT92 data file, slop98.dat	DTN: MO0106MWDTDG01.035 [DIRS 161791]	N/A	Qualified Data	All
Thermodynamic data for various mineral phases	Robie et al. 1979 [DIRS 107109]	N/A	Established Fact	4.1.7
Thermodynamic data and updated stoichiometry for PuO ₂ (OH) ₂ :H ₂ O	Lemire 2001 [DIRS 159027]	N/A	Established Fact	4.1.1
Thermodynamic data for SiO ₂ (aq) and quartz	BSC 2004 [DIRS 170268], Table 4-7, Section 6.3, and Table 6.4-1	I-7, Section 6.3, and N/A Qua		4.1.4
Handbook thermodynamic data	Binnewies and Milke 1999 [DIRS 158955]	N/A	Established Fact	4.1.7 4.1.8
Handbook thermodynamic data	Barin and Platzki 1995 [DIRS 157865]	N/A	Established Fact	4.1.7 4.1.8
Handbook solubility data (Mo species)	Martell and Smith 1982 [DIRS 159196]	N/A	Established Fact	4.1.2
Volume data for CaUO ₄	Loopstra and Rietveld 1969 [DIRS 172264]	С	Justified in this Report	4.1.9 ^b
Volume data for Cr-ferrihydrite	Towe and Bradley 1967 [DIRS 155334]	С	Justified in this Report	4.1.9 ^b
Volume data for Fe ₂ (MoO ₄) ₃	Johnson et al. 1992 [DIRS 101632]	С	Justified in this Report	4.1.9 ^b
Volume data for Ni ₃ (PO ₄) ₂	Calvo and Faggiani 1975 [DIRS 172265]	Т	Justified in this Report	4.1.9 ^b
Volume data for Na ₄ UO ₂ (CO ₃) ₃	Douglass 1956 [DIRS 172266]	С	Justified in this Report	4.1.9
Volume data for uranophane (alpha)	Hemingway 1982 [DIRS 157905]	С	Justified in this Report	4.1.9

Table 4-1. Direct Input Data (Continued)

Description	Source	Qualification Method ^a	Status	Where Discussed in Section 4.1
Volume data for Na-weeksite	Hemingway 1982 [DIRS 157905]	С	Justified in this Report	4.1.9
Np and Pu thermodynamic data	Lemire 2001 [DIRS 159027]	N/A	Established Fact	4.1.1 4.1.2 4.1.7
Soddyite log K data	Moll et al. 1996 [DIRS 106349]	С	Justified in this Report	4.1.7
Uranophane log K data	Pérez et al. 2000 [DIRS 157910]	С	Justified in this Report	4.1.7
Na-Weeksite log K data	Nguyen et al. 1992 [DIRS 100809]	С	Justified in this Report	4.1.7
Na-Boltwoodite log K data	Nguyen et al. 1992 [DIRS 100809]	С	Justified in this Report	4.1.7
Zeolite thermodynamic and volume data	Chipera et al. 1995 [DIRS 100025], Table 1	T,C	Justified in this Report	4.1.5 4.1.9
Zeolite thermodynamic data (above 100°C)	Viani and Bruton 1992 [DIRS 101407]	Т	Justified in this Report	4.1.5
Thermodynamic data for calcium silicates, aluminates, and ferrites	Babushkin et al. 1985 [DIRS 116981], Appendix 1	N/A	Established Fact	4.1.6
Calcium silicate hydrate data	Fujii and Kondo 1983 [DIRS 144876]	Т	Justified in this Report	4.1.6
Cr-ettringite data	Perkins and Palmer 2000 [DIRS 153349]	Т	Justified in this Report	4.1.6
CaCl₂ data	Chase 1998 [DIRS 157874], p. 711	N/A	Established Fact	4.1.6
Gehlenite Hydrate	Atkins et al. 1992 [DIRS 100700]	С	Justified in this Report	4.1.6
Hydrotalcite	Bennett et al. 1992 [DIRS 116990]	Т	Justified in this Report	4.1.6
Monocarboaluminate and Hemicarboaluminate	Damidot et al. 1994 [DIRS 144866], Appendix 1	Т	Justified in this Report	4.1.6
Syngenite (updated)	DTN: SN0302T0510102.002 [DIRS 162572]	N/A	Qualified Data	4.1.6
Gismondine	Atkins et al. 1993 [DIRS 131758]	Т	Justified in this Report	4.1.6
Ti-hydroxy (aq)	Ti-hydroxy (aq): Knauss et al. 2001 [DIRS 158998] Rutile: Robie et al. 1979 [DIRS 107109]	C, T	Justified in this Report	4.1.2
Am*** data	Silva et al. 1995 [DIRS 102087], p. 37	N/A	Established Fact	4.1.2
β-UO₃ data	Grenthe et al. 1992 [DIRS 101671], Tables III.1 and III.3	N/A	Established Fact	4.1.7
Mineral data used for estimation of thermodynamic properties of clays	Helgeson et al. 1978 [DIRS 101596]	C, T	Justified in this Report	4.1.4 4.1.6 4.1.9
HF ₂ ⁻ and HF data	Clark 1966 [DIRS 153163], Table 18-4	N/A	Established Fact	4.1.8

Description	Source	Qualification Method ^a	Status	Where Discussed in Section 4.1
HF data	Ellis and Mahon 1977 [DIRS 159230], Table 8.4	C, T	Justified in this Report	4.1.8
R Constant value of 1.9872 cal/mol-K	Weast and Astle 1979 [DIRS 102865]	N/A	Established Fact	All

N/A

Established Fact

ΑII

Table 4-1. Direct Input Data (Continued)

Conversion factor: 1 calorie =

4.184 Joules

4.1.1 Compilation of Thermodynamic Data for Np and Pu Species

Weast and Astle 1979

[DIRS 102865]

Thermodynamic data for Np and Pu solids and aqueous species were obtained from the OECD/NEA compilation of Lemire (2001 [DIRS 159027]). This source is considered "established fact" because it was developed from a comprehensive evaluation of available thermodynamic data and published in handbook form by the NEA. The species for which data were added, or for which the data in data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]) were updated, are listed in Table 4-2. In many cases, data needed to calculate thermodynamic properties at elevated temperature were unavailable. For some plutonium and neptunium species, sufficient thermodynamic properties were available to estimate log K values as a function of temperature using correlation algorithms, such as isocoulombic extrapolation discussed in Section 6.1.3. For most species, however, thermodynamic properties for temperatures other than 25°C were not available, and no extrapolation of log K for other temperatures was possible. Evaluation of these data is presented in Section 6.2.1.

A modification of the Pu solid PuO₂(OH)₂:H₂O was made to correct an error found in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) related to the stoichiometry of this species (the incorrect PuO₂(OH)₂:2H₂O was corrected to PuO₂(OH)₂:H₂O). This correction is consistent with the usage in Lemire (2001 [DIRS 159027], Section 17.2.2.1) and was made originally in data0.ymp.R3 (DTN: MO0312SPATDMIF.000 [DIRS 167800]). This correction is carried into the new data0.ymp.R4 database (output DTN: SN0410T0510404.002).

^a These unqualified inputs are to be qualified for intended use in Section 6 using the following qualification methods:

C (corroborating data)

T (technical assessment)

N/A (not applicable).

b The source shown is the original source of molar volume data for the indicated phase, as the data appear in data0.ymp.R2 (DTN: MO0302SPATHDYN.001 [DIRS 152576]). The data are tabulated in Table 4-21 and qualified in Section 6.6.

Table 4-2. Np and Pu Species for which Thermodynamic Data Were Added, or Existing Data Were Modified, in the Data0.ymp.R2 Database (DTN: MO0302SPATHDYN.000 [DIRS 161756])

Data0 Species Designation	Change	ΔG _f ° (J/mol)	ΔH _f ° (J/mol)	S° (J/mol-K)	Source
(NpO ₂) ₂ (OH) ₂ ⁺⁺	new	-2,030,400	-	-	1
(NpO ₂) ₂ CO ₃ (OH) ₃ ⁻	new	-2,814,900	-	-	1
(NpO ₂) ₃ (CO ₃) ₆ ⁽⁻⁶⁾	new	-5,839,700	-	-	1
(NpO ₂) ₃ (OH) ₅ ⁺	new	-3,475,800	-	-	1
(UO ₂) ₂ (NpO ₂)(CO ₃) ₆ ⁽⁻⁶⁾	new	-6,174,300	-	-	1
Np(CO ₃) ₃	new	-2,185,900	-	-	1
Np(CO ₃) ₄	updated	-2,812,800	-	-	1
$Np(CO_3)_5^{(-6)}$	updated	-3,334,600	-	-	1
NpCl ⁺⁺⁺	new	-631,550	-	-	1
NpF ⁺⁺⁺	updated	-824,441	-889,872	-263.621	1
NpF ₂ ⁺⁺	updated	-1,144,400	-	-	1
NpI***	new	-552,060	-	-	1
NpNO ₃ ⁺⁺⁺	new	-613,410	-	-	1
NpO ₂ (CO ₃) ₂	new	-1,946,000	-	-	1
NpO ₂ (CO ₃) ₂	updated	-2,000,900	-	-	1
NpO ₂ (CO ₃) ₂ OH	new	-2,170,400	-	-	1
NpO ₂ (CO ₃) ₃	new	-2,490,208	-2,928,323	-12.070	1
NpO ₂ (CO ₃) ₃ ⁽⁻⁵⁾	updated	-2,522,859	-3,017,120	-135.050	1
NpO ₂ (HPO ₄) ₂	new	-3,042,100	-	-	1
NpO ₂ (OH) ₂	updated	-1,247,336	-1,431,230	40.000	1
NpO ₂ (OH) ₂ CO ₃	removed	-	-	-	-
NpO ₂ OH(CO ₃) ₂	removed	-	-	-	-
NpO ₂ (SO ₄) ₂	new	-2,310,775	-2,653,413	121.798	1
NpO ₂ Cl ⁺	new	-929,440	-	-	1
NpO ₂ CO ₃ ⁻	updated	-1,464,000	-	-	1
NpO ₂ CO ₃ (aq)	new	-1,377,000	-	-	1
NpO ₂ F(aq)	updated	-1,196,100	-	-	1
NpO ₂ F ⁺	new	-1,103,600	-	-	1
NpO ₂ F ₂ (aq)	new	-1,402,400	-	-	1
NpO ₂ H ₂ PO ₄ ⁺	new	-1,952,000	-	-	1
NpO ₂ HPO ₄ ⁻	new	-2,020,600	-	-	1
NpO ₂ HPO ₄ (aq)	new	-1,927,300	-	-	1
NpO ₂ IO ₃ (aq)	new	-1,037,000	-	-	1
NpO ₂ IO ₃ ⁺	new	-929,130	-		1
NpO ₂ OH(aq)	updated	-1,080,405	-1,199,226	25.000	1
NpO ₂ OH ⁺	new	-1,004,000	-	-	1
NpO ₂ SO ₄	new	-1,654,281	-1,864,321	58.833	1
NpO ₂ SO ₄ (aq)	new	-1,558,666	-1,753,373	44.920	1
NpOH ⁺⁺	new	-711,190	-	-	1
NpOH***	updated	-727,260	-	-	1
NpSO ₄ ⁺⁺	new	-1,274,887	-1,435,522	-176.635	1

Table 4-2. Np and Pu Species for which Thermodynamic Data Were Added, or Existing Data Were Modified, in the Data0.ymp.R2 Database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) (Continued)

Data0 Species Designation	Change	ΔG _f ° (J/mol)	ΔH _f ° (J/mol)	S° (J/mol-K)	Source
Np(SO ₄) ₂ (aq)	new	-2,042,873	-2,319,322	7.964	1
Np(SCN)***	new	-416,198	-486,622	-248.165	1
Np(SCN)2 ⁺⁺	new	-329,777	-412,222	-248.165	1
Np(SCN)3 ⁺	new	-241,072	-339,822	54.707	1
(PuO ₂) ₂ (OH) ₂ ⁺⁺	updated	-1,956,180	-	-	2
(PuO ₂) ₃ (CO ₃) ₆ ⁽⁻⁶⁾	new	-5,740,431	-	-	2
(UO ₂) ₂ (PuO ₂)(CO ₃) ₆ ⁽⁻⁶⁾	new	-6,135,670	-	-	2
Pu(SO ₄) ₂ ⁻	new	-2,099,545	-2,398,590	1.520	2
Pu(SO ₄) ₂ (aq)	new	-2,029,601	-	-	2
PuBr ⁺⁺⁺	new	-590,971	-	-	2
PuCl ⁺⁺	new	-717,051	-	-	2
PuCI***	new	-619,480	-	-	2
PuF ⁺⁺⁺	updated	-809,970	-866,145	-228.573	2
PuF ₂ ⁺⁺	updated	-1,130,651	-1,199,595	-104.666	2
PuH ₃ PO ₄ ⁺⁺⁺⁺	new	-1,641,050	-	-	2
Pul ⁺⁺	new	-636,987	-	-	2
PuNO ₃ ⁺⁺⁺	new	-599,913	-	-	2
PuO ₂ (CO ₃) ₂	updated	-1,900,920	-2,199,496	15.796	2
PuO ₂ (CO ₃) ₂	removed	-	-	-	-
PuO ₂ (CO ₃) ₃	updated	-2,447,085	-2,886,326	-11.847	2
PuO ₂ (CO ₃) ₃ ⁽⁻⁵⁾	updated	-2,465,031	-2,954,927	-116.406	2
Pu(CO ₃) ₅ ⁽⁻⁶⁾	removed	-	-	-	-
PuO ₂ (OH) ₂ (aq)	updated	-1,161,290	-	-	2
PuO ₂ (SO ₄) ₂	new	-2,275,477	-2,597,716	194.214	2
PuO ₂ Cl ⁺	new	-897,566	-	-	2
PuO ₂ Cl ₂ (aq)	new	-1,021,360	-	-	2
PuO ₂ CO ₃ -	Updated	-1,409,771	-	-	2
PuO ₂ CO ₃ (aq)	updated	-1,356,466	-	-	2
PuO ₂ F ⁺	updated	-1,069,900	-	-	2
PuO ₂ F ₂ (aq)	updated	-1,366,780	-	-	2
PuO ₂ OH(aq)	updated	-1,034,250	-	-	2
Pu(OH) ₄ (aq)	removed	-	-	1	-
PuO ₂ OH ⁺	updated	-968,099	-1,079,866	-12.680	2
PuO ₂ SO ₄ (aq)	new	-1,525,650	-1,715,276	65.963	2
PuOH ⁺⁺	updated	-776,739	-	-	2
PuOH ⁺⁺⁺	updated	-710,676	-789,725	-238.773	2
PuSCN ⁺⁺	new	-493,704	-	-	2
PuSO ₄ ⁺	new	-1,345,315	-1,483,890	-33.301	2
PuSO ₄ ⁺⁺	new	-1,261,329	-	-	2

Sources: 1 Lemire 2001 [DIRS 159027], Table 3.1 pp. 41 to 46. 2 Lemire 2001 [DIRS 159027], Table 4.1, pp. 55 to 59.

4.1.2 Compilation of Thermodynamic Data for Other Aqueous Species

In the development of the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), a variation on the isocoulombic/isoelectric spreadsheet (see Section 6.1.3 for an explanation of special function spreadsheets) was used to obtain the Gibbs free energy grids for species not previously defined strictly as basis species in data0.vmp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]). These basis species are Am⁺⁺, Am⁺⁺⁺. Am⁺⁺⁺⁺, AmO₂⁺, AmO₂⁺⁺, Np⁺⁺⁺⁺, NpO₂⁺, NpO₂⁺⁺, Pu⁺⁺⁺, Pu⁺⁺⁺, PuO₂⁺, PuO₂⁺⁺, and Ti(OH)₄(aq) (Table 4-3). The major difference from the regular isocoulombic/isoelectric spreadsheet was that the final step of calculating log K values for associated reactions was omitted in the case of species chosen as strict basis species (as these have no associated EO3/6 The Am data were taken from Silva et al. (1995 [DIRS 102087]), which is a comprehensive review of the thermochemistry of Am published by the OECD/NEA. The Np and Pu data were taken from the OECD/NEA Np and Pu volume (Lemire 2001 [DIRS 159027]), while the data for the secondary basis species Ti(OH)₄(aq), Ti(OH)₃⁺, and Ti(OH)₅⁻ were taken from Knauss et al. (2001 [DIRS 158998]). Data for the molybdenum aqueous species were obtained from Martell and Smith (1982 [DIRS 159196], p. 399). The OECD/NEA sources are considered "established fact" because they were developed from a comprehensive evaluation of available thermodynamic data and published in handbook form. Also, the Martell and Smith (1982 [DIRS 159196]) source is considered "established fact" because it represents a widely used comprehensive compilation of stability constants for aqueous species reactions. Evaluations of these and the Ti and Mo species data are given in Section 6.2.2. Standard for the solid phase rutile (TiO₂) are from data0.ymp.R0 thermodynamic data (DTN: MO0009THRMODYN.001 [DIRS 152576]), which also corresponds to the value reported by Robie et al. (1979 [DIRS 107109]), an "established fact" source.

Table 4-3. Thermodynamic Data for Actinide Basis Species, Redox Species, Titanium, and Molybdenum Species

	400	4110	S°				
Species	∆G _f ° (J/mol)	ΔH _f ° (J/mol)	(J/ mol-K)	Source			
•	Basis S		,				
Am ⁺⁺⁺	-598,698	-616,700	-201.000	1			
NpO ₂ ⁺	-907,765	-978,181	-45.904	2			
PuO ₂ ⁺	-852,646	-910,127	1.480	3			
Ti(OH) ₄ (aq)	-1,322,665	ı	39.207	4			
Secondary Basis Species (Redox)							
Am ⁺⁺	-376,780	-354,633	-1.000	1			
Am ⁺⁺⁺⁺	-346,358	-406,000	-406.000	1			
AmO ₂ ⁺	-739,796	-804,260	-21.000	1			
AmO ₂ ⁺⁺	-585,801	-650,760	-88.000	1			
Np ⁺⁺⁺	-512,866	-527,184	-193.584	2			
Np****	-491,774	-556,022	-426.390	2			
NpO ₂ ⁺⁺	-795,939	-860,733	-92.387	2			
Pu ⁺⁺⁺	-578,984	-591,790	-184.510	3			
Pu ⁺⁺⁺⁺	-477,988	-539,895	-414.535	3			
PuO ₂ ⁺⁺	-762,353	-822,036	-71.246	3			

Table 4-3. Thermodynamic Data for Actinide Basis Species, Redox Species, Titanium, and Molybdenum Species (Continued)

Species	∆G _f ° (J/mol)	∆H _f ° (J/mol)	S° (J/ mol-K)	Source			
	Titanium	Species					
Ti(OH) ₃ ⁺	-1,092,824	-	55.779	4			
Ti(OH) ₅	-1,482,898	-	154.242	4			
TiO ₂ (rutile)	-890,700	-	-	5			
Molybdenum Species							
Species	Log K	Reac	tion	Source			
		$H^{+} + HN$	loO ₄ =				
H ₂ MoO ₄ (aq)	4.00	H ₂ MoO ₄ (aq)		6			
HMoO ₄ -	4.24	H ⁺ + MoO ₄	= HMoO ₄ -	6			

Sources: 1 Silva et al. 1995 [DIRS 102087], Table III.1, pp. 37-38.

- 2 Lemire 2001 [DIRS 159027], Table 3.1, p. 41.
- 3 Lemire 2001 DIRS 159027, Table 4.1, p. 55.
- 4 Knauss et al. 2001 [DIRS 158998]. 5 Data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]); Robie et al. 1979 [DIRS 107109].
- 6 Martell and Smith 1982 [DIRS 159196], p. 399.

4.1.3 "Azero" Ion Size Parameters

In the development of the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), the "azero" ion size parameters were used in the B-dot equation (Helgeson 1969 [DIRS 137246]) for estimation of activity coefficients for aqueous species (see Section 6.5). Table 4-4 shows the "azero" values within the valence-type scheme as adopted in this database. This is the scheme used in data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]); therefore. this input is qualified for use in data0.vmp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) and data0.ymp.R4 (output DTN: SN0410T0510404.002).

Table 4-4. Suggested "Azero" Values for Various Charge Numbers

Charge Number (Z)	Ion Size (Å)		
<-1	4.0		
-1	4.0		
0	3.0		
+1	4.0		
+2	4.5		
+3	5.0		
+4	5.5		
>+4	6.0		

DTN: MO0009THRMODYN.001 [DIRS 152576] (Data0.ymp.R0).

4.1.4 Compilation of Thermodynamic Data for Clay Minerals

In the development of the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), the data for clay minerals were recalculated using thermodynamic data developed more recently than the sources used in the data0.ymp.R0 database (DTN: MO0009THRMODYN.001 [DIRS 152576]; Wolery 1978 [DIRS 151346]). The approach of Tardy and Garrels (1974 [DIRS 159209]) was implemented for data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) using Microsoft Excel spreadsheets for reestimating these data. Its implementation is discussed in Section 6.3.1. This approach uses standard molal thermodynamic data mainly from sheet silicates and simple oxides. These data are direct inputs in the thermodynamic calculations and, with one exception (described below) were taken from Helgeson et al. (1978 [DIRS 101596]). The standard thermodynamic data include ΔG_f° , S°, and V°. In addition, the C_p° parameters "a," "b," and "c" of the Maier-Kelly equation for extrapolation of C_p° values for the solids (Eq. 4-1) are included.

The ΔG_f° data for oxides summarized in Table 4-5 were taken from Helgeson et al. (1978 [DIRS 101596], Table 8, pp. 120-121). All of the other thermodynamic data for the oxides (S°, V°, and C_p° parameters a, b, and c) were from Helgeson et al. (1978 [DIRS 101596], Table 2, p. 48). The exceptions were the ΔG_f° and S° values for SiO₂, which was selected for consistency with revision to the Rimstidt paradigm discussed in Section 6.1.5, as documented by BSC (2004 [DIRS 170268], Section 6.3 and Table 6.4-1). Although the values of -204646.0 cal/mol and 9.88 cal/mol-K (reported by Helgeson et al. 1978 [DIRS 101596] for ΔG_f° and S°, respectively) were used in comparisons with previously calculated values, the final values used to calculate the thermodynamic properties were -204656.0 cal/mol and 9.904 cal/mol-K. These values are taken from *Data Qualification for Thermodynamic Data Used to Support THC Calculations* (BSC 2004 [DIRS 170268], Table 4-7).

Table 4-5. Oxide Thermodynamic Parameters Used to Estimate Thermodynamic Properties of Clays

				Heat Capacity Coefficients ^a		
Oxide Formula	ΔG _f ° (cal/mol)	V° (cm³/mol)	S° (cal/mol-K)	a (cal/mol-K)	b x 10 ³ (cal/mol-K ²)	c x 10 ⁻⁵ (cal-K/mol)
Al ₂ O ₃	-374824.0	25.575	12.180	27.490	2.820	8.380
CaO	-144366.0	16.764	9.500	11.670	1.080	1.560
Fe ₂ O ₃	-178155.0	30.274	20.940	23.490	18.600	3.550
FeO	-60097.0	12.000	14.520	12.120	2.070	0.750
K₂O	-77056.0	40.380	22.500	18.510	8.650	0.880
Mg(OH) ₂	-199646.0	24.630	_b	_b	_b	_b
MgO	-136086.0	11.248	6.440	10.180	1.740	1.480

Table 4-5. Oxide Thermodynamic Parameters Used to Estimate Thermodynamic Properties of Clays (Continued)

			Heat	Capacity Coeff	icients ^a	
Oxide Formula	∆G _f ° (cal/mol)	V° (cm³/mol)	S° (cal/mol-K)	a (cal/mol-K)	b x 10 ³ (cal/mol-K ²)	c x 10 ^{−5} (cal-K/mol)
Na₂O	-89883.0	25.000	17.935	18.250	4.890	2.890
SiO ₂	-204646.0°	22.688	9.88 ^c	11.220	8.200	2.700

Sources: ΔG_f° from Helgeson et al. 1978 [DIRS 101596], Table 8, pp. 120-121; all other data from Helgeson et al. 1978 [DIRS 101596], Table 2, p. 48.

The ΔG_f° data for sheet silicates used in the estimation of free energies of the silicated oxide components by the Tardy and Garrels (1974 [DIRS 159209]) method are from Helgeson et al. (1978 [DIRS 101596], Table 8, pp. 120-125) (Table 4-6). However, there are exceptions to this Ca-bearing source including several silicate phases present slop98.dat (DTN: MO0106MWDTDG01.035 [DIRS 161791]) and data0.ymp.R0 in (DTN: MO0009THRMODYN.001 [DIRS 152576]), that were incorporated in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). These exceptions are discussed in Section 6.1.6.

The V° values for the clays used to calculate molar volumes of other clays are from Helgeson et al. (1978 [DIRS 101596], Table 3, pp. 53-56, and Table 8, pp. 120-125) (Table 4-6). S° and the C_p ° parameters "a," "b," and "c" for the silicated components of clay minerals were calculated from the thermodynamic data for the base silicate minerals (Table 4-7) listed. The source of these thermodynamic data is Helgeson et al. (1978 [DIRS 101596], Table 8, pp. 120-125). The list of clay phases for which mineral volumes were estimated is discussed in Section 6.3.1 and shown in Table 4-8.

Table 4-6. ΔG_f° and V° of Minerals Used to Estimate ΔG_f° and V° of Silicated Components of Clay Minerals

Reference Mineral Formula		ΔG _f ° (cal/mol)	V° (cm³/mol)
14A-Amesite	Mg ₄ Al ₄ Si ₂ O ₁₀ (OH) ₈	_a	205.400
14A-Clinochlore	Mg ₅ Al ₂ Si ₃ O ₁₀ (OH) ₈	-1961703	207.110
14A-Daphnite	Fe ₅ Al ₂ Si ₃ O ₁₀ (OH) ₈	_a	213.420
7A-Amesite	Mg ₂ Al ₂ SiO ₅ (OH) ₄	_a _	103.000
7A-Chamosite	Fe ₂ Al ₂ SiO ₅ (OH) ₄	_a _	106.200
7A-Clinochlore	Mg ₅ Al ₂ Si ₃ O ₁₀ (OH) ₈	-1957101	211.500
7A-Cronstedtite	Fe ⁺⁺ ₂ Fe ⁺⁺⁺ ₂ SiO ₅ (OH) ₄	_a	110.900
7A-Daphnite	Fe ₅ Al ₂ Si ₃ O ₁₀ (OH) ₈	_a _	221.200
Annite	KFe ₃ AlSi ₃ O ₁₀ (OH) ₂	-1147156	154.320
Antigorite	Mg ₄₈ Si ₃₄ O ₈₅ (OH) ₆₂	-15808020	1749.130

^a Heat capacity coefficients a, b, and c defined in Eq. 4-1.

^b Values not used in any calculations.

 $^{^{\}rm c}$ Value of –204656.0 cal/mol for $\Delta G_{\rm f}^{\circ}$, and 9.904 cal/mol-K for S°, from BSC (2004 [DIRS 170268], Table 4-7) were used in DTN: MO0302SPATHDYN.000 [DIRS 161756]. This is consistent with the Rimstidt paradigm for quartz solubility.

Table 4-6. ΔG_f° and V° of Minerals Used to Estimate ΔG_f° and V° of Silicated Components of Clay Minerals (Continued)

Reference Mineral	Reference Mineral Formula		V° (cm³/mol)
Celadonite	KMgAlSi ₄ O ₁₀ (OH) ₂	_a	157.100
Chrysotile	$Mg_3Si_2O_5(OH)_4$	-964871	108.500
Greenalite	Fe ₃ Si ₂ O ₅ (OH) ₄	_a -	115.000
Hematite	Fe ₂ O ₃	-178155	_a
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	-905614	99.520
Margarite	CaAl ₄ Si ₂ O ₁₀ (OH) ₂	-1394370 ^b	129.400
Minnesotaite	Fe ₃ Si ₄ O ₁₀ (OH) ₂	_a	147.860
Muscovite	KAI ₃ Si ₃ O ₁₀ (OH) ₂	-1336301	140.710
Paragonite	NaAl ₃ Si ₃ O ₁₀ (OH) ₂	-1326012	132.530
Phlogopite	KAIMg ₃ Si ₃ O ₁₀ (OH) ₂	-1396187	149.660
Pyrophyllite	Al ₂ Si ₄ O ₁₀ (OH) ₂	-1255997	126.600
Quartz	SiO ₂	-204646	22.688
Sepiolite	Mg ₄ Si ₆ O ₁₅ (OH) ₂ :6H ₂ O	_a	285.600
Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	-1320188	136.250

Sources: Column 3: Helgeson et al. 1978 [DIRS 101596], Table 8, pp. 120-125. Column 4: Helgeson et al. 1978 [DIRS 101596], Table 3, pp. 53-56, and Table 8, pp. 120-125.

Table 4-7. Thermodynamic Data for Reference Minerals Used to Estimate S° and the a, b, and c Heat Capacity Parameters of the Silicated Components of Clay Minerals

				Heat (Capacity Coef	ficients ^a
Reference Mineral	Formula	S° (cm³/mol-K)	V° (cm³/mol)	a (cal/mol-K)	b x 10 ³ (cal/mol-K ²)	c x 10 ^{−5} (cal-K/mol)
7A-Clinochlore	Mg ₅ Al ₂ Si ₃ O ₁₀ (OH) ₈	106.500	211.500	162.820	50.620	40.880
14A-Clinochlore	Mg ₅ Al ₂ Si ₃ O ₁₀ (OH) ₈	111.200	207.110	166.500	42.100	37.470
Chrysotile	Mg ₃ Si ₂ O ₅ (OH) ₄	52.900	108.500	75.820	31.600	17.580
Muscovite	KAI ₃ Si ₃ O ₁₀ (OH) ₂	_b	_b	97.560	26.380	25.440
Pyrophyllite	Al ₂ Si ₄ O ₁₀ (OH) ₂	57.200	126.600	79.432	39.214	17.282
Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	62.340	136.250	82.480	41.610	13.340

Source: Helgeson et al. 1978 [DIRS 101596], Table 8, pp. 120-125.

^a Values are not used in any calculations.

^b Value of −1394150 cal/mol used in final calculations. The change is a result of making the Gibbs free energies and enthalpies consistent with updated values of Gibbs free energies of Ca⁺⁺ (Shock and Helgeson 1988 [DIRS 144817]). Margarite properties are included in the SUPCRT92 data file *slop98.dat* (DTN: MO0106MWDTDG01.035 [DIRS 161791]).

^a Coefficients defined in Eq. 4-1.

^b Values are not used in any calculations.

Table 4-8. Clay Minerals for which Molar Volumes Will Be Evaluated in this Report

Phase	Formula
14A-Ripidolite	$Mg_3Fe_2Al_2Si_3O_{10}(OH)_8$
7A-Ripidolite	$Mg_3Fe_2Al_2Si_3O_{10}(OH)_8$
Ca-Beidellite	Ca _{0.165} Al _{2.33} Si _{3.67} O ₁₀ (OH) ₂
Ca-Montmorillonite	Ca _{0.165} Mg _{0.33} Al _{1.67} Si ₄ O ₁₀ (OH) ₂
Ca-Nontronite	Ca _{0.165} Fe ₂ Al _{0.33} Si _{3.67} O ₁₀ (OH) ₂
Ca-Saponite	Ca _{0.165} Mg ₃ Al _{0.33} Si _{3.67} O ₁₀ (OH) ₂
Ferroaluminoceladonite	KFeAlSi ₄ O ₁₀ (OH) ₂
Ferroceladonite	$KFe^{++}Fe^{+++}Si_4O_{10}(OH)_2$
H-Beidellite	H _{0.33} Al _{2.33} Si _{3.67} O ₁₀ (OH) ₂
High Fe-Mg Smectite	$Na_{0.1}K_{0.2}Ca_{0.025}(Mg_{1.15}Fe^{+++}_{0.2}Fe^{++}_{0.5}Al_{0.75})(Al_{0.5}Si_{3.5})O_{10}(OH)_2$
H-Montmorillonite	H _{0.33} Mg _{0.33} Al _{1.67} Si ₄ O ₁₀ (OH) ₂
H-Nontronite	$H_{0.33}Fe_2AI_{0.33}Si_{3.67}O_{10}(OH)_2$
H-Saponite	H _{0.33} Mg ₃ Al _{0.33} Si _{3.67} O ₁₀ (OH) ₂
Illite	K _{0.6} Mg _{0.25} Al _{2.3} Si _{3.5} O ₁₀ (OH) ₂
K-Beidellite	K _{0.33} Al _{2.33} Si _{3.67} O ₁₀ (OH) ₂
K-Montmorillonite	K _{0.33} Mg _{0.33} Al _{1.67} Si ₄ O ₁₀ (OH) ₂
K-Nontronite	K _{0.33} Fe ₂ Al _{0.33} Si _{3.67} O ₁₀ (OH) ₂
K-Saponite	K _{0.33} Mg ₃ Al _{0.33} Si _{3.67} O ₁₀ (OH) ₂
Low Fe-Mg Smectite	$Na_{0.15}K_{0.2}Ca_{0.02}(Mg_{0.9}Fe^{+++}_{0.16}Fe^{++}_{0.29}AI)(AI_{0.25}Si_{3.75})O_{10}(OH)_2$
Mg-Beidellite	Mg _{0.165} Al _{2.33} Si _{3.67} O ₁₀ (OH) ₂
Mg-Montmorillonite	Mg _{0.495} Al _{1.67} Si ₄ O ₁₀ (OH) ₂
Mg-Nontronite	$Mg_{0.165}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$
Mg-Saponite	Mg _{0.165} Mg ₃ Al _{0.33} Si _{3.67} O ₁₀ (OH) ₂
Na-Beidellite	Na _{0.33} Al _{2.33} Si _{3.67} O ₁₀ (OH) ₂
Na-Montmorillonite	Na _{0.33} Mg _{0.33} Al _{1.67} Si ₄ O ₁₀ (OH) ₂
Na-Nontronite	Na _{0.33} Fe ₂ Al _{0.33} Si _{3.67} O ₁₀ (OH) ₂
Na-Saponite	Na _{0.33} Mg ₃ Al _{0.33} Si _{3.67} O ₁₀ (OH) ₂
Reykjanes Smectite	$Na_{0.33}K_{0.03}Ca_{0.66}(Mg_{1.29}Fe^{+++}_{0.35}Fe^{++}_{0.33}Mn_{0.01}Al_{0.28})(Al_{0.83}Si_{3.17})O_{10}(OH)_2$

Output DTN: SN0410T0510404.001 (Spreadsheet *Volume_Q_DS_11-01-04.xls*).

4.1.5 Compilation of Thermodynamic Data for Zeolites

Zeolite minerals are commonly found in the rock matrix and fractures at Yucca Mountain (Vaniman and Bish 1995 [DIRS 101496]; Carlos et al. 1995 [DIRS 105213]). Therefore, consideration of these minerals is important in modeling water/rock reactions. The previous database data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]) contained 16 zeolite mineral phases. The data (ΔG_f° , ΔH_f° , S°, V°, and C_p°) for these 16 minerals were originally taken from work done by Viani and Bruton (1992 [DIRS 101407], Tables 1 and 2; Appendix E, Tables 1 and 2), but were truncated at temperatures beyond 100°C. Viani and Bruton (1992 [DIRS 101407]) provide heat capacity data (C_p°) at elevated temperatures that would allow for extrapolation of ΔG_f data to temperatures beyond 100°C. The requisite thermodynamic data were entered into the spreadsheets to establish the log K grid beyond 100°C. Estimated data for

 ΔG_f° , ΔH_f° , S° , V° , and C_p° for an additional five zeolite minerals were taken from Table 1 of Chipera et al. (1995 [DIRS 100025]), included in a recent book on natural zeolites published by the International Committee on Natural Zeolites. A typographical error in Table 1 of Chipera et al. (1995 [DIRS 100025]) expressed the standard entropy in kJ/mol K instead of J/mol K. To confirm this, standard entropy values for one of the zeolites (e.g., analcime) were checked against handbook data (Robie and Hemingway 1995 [DIRS 153683]), indicating a difference within a few kJ/mol and not by a factor of a 1000. The list of updated zeolite phases in the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) is given in Table 4-9. Thermodynamic data for these minerals are listed in Table 4-10. The analysis used to generate the computed log K values (over the entire temperature range) and associated corrections using updated quartz solubility data are discussed in Section 6.3.2.

4.1.6 Compilation of Thermodynamic Data for Cement Phases

Previous work to derive a thermodynamic database to investigate seepage-cement interactions resulted in the creation of a cement database that was compatible with EQ3/6 (Hardin 1998 [DIRS 100350], pp. 7-28). However, this database was not developed under a qualified process and lacks cement phases common to grouts. Even though it contains many cement minerals of interest, it does not include many known minerals associated with the production of cement pastes or the dissolution of hardened concretes and grouts.

In development of the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), the cement data were developed using the existing qualified data0.ymp.R0 database (DTN: MO0009THRMODYN.001 [DIRS 152576]) with added data from Perkins and Palmer (2000 [DIRS 153349]) for Cr-ettringite (chromium ettringite). This source also generated a log K value at 25°C (log K = -2.77) for the reaction CaCrO₄(aq) = Ca⁺⁺ + CrO₄⁻⁻ consistent with the retrieved solubility data for Cr-ettringite.

Numerous data sources were reviewed for thermodynamic data of cement phases but the compilation by Babushkin et al. (1985 [DIRS 116981]) was deemed sufficiently comprehensive and was selected for inclusion in the database. Certain data from Perkins and Palmer (1999 [DIRS 152703]) are used in this report to corroborate the data used from Babushkin et al. (1985 In addition, data from Perkins and Palmer (2000 [DIRS 153349]) for [DIRS 116981]). Cr-ettringite were added to the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) (this mineral was not included data0.vmp.R0; DTN: MO0009THRMODYN.001 [DIRS 152576]). These data are listed in Table 4-11. Other sources such as Fujii and Kondo (1983 [DIRS 144876]), Atkins et al. (1993 [DIRS 131758]), Bennett et al. (1992 [DIRS 116990]), and Damidot et al. (1994 [DIRS 144866]) report solubility data for various cement phases which are also used as direct input.

Table 4-9. Zeolite Minerals Included in Data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756])

Mineral	Formula	Reaction	Source
Analcime	Na _{0.96} Al _{0.96} Si _{2.04} O ₆ :H ₂ O	Analcime + $3.84H^{+}$ = 0.96 Al^{+++} + 0.96 Na^{+} + 2.04SiO_{2} + $2.92 \text{H}_{2}\text{O}$	1
Analcime-dehy	Na _{0.96} Al _{0.96} Si _{2.04} O ₆	Analcime-dehy + $3.84H^{+}$ = 0.96 Al^{+++} + 0.96 Na^{+} + 2.04SiO_2 + $1.92 \text{H}_2 \text{O}$	1
Clinoptilolite	$\begin{array}{l} Na_{0.954}K_{0.543}Ca_{0.761}Mg_{0.124}Sr_{0.036}Ba_{0.062} \\ Mn_{0.002}Al_{3.45}Fe_{0.017}Si_{14.533}O_{46.922}H_{21.844} \end{array}$	Clinoptilolite + 13.868 H^+ = 0.002Mn^{++} + 0.017Fe^{+++} + 0.036Sr^{++} + 0.062Ba^{++} + 0.124Mg^{++} + 0.543K^+ + 0.761Ca^{++} + 0.954Na^+ + 3.45Al^{+++} + $14.533 \text{SiO}_2(\text{aq})$ + $17.856 \text{H}_2 \text{O}$	1
Clinoptilolite- dehy	$\begin{array}{l} Na_{0.954}K_{0.543}Ca_{0.761}Mg_{0.124}Sr_{0.036}Ba_{0.062} \\ Mn_{0.002}Al_{3.45}Fe_{0.017}Si_{14.533}O_{36} \end{array}$	Clinoptilolite + 13.868 H^+ = 0.002Mn^{++} + 0.017Fe^{+++} + 0.036Sr^{++} + 0.062Ba^{++} + 0.124Mg^{++} + 0.543K^+ + 0.761Ca^{++} + 0.954Na^+ + 3.45Al^{+++} + $14.533 \text{SiO}_2(\text{aq})$ + $6.934 \text{H}_2 \text{O}$	1
Clinoptilolite-Ca	Ca _{1.7335} Al _{3.45} Fe _{0.017} Si _{14.533} O ₃₆ : 10.922H ₂ O	Clinoptilolite-Ca + $13.868H^{+}$ = $0.017Fe^{+++}$ + $1.7335Ca^{++}$ + $3.45Al^{+++}$ + $14.533SiO_{2}(aq)$ + $17.856H_{2}O$	1
Clinoptilolite-Cs	Cs _{3.467} Al _{3.45} Fe _{0.017} Si _{14.533} O ₃₆ :10.922H ₂ O	Clinoptilolite-Cs + $13.868H^{+}$ = $0.017Fe^{+++}$ + $3.467Cs^{+}$ + $3.45Al^{+++}$ + $14.533SiO_{2}(aq)$ + $17.856H_{2}O$	1
Clinoptilolite-K	K _{3.467} Al _{3.45} Fe _{0.017} Si _{14.533} O ₃₆ :10.922H ₂ O	Clinoptilolite-K + $13.868H^{+}$ = $0.017Fe^{+++}$ + $3.467K^{+}$ + $3.45Al^{+++}$ + $14.533SiO_{2}(aq)$ + $17.856H_{2}O$	1
Clinoptilolite-NH ₄	(NH ₄) _{3.467} Al _{3.45} Fe _{0.017} Si _{14.533} O ₃₆ : 10.922H ₂ O	Clinoptilolite-NH ₄ + 10.401 H ⁺ = 0.017 Fe ⁺⁺⁺ + 3.45 Al ⁺⁺⁺ + 3.467 NH ₃ (aq) + 14.533 SiO ₂ (aq) + 17.856 H ₂ O	1
Clinoptilolite-Na	Na _{3.467} Al _{3.45} Fe _{0.017} Si _{14.533} O ₃₆ :10.922H ₂ O	Clinoptilolite-Na + $13.868H^{+}$ = $0.017Fe^{+++}$ + $3.467Na^{+}$ + $3.45Al^{+++}$ + $14.533SiO_{2}(aq)$ + $17.856H_{2}O$	1
Clinoptilolite-Sr	Sr _{1.7335} Al _{3.45} Fe _{0.017} Si _{14.533} O ₃₆ : 10.922H ₂ O	Clinoptilolite-Sr + $13.868H^{+}$ = $0.017Fe^{+++}$ + $1.7335Sr^{++}$ + $3.45Al^{+++}$ + $14.533SiO_{2}(aq)$ + $17.856H_{2}O$	1
Heulandite	Ba _{0.065} Sr _{0.175} Ca _{0.585} K _{0.132} Na _{0.383} Al _{2.165} Si _{6.835} O ₁₈ :6H ₂ O	Heulandite + $8.66H^{+}$ = $0.065Ba^{++}$ + $0.132K^{+}$ + $0.175Sr^{++}$ + $0.383Na^{+}$ + $0.585Ca^{++}$ + $2.165Al^{+++}$ + $6.835SiO_{2}(aq)$ + $10.33H_{2}O$	1
Mesolite	Na _{0.676} Ca _{0.657} AI _{1.99} Si _{3.01} O ₁₀ :2.647H ₂ O	Mesolite + $7.96H^{+}$ = $0.657Ca^{++}$ + $0.676Na^{+}$ + $1.99Al^{+++}$ + $3.01SiO_{2}(aq)$ + $6.627H_{2}O$	1
Mordenite	Ca _{0.2895} Na _{0.361} Al _{0.94} Si _{5.06} O ₁₂ :3.468H ₂ O	Mordenite + $3.76H^{+}$ = $0.2895Ca^{++}$ + $0.361Na^{+}$ + $0.94Al^{+++}$ + $5.06SiO_{2}(aq)$ + $5.348H_{2}O$	1
Natrolite	Na ₂ Al ₂ Si ₃ O ₁₀ :2H ₂ O	Natrolite + $8H^{+}$ = $2AI^{+++}$ + $2Na^{+}$ + $3SiO_{2}(aq)$ + $6H_{2}O$	1
Scolecite	CaAl ₂ Si ₃ O ₁₀ :3H ₂ O	Scolecite + $8H^{+}$ = Ca^{++} + $2AI^{+++}$ + $3SiO_{2}(aq)$ + $7H_{2}O$	1
Stilbite	Ca _{1.019} Na _{0.136} K _{0.006} Al _{2.18} Si _{6.82} O ₁₈ : 7.33H ₂ O	Stilbite + $8.72H^{+}$ = $0.006K^{+}$ + $0.136Na^{+}$ + $1.019Ca^{++}$ + $2.18Al^{+++}$ + $6.82SiO_{2}(aq)$ + $11.69H_{2}O$	1
Chabazite	K _{0.6} Na _{0.2} Ca _{1.5} Al _{3.8} Si _{8.2} O ₂₄ :10H ₂ 0	Chabazite + $15.2H^{+}$ = $0.6K^{+}$ + $0.2Na^{+}$ + $1.5Ca^{++}$ + $3.8Al^{+++}$ + $8.2SiO_{2}(aq)$ + $17.6H_{2}O$	2
Erionite	K _{1.5} Na _{0.9} Ca _{0.9} Al _{4.2} Si _{13.8} O ₃₆ :13.0H ₂ O	Erionite + $16.8H^{+}$ = $1.5K^{+}$ + $0.9Na^{+}$ + $0.9Ca^{++}$ + $4.2Al^{+++}$ + $13.8SiO_{2}$ + $21.4H_{2}O$	2
Laumontite	K _{0.2} Na _{0.2} Ca _{1.8} Al ₄ Si ₈ O ₂₄ :8H ₂ O	Laumontite + $16H^{+}$ = $0.2K^{+}$ + $0.2Na^{+}$ + $1.8Ca^{++}$ + $4AI^{+++}$ + $8SiO_2$ + $16H_2O$	2
Phillipsite	K _{0.7} Na _{0.7} Ca _{1.1} Al _{3.6} Si _{12.4} O ₃₂ :12.6H ₂ O	Phillipsite + $14.4H^{+}$ = $0.7K^{+}$ + $0.7Na^{+}$ + $1.1Ca^{++}$ + $3.6Al^{+++}$ + $12.4SiO_{2}$ + $19.8H_{2}O$	2
Stellerite	Ca _{2.0} Al _{4.0} Si ₁₄ O ₃₆ :14H ₂ O	Stellerite + $16H^{+}$ = $2.0Ca^{++}$ + $4.0Al^{+++}$ + $14SiO_2$ + $22H_2O$	2

Sources: 1 Viani and Bruton 1992 [DIRS 101407], Tables 1 and 2; Appendix E, Tables 1 and 2. 2 Chipera et al. 1995 [DIRS 100025], Table 1.

Table 4-10. Thermodynamic Data for Zeolite Minerals

						Empirical (Coefficients	for the Heat	Canacity Fo	uuation ^a		
Phase	ΔG _f ° (J/mol)	ΔH _f ° (J/mol)	S° (J/mol-K)	V° (cm³/mol)	C _p ° (J/mol-K)	T (J/mol-K²)	T ² (J/mol-K ³)	T³ (J/mol-K⁴)	T ⁻² (J-K ² /mol)	T ⁻³ (J-K ⁴ /mol)	T ^{-0.5} (J-K ^{0.5} / mol)	Source
Analcime	-3,077,200	-3,296,900	226.75	-	2.376E+02	-4.743E+00	1.663E-03	-1.236E-06	-	-	-	1
Analcime-dehy	-2,803,700	-2,970,200	171.71	-	1.108E+02	2.717E-01	-1.172E-03	-	-1.583E+06	-	-	1
Clinoptilolite ^b	-19,021,200	-20,587,800	1,483.06	-	5.016E+01	6.365E+00	-4.616E-03	ı	-	ı	ı	1
Clinoptilolite-dehyb	-16,227,300	-17,210,200	893.31	-	-4.781E+02	6.910E+00	-9.031E-03	3.902E-06	-	-	ı	1
Clinoptilolite-Cab	-19,027,912	-	1,462.73	632.050	2.990E+01	6.348E+00	4.616E-03	-	1.696E+05	-	-	1
Clinoptilolite-Csb	-19,115,382	-	1,561.18	632.050	5.971E+01	6.398E+00	4.616E-03	-	1.301E+06	-	-	1
Clinoptilolite-K ^b	-19,071,429	ı	1,509.29	632.050	7.951E+01	6.403E+00	4.616E-03	ı	6.628E+05	ı	ı	1
Clinoptilolite-NH ₄ ^b	-18,364,701	ı	ı	-	-	i	-	ı	-	ı	ı	1
Clinoptilolite-Nab	-18,978,314	ı	1,507.16	632.050	7.762E+01	6.365E+00	4.616E-03	ı	-	ı	ı	1
Clinoptilolite-Srb	-19,047,857	ı	1,480.22	632.050	3.476E+01	6.348E+00	4.616E-03	ı	-1.173E+04	ı	ı	1
Heulandite	-9,779,100	-10,594,600	767.18	-	7.456E+02	6.513E-01	-	ı	-1.411E+07	ı	ı	1
Mesolite	-5,513,200	-5,947,154	363.00	-	1.908E+02	6.793E-01	-	ı	-1.633E+06	ı	ı	1
Mordenite	-6,228,100	-6,736,700	486.54	-	5.281E+02	1.625E-01	-	ı	-8.197E+06	1	1	1
Natrolite	-5,316,600	-5,718,600	359.73	-	3.020E+02	3.769E-01	-	ı	-4.898E+06	ı	ı	1
Scolecite	-5,597,900	-6,049,000	367.42	-	1.352E+02	8.305E-01	-	ı	-	ı	ı	1
Stilbite	-10,114,100	-11,005,700	805.54	-	4.430E+02	6.173E-01	3.609E-03	-5.247E-06	-	ı	ı	1
Chabazite	-13,850,300	-15,047,400	1,194.30	499.400	2.023E+03	-	-	-	-3.016E-03	4.195E-05	-1.385E+00	2
Erionite	-19,813,000	-21,497,500	1,640.50	672.000	2.853E+03	-	-	1	-4.704E-03	6.723E-05	-1.923E+00	2
Laumontite	-13,431,200	-14,525,900	1,011.20	406.400	1.843E+03	-	-	-	-3.012E-03	4.147E-05	-1.227E+00	2
Phillipsite	-17,817,700	-19,375,100	1,491.90	609.200	2.609E+03	-	-	-	-4.158E-03	5.918E-05	-1.778E+00	2
Stellerite	-19,996,800	-21,751,300	1,611.70	665.500	2.887E+03	-	-	-	-4.478E-03	6.259E-05	-1.983E+00	2

Sources: 1 Viani and Bruton 1992 [DIRS 101407], Tables 1 and 2; Appendix E, Tables 1 and 2. Chipera et al. 1995 [DIRS 100025], Table 1.

^a Empirical coefficients based on the equation given by Viani and Bruton (1992 [DIRS 101407], p. 60, Table E.2, Footnote 1). ^b Units for partial molal thermodynamic properties originally given in cal/mol basis. Converted to J/mol basis in this table.

The following minerals associated with cement already existed in data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]), with log K values up to 100°C: gypsum, wollastonite, brucite, portlandite, lime, ferrite-Mg, ferrite-Ca, ferrite-dicalcium, sepiolite, gibbsite, anhydrite, and periclase. For data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) the log K values for these minerals were calculated up to 300°C (except for gypsum and sepiolite) using the input thermodynamic data listed in Table 4-17. Since the sources of these data were already qualified, no further evaluation is necessary.

Data for the calcium silicate hydrate (CSH) cement phase (examined for qualification, although not active in the data0.ymp.R2 database; DTN: MO0302SPATHDYN.000 [DIRS 161756]) are from Fujii and Kondo (1983 [DIRS 144876]). Table 4-12 shows the values adopted for the analysis of log K values for this phase. For evaluation of heat capacities as applied to this phase, C_p° data for portlandite, alpha-quartz, and H_2O (Table 4-13) were used (see Section 6.3.3.1). Also, heat capacity data for $CaCl_2(cr)$ are listed in Table 4-14 for use in the extrapolation of log K values for CSH and Friedl salt phases at higher temperatures. The log K temperature extrapolation uses an approximation of the cement heat capacity based on a linear representation of heat capacity values of the constituent oxides, hydroxides, and salts making up the cement.

Gibbs free energy of formation data for Na-gismondine and Ca-gismondine (-1179160 and -1187450 cal/mol, respectively, Table 4-15) were obtained from Atkins et al. (1993 [DIRS 131758], Section 5.2.6). The log K value (73.78) for hydrotalcite dissociation was obtained from Bennett et al. (1992 [DIRS 116990]). The log K values for monocarboaluminate (3CaO•Al₂O₃•CaCO₃•10H₂O) and hemicarboaluminate (3CaO•Al₂O₃•0.5CaCO₃•0.5Ca(OH)₂ •10.5H₂O) were obtained from Damidot et al. (1994 [DIRS 144866], Appendix 1) reporting log K values of 69.99 and 85.76, respectively.

The log K value at 25C for the dissociation reaction of the cement phase syngenite is −7.6 as given in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). This log K value is evaluated in Section 6.3.3.9.

Table 4-11. Thermodynamic Properties for Calcium Silicates and Aluminates

					Heat Ca	pacity Coeffi	icients ^a
Solid Phase	Formula	∆G° _f (cal/mol)	ΔH° _f (cal/mol)	S° ₂₉₈ (cal/mol)	a (cal/mol-K)	b× 10 ³ (cal/mol-K ²)	c × 10 ^{−5} (cal-K/mol)
Allite (C ₃ S) ^b	3CaO⋅SiO₂	-665470	-700430	40.3	49.85	8.62	-10.15
$(C_{12}A_7)^b$	12CaO·7Al ₂ O ₃	-4410000	-4640160	249.7	301.96	65.5	-55.3
(C ₂ AH ₈) ^b	2CaO·Al ₂ O ₃ ·8H ₂ O	-1151540	-1299200	106.4	68.38	153.45	-
$(C_3A)^b$	3CaO·Al ₂ O ₃	-808400	-851000	49.1	62.28	4.58	-12.1
(C ₄ AF) ^b	4CaO·Al ₂ O ₃ ·Fe ₂ O ₃	-1144000	-1214200	78	89.49	17.4	ı
(C ₄ AH ₁₃) ^b	4CaO·Al ₂ O ₃ ·13H ₂ O	-1756170	-1988000	171.6	109.6	242.19	ı
(C ₄ AH ₁₉) ^b	4CaO·Al₂O3·19H₂O	-2096330	-2411000	228	122.36	394	-
(CA) ^b	CaO·Al ₂ O ₃	-527700	-556180	27.3	36.01	9.98	-7.96
(CA ₂) ^b	CaO·2Al ₂ O ₃	-907100	-957060	42.5	66.09	5.48	-17.8
(CAH ₁₀) ^b	CaO·Al ₂ O ₃ ·10H ₂ O	-1103700	-1271400	116.1	67.85	182.46	-
Afwillite	Ca ₃ Si ₂ O ₄ (OH) ₆	-1052950	-1143200	74.6	81.54	45.1	-14.7
Bellite (C ₂ S) ^b	2CaO⋅βSiO₂	-524190	-551740	30.5	36.25	8.83	-7.24

Table 4-11. Thermodynamic Properties for Calcium Silicates and Aluminates (Continued)

					Heat Ca	pacity Coeff	icients ^a
Solid Phase	Formula	∆G° _f (cal/mol)	ΔH° _f (cal/mol)	S° ₂₉₈ (cal/mol)	a (cal/mol-K)	b× 10 ³ (cal/mol-K ²)	c × 10 ⁻⁵ (cal-K/mol)
Ettringite	3CaO·Al₂O₃·3CaSO₄·32H₂O	-3634260	-4201320	417.6	208	740.93	-
Cr-ettringite	Ca ₆ Al ₂ (CrO ₄) ₃ (OH) ₁₂ ·26H ₂ O	-3616395.8	-4141969.4	-	-	-	-
Foshagite	Ca ₄ Si ₃ O ₉ (OH) ₂ ·0.5H ₂ O	-1347900	-1439900	78.95	87.95	3.95	-13.5
Friedl Salt	CaCl ₂ ·3CaO·16H ₂ O	-	-1833000	-	-	-	-
Gyrolite	Ca ₂ Si ₃ O ₇ (OH) ₂ ·1.5H ₂ O	-1085650	-1175850	64	79.47	36.3	-17.6
Hillebrandite	Ca ₂ SiO ₃ (OH) ₂ ·0.17H ₂ O	-592900	-637150	38.4	41.4	22.4	-7.4
Hydrogarnet	3CaO·Al₂O₃·6H₂O	-1198400	-1326000	96.7	68.91	127.17	-
Monosulphate	3CaO·Al₂O₃·CaSO₄·12H₂O	-1859140	-2096440	178.6	113.71	246.84	-
Okenite	CaSi ₂ O ₄ (OH) ₂ ·H ₂ O	-686400	-750300	40.9	44.81	18.7	-10.4
Plombierite	5CaO·6SiO₂·10.5H₂O	-2647300	-2911250	193.15	132.2	270	-
Riversideite	Ca ₅ H ₂ (SiO ₃) ₆ ·2H ₂ O	-2215000	-2375000	122.65	143.55	74.7	-20.8
Tobermorite	5CaO·6SiO₂·5.5H₂O	-2361450	-2556300	146.15	110.6	189	-
Xonotlite	Ca ₆ [Si ₆ O ₁₇](OH) ₂	-2259400	-2396700	121.3	132.25	65.2	-18.4

Sources: Babushkin et al. 1985 [DIRS 116981], Appendix 1.

Cr-ettringite data, which are for 25°C, are from Perkins and Palmer 2000 [DIRS 153349].

Table 4-12. Thermodynamic Data for CSH with Ca to Si Ratio of 1.7

ΔH° _f	$\Delta G^_f$	S°
-2890 kJ/mol	-2630 kJ/mol	200 J/mol-K

Source: Fujii and Kondo 1983 [DIRS 144876].

Table 4-13. Heat Capacity Coefficient Data for Portlandite, Alpha-Quartz, and H₂O

Phase	a (cal/mol-K) ^a	b × 10 ³ (cal/mol-K ²) ^a	c × 10 ⁻⁵ (cal-K/mol) ^a	Source
Portlandite (Ca[OH] ₂)	101.79	1.80E+01	-1.74E+00	1
SiO ₂ (alpha-quartz)	11.22	8.20E+00	-2.70E+00	2
H ₂ O(s)	7.11	8.24E+00	0	2
H ₂ O(zw) ^b	11.4	0	0	2

Sources: 1 Binnewies and Milke 1999 [DIRS 158955].

^a Heat capacity coefficients refer to those in Eq. 4-1.

^b For the cement phases in parentheses, the letter "A" stands for Al₂O₃, "C" for CaO, "S" for SiO₂, and "H" for H₂O components in the cement. This is customary notation for cement phase composition.

² Helgeson et al. 1978 [DIRS 101596], Table 2, p. 48.

^a Heat capacity coefficients refer to those in Eq. 4-1.

^b H₂O(zw) refers to "zeolitic water" after Helgeson et al. (1978 [DIRS 101596], Table 2, p. 48).

Table 4-14. Heat Capacity Data for CaCl₂(cr)

T (K)	C _p °
100	48.812
200	67.357
298.15	72.856
300	72.927
400	75.647
500	77.153
600	78.199
700	79.370

Source: Chase 1998 [DIRS 157874], Part I, Al.-Co, p. 711.

Table 4-15. Gibbs Free Energy of Formation for Na- and Ca-Gismondine Minerals

Mineral	Formula	ΔG° _f kcal/mol	Source
Gismondine-Na	Na ₂ Al ₂ Si ₂ O ₈ •4H ₂ O	-1179.16	Atkins et al. 1993 [DIRS 131758]
Gismondine-Ca	CaAl ₂ Si ₂ O ₈ •4H ₂ O	-1187.45	Atkins et al. 1993 [DIRS 131758]

4.1.7 Compilation of Thermodynamic Data for Additional Solid Phases

Uranyl silicates are expected to be the major alteration products of spent nuclear fuel and high-level waste glass in the repository. Geochemical calculations require thermodynamic data for these minerals. Data for four uranyl silicates that have been observed in both laboratory spent fuel corrosion experiments and natural analog sites were included in the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]): soddyite, uranophane, Na-weeksite, and Na-boltwoodite. The sources of log K data are described in Table 4-16. Analysis of these data is discussed in Sections 6.3.4.1 through 6.3.4.4.

Data for β-UO₃ in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) were obtained from the qualified database data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]); their original source was Grenthe et al. (1992 [DIRS 101671), which is "established fact." Review of the thermodynamic data for this phase indicates that the retrieved log K data are correct and since the source is qualified for Yucca Mountain Project (YMP) use, no further evaluation is necessary.

Table 4-16. Sources of Thermodynamic Data for Inputs for Uranium Silicate Minerals

Mineral	Source	Data Extracted	Log K
Soddyite	Moll et al. 1996 [DIRS 106349], p. 6	Log K (N ₂ atmosphere experiments at 25°C)	6.03 ± 0.45
Uranophane	Pérez et al. 2000 [DIRS 157910], p. 606	Log K (25°C)	11.7 ± 0.6
Sodium weeksite	Nguyen et al. 1992 [DIRS 100809], Table 6, p. 374	Log K (30°C)	1.50 ± 0.08
Sodium boltwoodite	Nguyen et al. 1992 [DIRS 100809], Table 6, p. 374	Log K (30°C)	≥ 5.82 ± 0.16
β-UO₃ data	data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]); Grenthe et al. 1992 [DIRS 101671], Tables III-1 and III-3	Log K values at a temperature range from 0.01°C to 100°C	9.6847, 8.3205, 6.7706, and 5.3656 at 0.01°C, 25°C, 60°C, and 100°C, respectively

Thermodynamic data for various solid phases are used for modeling of in-package chemical reactions and reactions involving degraded waste forms at relevant environmental conditions. For construction of the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), large data sets were obtained from well-known compilations including the OECD/NEA Database (Lemire 2001 [DIRS 159027]), Binnewies and Milke (1999 [DIRS 158955]), and Barin and Platzki (1995) [DIRS 157865]. These handbooks were chosen because they are recent, comprehensive, and accepted within the scientific community. Table 4-17 presents the thermodynamic data which were either updated or added in the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]).

During data qualification with this report, an error was identified in the calculation of log K values for Np and Pu solids. Calculation spreadsheets for neptunium and plutonium that took Maier-Kelley parameters from Tables 3.3 and 4.3 of Lemire (2001 [DIRS 159027]) were not scaled for the factor of 1000 on the "b" parameter, did not use the "c" parameter, and sometimes applied inappropriate parameters as Maier-Kelly parameters. Therefore, the temperature extrapolations of log K for solids calculated in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) using thermodynamic data from these two tables in Lemire (2001 [DIRS 159027]) are incorrect. The log K values at 25°C are correct, and in many cases the maximum deviations in the log K values are relatively small, generally less than 0.2 log K units at 300°C. In general, these deviations increase with increasing temperature. The affected log K values are corrected in the data0.ymp.R4 database (output DTN: SN0410T0510404.002) and an evaluation is given in Section 6.3.4. Transcription errors were identified for solid species in the scaling of the "c" coefficient for heat capacity from Binnewies and Milke (1999 [DIRS 158955]) into the calculation spreadsheet for the species listed in Table 4-17 using this source. This error is further discussed in Section 6.3.4.5.

4.1.8 Compilation of Thermodynamic Data for Gases and Associated Aqueous Species

Additional gas data and their associated aqueous species were added to the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]). The values included in the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) are those developed using the same SUPCRT92 approach with the template spreadsheets as was used for other species extrapolated to temperatures above 25°C as will be discussed in Section 6.1.2 of this report.

Data for the dissociation of HF (aq) (Eq. 4-2) from ionic species were taken from two sources. The values selected from Ellis and Mahon (1977 [DIRS 159230], Table 8.4, p. 288) are for the pK_a (referring to the association constant) of HF between steam and water at various temperatures (250 to 300°C) (Table 4-18). This source is an excellent compilation of data collected from geothermal wells in New Zealand. In addition to this, data from Clark (1966 [DIRS 153163], Table 18-4, p. 407) for a temperature range of 15 to 200°C were also used to complement the data from Ellis and Mahon (1977 [DIRS 159230]).

$$HF(aq) = H^{+} + F^{-}$$
 (Eq. 4-2)

Table 4-17. Thermodynamic Data Used as Inputs to Calculate Log K Grids for Data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756])

		_			Heat	Capacity Coeffic	cients ^a]
Phase	ΔG° _f (J/mol)	ΔH° _f (J/mol)	S° (J/mol-K)	V° (cm³/mol)	a (J/mol-K)	b x 10 ³ (J/mol-K ²)	c x 10 ⁻⁵ (J-K/mol) ^b	Source
(NH4)4NpO2(CO3)3	-2,850,284	-	-	-	-	-	-	1
Portlandite Ca(OH) ₂	-898,470	-986,100	83.40	33.06	101.790	18.0000	-1.740	2, 3
Ferrite-Dicalcium Ca ₂ Fe ₂ O ₅	-2,001,686	-2,133,700	188.70	67.18	248.610	-4.8900	0.000	2, 3
Brucite	-835,319	-926,296	63.14	24.63	101.031	16.786	-25.564	4
CaO (lime)	-604,027	-635,089	39.75	16.764	48.827	4.519	-6.527	4
Periclase	-569384	-601659	26.94	11.25	42.593	7.280	-6.192	4
Ferrite-Mg	-1,317,429	-1,440,100	123.8	44.57	167.19	14.23	-2.99	2, 3
Gypsum (CaSO ₄ ·2H ₂ O)	-1,797,197	-2,022,628	194.14	74.69	5.220	0.3180	-	6
Anhydrite	-1,321,830	-1,434,108	106.69	45.94	70.208	98.742	0.000	4
Gibbsite	-1,155,487	-1,293,128	70.08	31.96	36.192	190.790	0.000	4
Sepiolite	-9,251,627	-10,116,912	613.37	285.6	-	-	-	4
Ca ₃ Al ₂ O ₆	-3,411,786	-3,587,800	205.90	88.94	260.580	19.1600	-5.030	2, 3
CaAl ₂ O ₄	-2,208,820	-2,326,300	114.20	53.02	150.620	24.9400	-3.330	2, 3
Wollastonite	-1,544,837	-1,630,045	82.0	39.93	111.462	15.062	27.280	2
Pseudo wollastonite CaSiO ₃	-1,544,739	-1,628,400	87.40	40.08	108.160	16.4800	-2.360	2, 3
Titanite CaSiTiO ₅	-2,461,780	-2,603,300	129.20	55.65	177.360	23.1800	-4.030	2, 3
Perovskite CaTiO ₃	-1,575,247	-1,659,000	93.70	33.63	127.490`	5.6900	-2.800	2, 3
Co(OH) ₂	-454,168	-541,300	93.30	24.74	82.840	47.7000	0.000	2, 3
Spinel-Co Co ₃ O ₄	-794,901	-918,700	109.30	-	131.650	66.0200	-2.480	2, 3
CoCl ₂	-269,650	-312,500	109.30	38.69	81.580	7.4100	-0.470	2, 3
CoF ₃	-718,899	-790,400	94.60	29.88	100.280	4.8800	-0.880	2, 3
Sphaerocobaltite CoCO ₃	-636,782	-713,000	87.90	28.80	88.280	38.9100	-1.800	2, 3
CoCr ₂ O ₄	-1,329,788	-1,438,300	126.80	-	167.650	17.7400	-1.400	2, 3
CoF ₂	-626,562	-672,400	82.00	21.73	80.910	6.1500	-1.240	2, 3
CoFe ₂ O ₄	-980,455	-1,088,700	142.70	-	173.220	54.3900	-3.280	2, 3
CoO	-241,198	-237,700	53.00	-	45.260	10.6900	0.600	2, 3

Table 4-17. Thermodynamic Data Used as Inputs to Calculate Log K Grids for Data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) (Continued)

					Heat			
Phase	ΔG° _f (J/mol)	ΔH° _f (J/mol)	S° (J/mol-K)	V° (cm³/mol)	a (J/mol-K)	b x 10 ³ (J/mol-K ²)	c x 10 ⁻⁵ (J-K/mol) ^b	Source
CoTiO ₃	-1,129,498	-1,207,400	96.90	-	123.470	9.7100	-1.650	2, 3
CoWO ₄	-1,035,813	-1,142,700	126.40	-	115.480	48.4900	0.000	2, 3
Eskolaite Cr ₂ O ₃	-1,058,067	-1,140,600	81.20	29.09	109.650	15.4600	0.000	2, 3
CrCl ₃	-486,316	-556,500	123.00	57.38	98.830	13.9800	-1.000	2, 3
CrF ₃	-1,103,441	-1,173,200	93.90	28.68	93.970	10.2500	-1.620	2, 3
Crl ₃	-205,530	-205,000	199.60	88.04	105.440	20.9200	0.000	2, 3
CrO ₃	-512,562	-587,000	73.20	35.14	71.760	87.8700	-1.670	2, 3
Cs₂NaPuCl ₆	-2,143,496	-2,294,200	440.00	-	-	·	-	1
Cs ₂ NpBr ₆	-1,620,121,	-1,682,300	469.00	-	1	i	-	1
Cs ₂ NpCl ₆	-1,833,039	-1,976,200	410.00	-	-	-	-	1
Cs ₂ PuBr ₆	-1,634,326	-1,697,400	470.00	-	-	-	-	1
Cs ₂ PuCl ₆	-1,838,243	-1,982,000	412.00	-	-	-	-	1
Cs ₃ PuCl ₆	-2,208,045	-2,364,415	454.92	-	256.600	34.60	-7.40	1
CsPu ₂ Cl ₇	-2,235,119	-2,399,380	424.00	-	237.800	51.50	1.55	1
Ferrite-Cu CuFe ₂ O ₄	-863,240	-1,025,100	177.70	44.53	200.080	20.2500	-3.360	2, 3
Iron Fe	0	0	27.30	7.09	14.950	28.0800	0.160	2, 3
Fe(OH) ₂	-486,975	-574,000	87.90	26.43	116.060	8.6500	-2.870	2, 3
Fe(OH) ₃	-696,486	-832,600	104.60	34.36	127.610	41.6400	-4.220	2, 3
Fe ₂ (SO ₄) ₃	-2,262,753	-2,583,000	307.50	130.77	361.300	54.7600	-10.640	2, 3
Hercynite FeAl ₂ O ₄	-1,879,669	-1,969,500	106.30	40.75	155.310	26.1500	-3.520	2, 3
Lawrencite FeCl ₂	-302,343	-341,600	117.90	-	78.260	9.9500	-0.420	2, 3
Molysite FeCl ₃	-333,926	-399,200	147.80	-	74.590	78.2700	-0.090	2, 3
Chromite FeCr ₂ O ₄	-1,355,891	-1,458,600	146.90	44.01	163.010	22.3400	-3.190	2, 3
FeF ₂	-633,179	-705,800	87.00	22.94	73.080	9.6100	-0.700	2, 3
FeF ₃	-972,303	-1,039,300	98.30	32.06	90.750	11.3100	-0.220	2, 3
Goethite FeOOH	-488,550	-558,100	60.40	20.82	49.370	83.6800	0.000	5
Ferrite-Ca	-1,412,731	-1,479,400	145.20	44.98	164.930	19.9200	-1.530	2, 3
Ferrite-Ni	-972,893	-1,084,500	125.90	-	152.670	77.8200	-1.490	2, 3

Table 4-17. Thermodynamic Data Used as Inputs to Calculate Log K Grids for Data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) (Continued)

					Heat			
Phase	ΔG° _f (J/mol)	ΔH° _f (J/mol)	S° (J/mol-K)	V° (cm³/mol)	a (J/mol-K)	b x 10 ³ (J/mol-K ²)	c x 10 ⁻⁵ (J-K/mol) ^b	Source
FeSO ₄	-824,892	-928,900	121.00	41.58	122.000	37.8200	-2.930	2, 3
Ilmenite FeTiO ₃	-1,158,045	-1,239,200	105.90	-	116.610	18.2400	-2.000	2, 3
$K_4NpO_2(CO_3)_3$	-3,660,395	-	-	-	-	-	-	1
MgBr ₂	-504,060	-524,300	117.20	49.49	70.510	18.0700	-0.110	2, 3
Chloro magnesite MgCl ₂	-592,074	-644,200	89.50	-	76.400	9.2500	-0.700	2, 3
MgSO ₄	-1,170,579	-1,261,800	91.40	45.25	106.440	46.2800	-2.190	2, 3
Bixbyite Mn ₂ O ₃	-881,114	-959,000	110.50	-	102.800	35.6700	-1.280	2, 3
Tephroite Mn ₂ SiO ₄	-1,632,130	-1,725,300	142.20	-	159.080	19.5000	-3.110	2, 3
Scacchite MnCl ₂	-440,478	-481,300	118.20	-	73.800	15.2300	-0.470	2, 3
MnSO ₄	-957,243	-1,065,300	112.10	-	122.420	37.3200	-2.950	2, 3
MoO_2CI_2	-623,302	-725,800	120.50	-	127.400	7.0300	-1.940	2, 3
Na ₂ CO ₃	-1,048,005	-1,130,800	138.80	41.86	11.000	244.0500	2.450	2, 3
Na ₂ CrO ₄	-1,234,795	-1,334,300	176.60	59.48	101.040	140.0000	0.000	2, 3
Na ₃ NpF ₈	-3,521,239	-3,714,000	369.00	-	270.000	56.60	-13.00	1
Na ₃ NpO ₂ (CO ₃) ₂	-2,833,333	-	-	-	-	ı	-	1
Nahcolite NaHCO ₃	-852,851	-936,300	101.20	38.62	45.310	143.1000	0.000	2, 3
NaNpO ₂ CO ₃	-1,764,157	-	-	-	-	-	-	1
NaNpO ₂ CO ₃ ·3.5H ₂ O	-2,591,287	-	-	-	-	-	-	1
Heazlewoodite Ni ₃ S ₂	-2,591,287	-210,396	133.90	40.95	110.790	51.6700	-0.750	2, 3
NiCl ₂	-259,139	-305,300	98.00	36.70	73.190	13.1200	-0.480	2, 3
NiCO ₃	-617,876	-696,300	86.20	27.05	88.700	38.9100	-1.230	2, 3
NiCr ₂ O ₄	-1,271,777	-1,392,400	129.70	-	167.150	17.8700	-2.110	2, 3
NiF ₂	-610,298	-657,700	73.60	20.88	66.600	13.9400	-0.590	2, 3
Trevorite NiFe ₂ O ₄	-972,893	-1,084,500	125.90	45.38	152.670	77.8200	-1.490	2, 3
NiSO ₄	-759,545	-873,200	101.30	42.05	125.940	27.8200	-3.260	2, 3
NiTiO ₃	-1,118,188	-1,201,400	82.60	-	115.100	15.9800	-1.830	2, 3
NiWO ₄	-1,023,620	-1,127,800	118.00	-	110.630	53.3900	-0.440	2, 3
Np	0	0	50.460	-	-4.054	82.555	8.0571	1

Table 4-17. Thermodynamic Data Used as Inputs to Calculate Log K Grids for Data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) (Continued)

					Heat	Capacity Coeffi	cients ^a	
Phase	ΔG° _f (J/mol)	ΔH° _f (J/mol)	S° (J/mol-K)	V° (cm³/mol)	a (J/mol-K)	b x 10 ³ (J/mol-K ²)	c x 10 ⁻⁵ (J-K/mol) ^b	Source
Np_2C_3	-192,427	-187,400	135.00	-	-	-	-	1
Np_2O_5	-2,031,574	-2,162,700	174.00	-	99.200	98.60	-	1
NpBr ₃	-705,521	-730,200	196.00	-	101.230	20.68	-3.20	1
NpBr ₄	-737,843	-771,200	243.00	-	119.000	30.00	-	1
NpC _{0.91}	-76,024	-71,100	72.20	-	_c	-	-	1
NpCl ₃	-829,811	-896,800	160.40	-	89.600	27.50	3.60	1
NpCl ₄	-895,562	-984,000	200.00	-	112.500	36.00	-1.10	1
NpF ₃	-1,460,501	-1,529,000	124.90	-	105.200	0.812	-10.00	1
NpF ₄	-1,783,797	1,874,000	153.50	-	122.635	9.684	-8.365	1
NpF ₅	-1,834,430	-1,941,000	200.00	-	126.000	30.00	-1.90	1
NpF ₆	-1,841,872	-1,970,000	229.09	-	62.333	352.55	-	1
Npl ₃	-512,498	-512,400	225.00	-	104.000	20.00	-	1
NpN	-270,043	-294,600	63.90	-	47.670	13.174	-2.576	1
NpO ₂	-1,021,371	-1,074,000	80.30	24.22	67.511	26.60	-8.19	1
NpO ₂ (hyd, aged)	-957,321	-	-	-	-	-	-	1
$NpO_2(NO_3)_2 \cdot 6H_2O$	-2,428,069	-3,008,241	516.31	-	-	-	-	1
NpO ₂ CO ₃	-1,407	1	-	-	-	-	-	1
NpO ₂ OH(am)	-1,118,078	-1,222,900	71.95	-	-	-	-	1
NpO ₂ OH(am, aged)	-1,114,652	-1,222,900	60.46	-	-	-	-	1
NpO ₃ ·H ₂ O	-1,238,997	1	-	-	-	-	-	1
NpOBr ₂	-906,933	-950,000	160.80	-	111.000	13.70	-15.00	1
NpOCl ₂	-960,645	-1,030,000	143.50	-	98.800	22.00	-9.20	1
Pu	0	0	54.46	-	18.126	44.82	-	1
Pu(HPO ₄) ₂ (am, hyd)	-2,843,768	-	-	-	-	-	-	1
Pu(OH) ₃	-1,200,218	-	-	-	-	-	-	1
Pu ₂ C ₃	-156,614	-149,400	150.00	-	_c	-	-	1
Pu ₂ O ₃	-1,580,375	-1,656,000	163.00	-	169.446	-79.98	-25.459	1
Pu ₃ C ₂	-123,477	-113,000	210.00	_	120.670	46.86	1.9456	1

Table 4-17. Thermodynamic Data Used as Inputs to Calculate Log K Grids for Data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) (Continued)

					Heat	Capacity Coeffi	cients ^a	
Phase	ΔG° _f (J/mol)	ΔH° _f (J/mol)	S° (J/mol-K)	V° (cm³/mol)	a (J/mol-K)	b x 10 ³ (J/mol-K ²)	c x 10 ⁻⁵ (J-K/mol) ^b	Source
PuAs	-241,413	-240,000	94.30	-	-	-	-	1
PuBi	-119,624	-117,000	120.00	-	-	-	-	1
PuBi ₂	-124,527	-126,000	163.00	-	-	-	-	1
PuBr ₃	-767,324	-792,600	198.00	-	104.5	15.00	-6.38	1
PuC _{0.84}	-49,827	-45,200	74.80	-	c -	-	-	1
PuCl ₃	-891,806	-959,600	161.70	-	91.350	24.00	2.40	1
PuCl ₃ ·6H ₂ O	-2,365,347	-2,773,400	420.00	-	-	-	-	1
PuCl ₄	-879,368	-968,700	201.00	-	-	-	-	1
PuF ₃	-1,517,369	-1,586,700	126.11	-	104.078	0.707	-10.355	1
PuF ₆	-1,729,856	1,861,350	221.80	-	72.348	32.13	-	1
Pul ₃	-579,000	-579,200	228.00	-	104.000	20.00	-	1
PuN	-273,719	-299,200	64.80	-	-	-	-	1
PuO _{1.61}	-834,771	-875,500	83.00	-	65.910	13.85	-8.757	1
PuO ₂	-998,113	-1,055,800	66.13	23.83	_c	-	-	1
PuO ₂ (hyd, aged)	-963,654	-	-	-	-	-	-	1
$PuO_2(NO_3)_2 \cdot 6H_2O$	-2,393,300	-	-	-	-	-	-	1
PuO ₂ (OH) ₂ ·2H ₂ O ^d	-	-	-	-	-	-	-	d
PuO ₂ (OH) ₂ ·H ₂ O	-1,442,379	-1,632,808	190.00	-	-	-	-	1
PuO ₂ CO ₃	-1,371,307	-	-	-	-	-	-	1
PuO ₂ OH(am)	-1,061,246	-1,159,793	97.00	-	-	-	-	1
PuOBr	-838,354	-870,000	127.00	-	73.700	17.00	-5.15	1
PuOCI	-882,409	-931,000	105.60	-	73.030	17.10	-5.83	1
PuOF	-1,091,571	-1,140,000	96.00	-	_c	-	-	1
PuOI	-776,626	-802,000	130.00	-	_c	-	-	1
PuP	-313,757	-318,000	81.32	-	-	-	-	1
PuPO ₄ (s, hyd)	-1,744,893	-	-	-	-	-	-	1
PuSb	-152,063	-150,000	106.90	-	-			1
Ti ₂ O ₃	-1,433,824	-1,520,900	77.30	_	53.070	163.4400	_	2, 3

Table 4-17. Thermodynamic Data Used as Inputs to Calculate Log K Grids for Data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) (Continued)

					Heat			
Phase	ΔG° _f (J/mol)	ΔH° _f (J/mol)	S° (J/mol-K)	V° (cm³/mol)	a (J/mol-K)	b x 10 ³ (J/mol-K ²)	c x 10 ⁻⁵ (J-K/mol) ^b	Source
Ti ₃ O ₅	-2,317,294	-2,459,100	129.40	-	231.040	-24.7700	-6.130	2, 3
TiB ₂	-319,648	-315,900	28.50	-	56.380	25.8600	-1.750	2, 3
TiBr ₃	-525,596	-551,900	176.60	-	73.070	87.2500	0.080	2, 3
TiBr ₄	-590,646	-619,700	243.50	-	80.930	169.6200	-	2, 3
TiCl ₂	-465,823	-5,155	87.30	-	68.370	18.0300	-0.350	2, 3
TiCl ₃	-654,451	-721,700	139.80	-	95.810	11.0600	-0.180	2, 3
TiF ₃	-1,361,861	-1,435,500	87.90	-	79.080	29.2900	0.340	2, 3
TiF ₄ (am)	-1,559,179	-1,649,300	134.00	-	123.310	36.2400	-1.770	2, 3
Til ₄	-370,647	-375,700	246.20	-	71.420	181.8700	-	2, 3
TiO	-513,278	-542,700	34.80	-	44.220	15.0600	-0.780	2, 3
Uranium U	0	0	50.30	-	27.590	-4.0400	-0.110	2, 3
U(SO ₄) ₂	-2,087,195	-2,318,000	164.00	-	104.600	230.9600	-	2, 3
U_2S_3	-854,730	-854,000	199.20	-	140.830	16.1100	-0.380	2, 3
UBr ₃	-673,463	-699,100	192.50	-	100.000	29.2900	-	2, 3
UBr ₄	-767,852	-802,500	238.50	-	134.730	20.5000	-1.130	2, 3
UCI ₃	-794,530	861,900	159.00	-	87.780	31.1300	0.490	2, 3
UCI ₄	-929,927	-1,018,800	197.20	-	113.810	35.8600	-0.0330	2, 3
UCI ₅	-950,061	-1,041,500	246.90	-	140.040	35.4400	-0.540	2, 3
UCI ₆	-962,649	-1,068,200	285.80	-	173.400	35.0600	-0.740	2, 3
UF ₃	-1,439,861	1,502,100	123.40	-	85.980	30.5400	-	2, 3
UF ₄	-1,830,173	1,914,200	151.70	46.88	123.560	9.6200	-0.930	2, 3
UF ₅ (beta)	-1,970,577	-2,083,200	179.50	-	125.520	30.2100	-0.200	2, 3
UF ₆	-2,068,477	-2,197,000	227.60	-	52.720	384.9300	-	2, 3
UI ₃	-459,962	-460,700	222.00	-	102.970	30.5400	-	2, 3
UI ₄	-506,462	-512,100	263.60	-	149.370	9.9600	-1.590	2, 3
UO ₂ Br ₂	-1,066,612	-1,137,600	169.50	-	117.950	17.5300	-1.070	2, 3
UO ₂ CI ₂	-1,146,105	-1,243,500	150.60	-	115.230	18.2000	-1.140	2, 3
UO ₂ F ₂	-1,551,873	-1,651,400	135.60	-	122.880	8.6200	-1.990	2, 3

Table 4-17. Thermodynamic Data Used as Inputs to Calculate Log K Grids for Data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) (Continued)

					Heat	Capacity Coeffic	cients ^a	
Phase	ΔG° _f (J/mol)	ΔH° _f (J/mol)	S° (J/mol-K)	V° (cm³/mol)	a (J/mol-K)	b x 10 ³ (J/mol-K ²)	c x 10 ⁻⁵ (J-K/mol) ^b	Source
UO ₂ SO ₄	-1,683,212	-1,845,100	154.80	-	112.470	108.7800	-	2, 3
UO₃(gamma)	-1,144,896	-1,226,500	98.80	-	90.370	11.0500	-1.110	2, 3
UOBr ₂	-929,638	-973,600	157.60	-	110.580	13.6800	-1.490	2, 3
UOBr ₃	-901,429	-954,000	205.00	-	130.540	20.5000	-1.380	2, 3
UOCI	-899,108	-833,900	102.50	-	75.810	14.3500	-0.830	2, 3
UOCI ₂	-996,062	-1,067,500	138.30	-	98.950	14.6400	-0.740	2, 3
UOCI ₃	-1,068,773	-1,151,600	170.70	-	122.590	20.9200	-1.190	2, 3
WCI ₂ (s)	-219,977	-260,300	130.50	-	71.280	21.9000	-	2, 3
WCI ₄ (s)	-359,433	-443,100	198.30	-	113.450	54.6000	-	2, 3
WCI ₅ (s)	-401,783	-513,000	217.60	-	124.450	109.9200	-0.140	2, 3
WCI ₆ (s)	-455,511	-593,700	238.50	-	125.560	167.2300	_	2, 3
WO ₂ CI ₂ (s)	-702,770	-780,300	200.80	-	79.510	94.1100	-0.290	2, 3
WOCI ₄ (s)	-549,270	-671,100	172.80	-	115.000	104.6900	-	2, 3
WOF ₄ (s)	-1,285,507	1,406,900	175.70	-	83.650	167.4200	_	2, 3

Sources: 1 Lemire 2001 [DIRS 159027].

- 2 Barin and Platzki 1995 [DIRS 157865].
- 3 Binnewies and Milke 1999 [DIRS 158955].
- 4 slop98.dat (DTN: MO0106MWDTDG01.035 [DIRS 161791]).
- 5 Robie et al. 1979 [DIRS 107109].
- 6 data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]).

^a Heat capacity coefficients a, b, and c defined in Eq. 4-1.

^b The coefficient c for heat capacity obtained from Binnewies and Milke (1999 [DIRS 158955]) is incorrectly scaled as given in this table. This item is corrected to the proper scaling factor given in the source as discussed in Section 6.3.4.5.

^c Lemire (2001 [DIRS 159027]) Tables 3.3 and 4.3 do not give Maier-Kelley parameters for this species.

d Phase PuO₂(OH)₂·2H₂O was an incorrect representation of PuO₂(OH)₂·H₂O in data0.ymp.R2. The data reported in data0.ymp.R2 are shown in this table for the correct phase PuO₂(OH)₂·H₂O, consistent with Lemire (2001 [DIRS 159027]).

Table 4-18. Log K Data for Dissociation of HF(aq)

T (°C)	15 ^a	25 ^a	35 ^a	50 ^a	75 ^a	100 ^a	125 ^a	150 ^a	175 ^a	200 ^a	250 ^b	300 ^b
Log K	-3.1	-3.18	-3.25	-3.40	-3.64	-3.85	-4.09	-4.34	-4.59	-4.89	-5.8	-6.8

Sources: ^a Clark 1966 [DIRS 153163], Table 18-4, p.407. ^b Ellis and Mahon 1977 [DIRS 159230], Table 8.4, p.288.

Data for the HF₂⁻ association reaction were taken from data in Clark (1966 [DIRS 153163], Table 18-4, p. 407) (Table 4-19).

$$HF(aq) + F^{-} = HF_{2}^{-}$$
 (Eq. 4-3)

Table 4-19. Log K Data for the HF₂⁻ Association Reaction Delineated by Eq. 4-3

T (°C)	25	50	75	100	125	150	175	200
Log K	3.4	4	4.7	4.8	4.9	5.7	5.8	8

Source: Clark 1966 [DIRS 153163], p.407, Table 18-4.

The values listed in Table 4-19 are for the reaction represented by Eq. 4-3 and not the reaction listed in the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), which is $HF_2^- = H^+ + 2F^-$. Therefore, these values were reassessed in the source spreadsheets and compared to those in data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]). Also, an "established fact" source (Wagman et al. 1982 [DIRS 159216]) was used for comparison. The analysis of these gas species is given in Section 6.4.

Additional gas-phase thermodynamic data were obtained from handbook compilations of Barin and Platzki (1995 [DIRS 157865]) and Binnewies and Milke (1999 [DIRS 158955]) and are listed in Table 4-20. Transcription errors were identified for gas species in the scaling of the "c" heat capacity coefficient from Binnewies and Milke (1999 [DIRS 158955]) into the calculation spreadsheet for the species listed in Table 4-20 using this source. This error is further discussed in Section 6.4.

Thermodynamic Data Input for Gas Phases Updated or Added to Data0.ymp.R2 Table 4-20. (DTN: MO0302SPATHDYN.000 [DIRS 161756])

				Heat C	cients ^a		
Gas Species	∆G _f ° (J/mol)	∆H _f ° (J/mol)	S° (J/mol-K)	a (J/mol-K)	b x 10 ³ (J/mol-K ²)	c x 10 ⁻⁵ (J-K/mol) ^b	Source
CoCl ₂ (g)	-107,220	-93,700	298.50	60.730	2.820	-0.170	1, 2
CoF ₂ (g)	-369,947	-356,500	278.00	55.410	2.680	-0.440	1, 2
CoCl ₃ (g)	-154,434	-163,600	334.20	87.610	-2.000	-0.960	1, 2
CrCl ₄ (g)	-395,322	-426,800	364.4	106.43	1.31	-0.95	1,2
FeCl ₂ (g)	-155,571	-141,000	299.30	59.950	2.920	-0.290	1, 2
FeCl ₃ (g)	-247,843	-253,100	344.20	82.880	0.160	-0.460	1, 2
FeF ₂ (g)	-400,055	-389,500	265.20	70.540	-3.320	-1.230	1, 2
FeF ₃ (g)	-812,795	-820,900	304.20	78.590	2.800	-1.230	1, 2
H₂O(g)	-228,620	-241,826	188.959	28.590	12.343	1.173	1
HNO ₃ (g)	-73,964	-134,306	266.475	42.278	61.932	-6.524	1

Table 4-20. Thermodynamic Data Input for Gas Phases Updated or Added to Data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) (Continued)

				Heat C			
Gas Species	∆G _f ° (J/mol)	ΔH _f ° (J/mol)	S° (J/mol-K)	a (J/mol-K)	b x 10 ³ (J/mol-K ²)	c x 10 ⁻⁵ (J-K/mol) ^b	Source
$N_2O(g)$	104,172	82,048	219.979	27.371	35.896	0.629	1
$N_2O_3(g)$	139,486	82,843	309.349	49.369	58.009	-0.755	1
$N_2O_4(g)$	97,788	9,079	304.37	58.598	79.906	-4.402	1
$N_2O_5(g)$	118,014	11,297	346.545	98.612	58.437	-17.578	1
NiCl ₂ (g)	-83,779	-70,200	298.20	68.290	-0.970	-0.660	1, 2
NiF ₂ (g)	-347,601	-335,600	273.10	64.310	1.040	-1.080	1, 2
NO(g)	86,599	90,291	210.761	25.034	9.523	1.754	1
NO ₂ (g)	51,262	33,095	240.02	38.108	15.389	-5.366	1
NO ₃ (g)	116,060	71,128	252.823	58.598	79.906	-4.402	1
TiCl(g)	122,516	154,400	249.20	43.940	0.250	-0.610	1, 2
TiCl ₂ (g)	-244,529	-237,200	278.30	60.120	2.220	-0.280	1, 2
TiCl₃(g)	-524,829	-539,300	316.90	87.260	-0.710	-1.290	1, 2
TiCl ₄ (g)	-726,764	-763,200	354.90	107.170	0.490	-1.050	1, 2
TiF(g)	-98,305	-66,900	237.30	43.480	0.340	-0.760	1, 2
TiF ₂ (g)	-694,886	-688,300	255.70	59.470	2.560	-0.650	1, 2
TiF ₃ (g)	-1,175,664	-1,188,200	291.20	86.280	-0.260	-2.070	1, 2
TiF₄(g)	-1,515,221	-1,551,400	314.90	104.250	1.980	-1.800	1, 2
TiO(g)	24,534	54,400	233.50	37.040	0.970	-0.490	1, 2
WCl ₂ (g)	-28,637	-12,600	309.40	58.170	4.510	-0.100	1, 2
WCl ₄ (g)	-306,245	-336,000	379.30	107.400	0.460	-0.780	1, 2
WCl ₆ (g)	-409,436	-493,700	419.20	157.540	0.190	-1.230	1, 2
WF(g)	351,397	386,200	251.10	37.810	2.900	-0.520	1, 2
WF ₆ (g)	-1,632,294	-1,721,700	341.10	152.650	2.750	-3.140	1, 2
$WO_2Cl_2(g)$	-639,675	-671,500	353.90	103.580	2.300	-1.570	1, 2
WOCl ₄ (g)	-512,272	-573,500	377.10	128.840	1.850	-2.230	1, 2
WOF ₄ (g)	-1,275,166	-1,336,600	334.70	125.690	4.140	-2.770	1, 2

Sources: 1 Barin and Platzki 1995 [DIRS 157865].

4.1.9 Compilation of Mineral Volume Data

Molar volume data for mineral phases excluding those used to estimate volume data for clay phases (discussed in Section 4.1.4) are given in Table 4-21. Mineral volume data from data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]) are already qualified and are not considered for qualification in this report. Also, volume data from "established fact" sources, which are rather extensive, are not considered for qualification. That is, only the data listed in Table 4-21 are qualified in this report. The qualification of the data given in the table below and those developed for clay phases is evaluated in Section 6.6. It is noted that cement

² Binnewies and Milke 1999 [DIRS 158955].

^a Heat capacity coefficients a, b, and c defined in Eq. 4-1.

The coefficient c for heat capacity is incorrectly scaled as given in this table. These data were corrected to the proper scaling factor given in the source as discussed in Section 6.4.

phases CSH:1.7, Friedl salt, and hydrogarnet are inactive in the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), and the molar volume data for these species are not considered for qualification of molar volume data in Section 6.6.

Table 4-21. Molar Volumes of Mineral/Solid Phases from Data0.ymp.R2

Reference Mineral	Chemical Formula	V° (cm³/mol)	
7A-Amesite	$Mg_2Al_2SiO_5(OH)_4$	103	
CaUO ₄	CaUO ₄	45.926	
Chabazite	K _{0.6} Na _{0.2} Ca _{1.55} Al _{3.8} Si _{8.2} O ₂₄ ·10.0H ₂ O	499.4	
Cr-ferrihydrite	Fe ₄ (CrO ₄)(OH) ₁₀	129	
7A-Cronstedtite	Fe ₂ Fe ₂ SiO ₅ (OH) ₄	110.9	
Erionite	$K_{1.5}Na_{0.9}Ca_{0.9}Al_{4.2}Si_{13.8}O_{36}\cdot 13.0H_2O$	672	
$Fe_2(MoO_4)_3$	$Fe_2(MoO_4)_3$	131.85	
Laumontite	K _{0.2} Na _{0.2} Ca _{1.8} Al ₄ Si _{8.0} O ₂₄ ·8.0H ₂ O	406.40	
$Ni_3(PO_4)_2$	$Ni_3(PO_4)_2$	83.36	
Na ₄ UO ₂ (CO ₃) ₃	Na ₄ UO ₂ (CO ₃) ₃	149.31	
Phillipsite	$K_{0.7}Na_{0.7}Ca_{1.1}Al_{3.6}Si_{12.4}O_{32}\cdot 12.6H_2O$	609.20	
Stellerite	Ca _{2.0} Al _{4.0} Si _{14.0} O ₃₆ ·14.0H ₂ O	665.50	
Uranophane (alpha)	Ca(UO ₂ SiO ₃ OH) ₂ ·5H ₂ O	251.34	
Weeksite-Na	$Na_2(UO_2)_2Si_5O_{13}\cdot 3H_2O$	246.04	

MO0302SPATHDYN.000 [DIRS 161756] (data0.ymp.R2). Included in output DTN: SN0410T0510404.001 (Spreadsheet *Volume_Q_DS_11-01-04.xls*).

4.2 CRITERIA

DTN:

The criteria for the development and qualification of the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) are specified in the Data Qualification Plan of *Technical Work Plan for: Near-Field Environment and Transport In-Drift Geochemistry Analyses* (BSC 2004 [DIRS 172402], Appendix A). These criteria were selected to incorporate the qualification methods and applicable qualification process attributes defined in AP-SIII.2Q, *Qualification of Unqualified Data*. The source data considered for qualification for YMP use are those that are directly used in the final database or are the bases for calculated data that are included in the final database. Corroborating data are not directly used in the final database and therefore do not require qualification.

The AP-SIII.2Q qualification methods specified in the Data Qualification Plan are:

Method 2. Corroborating Data. This method can be used when independently measured data can be used to substantiate or confirm parameter values. This method requires that data be available for comparison to the unqualified data sets, and that inferences drawn to corroborate the unqualified data be clearly identified, justified, and documented.

Method 5. *Technical Assessment.* This method is used when it is determined that independent assessment of the data, by a subject matter expert, is needed to raise the confidence of the data to the proper level for intended use. Technical assessments may be required if the confidence in the data is in question because data collection procedures are unavailable for review, or the procedures

are not adequate, or if documentation or proof of proper data acquisition is unavailable for review. The technical assessment must include one or more of the following: 1) determination that the employed *methodology* is acceptable; 2) determination that *confidence* in the data acquisition or developmental results in warranted; or 3) confirmation that the data have been *used* in similar applications (e.g., by the U.S. Nuclear Regulatory Commission or the State Department of Environmental Protection, by nationally/internationally recognized organizations, or by the scientific community including publications, peer reviews, etc.).

Data qualifications for the data listed in Table 4-1 were performed using Method 2 or 5, or a combination of these. These qualifications are documented in Section 6. It was not required (nor possible) to assess all of the attributes/criteria to qualify these data for their intended use. Data sufficiency and acceptability were assessed using those attributes that could be evaluated. Corroborative data in the form of independently derived parameter values or of thermodynamic data for chemical analogs were used where available. It was not necessary to use Method 4 (Peer (DTN: MO0302SPATHDYN.000 Review) qualify the data0.ymp.R2 database [DIRS 161756]) and its supporting calculations (DTNs: MO0302SPATHDYN.001 [DIRS 161886], and MO0303SPASPEQ2.000 [DIRS 162278]).

There was considerable overlap in the attributes that were considered in the qualification process. For instance, Technical Assessment involved both an evaluation of data collection procedures and comparisons with corroborating data. Conversely, use of corroborating data generally involved an evaluation, or assessment, of the methodology used in collecting both the data set of interest and the corroborating data. Each attribute was considered, to the degree possible, when assessing the data quality.

4.3 CODES, STANDARDS, AND REGULATIONS

This analysis was developed to support a demonstration of compliance with 10 CFR 63 [DIRS 156605]. No codes or standards are applicable to this analysis.

5. ASSUMPTIONS

Assumption 1: For purposes of qualifying the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756], qualified by this report) and developing the new data0.ymp.R4 database (output DTN: SN0410T0510404.002), it is assumed that systems modeled with the data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) or data0.ymp.R4 databases (output DTN: SN0410T0510404.002) at temperatures above the boiling point of water will have the pressure controlled so that aqueous solutions are stable. For example, if a dilute solution is modeled at temperatures above the boiling point, this assumption implies that pressure conditions are controlled (i.e., pressure is increased) to maintain the solution in liquid form. As another example, for the study of deliquescence the dryout temperature of an evaporatively concentrated solution is defined with respect to the estimated total pressure in the repository, which is limited to approximately 1 bar. This assumption is consistent with anticipated repository conditions.

In accordance with this assumption the temperature grid selected for calculations of log K values as used in the EQ3/6 calculations is computed along the liquid-vapor saturation curve of pure water given the required physical state of the solvent, and application to repository conditions above the boiling point of water is limited using a realistic total pressure limit. No confirmation or additional investigation of this assumption is needed because it is a realistic depiction of temperature and pressure conditions in the repository and the adjacent host rock. This assumption is used throughout Section 6 in the data qualification discussion.

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6. SCIENTIFIC ANALYSIS DISCUSSION

The primary source of data making up the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756], qualified by this report) is the previously existing database, data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]). support of the changes made in developing data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), a wide variety of published sources (listed in Section 4) was evaluated. In the following sections the sources are assessed for applicability and defensibility, and justified for use where appropriate.

Large data sets were obtained from well known compilations including the OECD/NEA Database (Lemire 2001 [DIRS 159027]) and the compilations in Babushkin et al. (1985 [DIRS 116981]), Binnewies and Milke (1999 [DIRS 158955]), Barin and Platzki (1995 [DIRS 157865]), and Chase (1998 [DIRS 157874]). Binnewies and Milke (1999 [DIRS 158955]) is a recent comprehensive compilation of thermodynamic data that draws on six references, four of which are pertinent to this effort. The six references each draw on many published and unpublished thermodynamic data, although those references are not listed in Binnewies and Milke (1999 [DIRS 158955]). Barin and Platzki (1995 [DIRS 157865]) and Babushkin et al. (1985 [DIRS 116981]) are likewise comprehensive compilations of thermodynamic data that include extensive lists of references. The handbooks (Lemire 2001 [DIRS 159027]; Babushkin et al. 1985 [DIRS 116981]; Barin and Platzki 1995 [DIRS 157865]; Chase 1998 [DIRS 157874]; Binnewies and Milke 1999 [DIRS 158955]) were chosen because they are recent, comprehensive, and generally accepted within the scientific community. Their data sources were reviewed and assessed (to varying degrees) with regard to data quality prior to publication.

The body of this section consists of two parts. The first part (Section 6.1) describes the approach used to convert the data into the forms and parameters used in the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]). In the second part (Sections 6.2 through 6.4), the data as collected from the sources, are evaluated and qualified for use using the approaches described in Section 4.2. In this manner, the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) is qualified. Data reduction consists of converting fundamental thermodynamic properties into temperature-dependent equilibrium constants for the species of interest, and is largely performed in Excel spreadsheets.

Qualified data from two sources were used: data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]), which was the existing project database used for geochemistry calculations, and *slop98.dat* (DTN: MO0106MWDTDG01.035 [DIRS 161791]), a SUPCRT92 database that supports the data0.ymp.R0 database (DTN: MO0009THRMODYN.001 [DIRS 152576]) and contains organic data. The *slop98.dat* database (DTN: MO0106MWDTDG01.035 [DIRS 161791]) was qualified along with the data0.ymp.R0 database (DTN: MO0009THRMODYN.001 [DIRS 152576]) but was posted under a separate Data Tracking Number (DTN).

It should be noted that most of the available thermodynamic data originate in external university and international government laboratories. The data are therefore available only in published reports sponsored by government agencies and in international refereed technical journals.

This section includes discussion of the data sources considered and the calculation methods used in developing the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]). The data sources are identified, and justification for using data from those sources is presented. In addition, the conversions used to produce appropriate parameter values are discussed. All of the Excel spreadsheets used in performing the calculations to develop the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) are contained on a supplemental compact disk-read-only memory (CD-ROM) (DTN: MO0302SPATHDYN.001 [DIRS 161886]).

6.1 APPROACH TO DATA REDUCTION

While the basic thermodynamic data used in the development of the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) were obtained from published sources, most of the values actually included in the database were derived using various calculational techniques which are conventionally used in the retrieval and manipulation of thermodynamic data for solids, aqueous species, and gases. These methods generally calculate equilibrium constants from Gibbs free energy data and extrapolate those equilibrium constants to higher temperatures. The approaches adopted in this report for retrieval and extrapolation of thermodynamic data follow those adopted in the previous report *Data Qualification Report for Thermodynamic Data File, Data0.ympR0 for Geochemical Code, EQ3/6* (CRWMS M&O 2000 [DIRS 152575]). Therefore consistency is maintained between the various methods used in the extraction and extrapolation of data considered for the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]). The calculations are discussed in detail below.

6.1.1 The Heat Capacity of Solids as a Function of Temperature and its Relationship to Gibbs Free Energies at Higher Temperatures

The Maier-Kelley heat capacity equation (Maier and Kelley 1932 [DIRS 101691]) is used in the software code SUPCRT92 (e.g., Johnson et al. 1992 [DIRS 101632]) to represent the temperature dependence of the standard molal heat capacities (C_p°) of minerals and gases. As it is generally used, this empirical equation applies to conditions of 1 bar pressure. It can be written as (see Helgeson et al. 1978 [DIRS 101596], p. 29):

$$C_p^o = a + bT - \frac{c}{T^2}$$
 (Eq. 6-1)

where T is the absolute temperature (K). There is no generally accepted convention about the sign of the third term and hence the "c" coefficient. The above formulation was embedded in the original version of the SUPCRT software used in Helgeson et al. (1978 [DIRS 101596]). However, Johnson et al. (1992 [DIRS 101632], p. 910) writes the equation as:

$$C_p^o = a + bT + \frac{c}{T^2}$$
 (Eq. 6-2)

with a positive sign for the "c" coefficient. This convention is embedded in the more recent version of SUPCRT92 (Johnson et al. 1992 [DIRS 101632]) and is the form that is followed in

qualification of the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), except as noted in the following discussion.

Usually some temperature range is associated with any set of values. If a solid undergoes a phase transition at some temperature, one set of coefficients applies below that temperature and another applies above it. In addition, transitions involve changes in enthalpy and entropy (and volume) but not Gibbs free energy. In the temperature range of interest to YMP applications, generally less than 300°C (BSC 2004 [DIRS 169565], Section 6.3), only a small fraction of solids exhibits such transitions.

Values of Maier-Kelley heat capacity coefficients along with corresponding temperature ranges are given for many common rock-forming minerals by Helgeson et al. (1978 [DIRS 101596], Table 2, p. 48, Table 5, p. 61, and Table 7, pp. 68-73) (in all instances the old sign convention for "c" is employed as in Eq. 6-4). Some of these data have since been revised (apart from changing the sign of "c"); therefore, one should consult a recent copy of the SUPCRT92 database (e.g., slop98.dat; DTN: MO0106MWDTDG01.035 [DIRS 161791]) if values are desired as input for new calculations. These updated data also include a broader range of solids and gases. In both Helgeson et al. (1978 [DIRS 101596]) and in SUPCRT92 data files, the coefficients are treated such that the heat capacity is yielded in units of cal/mol-K (1 cal = 4.184 joules). Also in both places the tabulated values are actually expressed as a, b × 10³, and c × 10⁻⁵. Thus, from Helgeson et al. (1978 [DIRS 101596], Table 2) (going back to the old convention for "c"), the coefficients for α -quartz are a = 11.22, b × 10³ = 8.20, and c × 10⁻⁵ = -2.70, meaning a = 11.22, b = 8.20 × 10⁻³, and c = -2.70 × 10⁵.

Heat capacity temperature functions such as the Maier-Kelley equation are important because they are needed to calculate thermodynamic properties such as the Gibbs free energy as a function of temperature. In relation to EQ3/6, their role is to provide the Gibbs free energies of solids and gases, thus the Gibbs free energy change for reactions involving these species, and finally the corresponding equilibrium constants (log K values) on the EQ3/6 temperature grid. The "classic" grid of relevance to the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) consists of values for 0°C, 25°C, 60°C, 100°C, 150°C, 200°C, 250°C, and 300°C; corresponding pressures are 1 atm (1.013 bar) for temperatures between 0°C and 100°C and the steam/liquid water pressure for temperatures between 100°C and 300°C.

The mechanics of using heat capacity temperature functions to calculate apparent standard partial molar Gibbs free energies is discussed in both Helgeson et al. (1978 [DIRS 101596], pp. 28-30) and Johnson et al. (1992 [DIRS 101632], pp. 909-911). The equations as given in Johnson et al. (1992 [DIRS 101632]) are for the special case of Gibbs free energy of reactions among minerals. To obtain the equations for the Gibbs free energy for a single mineral, one is better served by referring to Helgeson et al. (1978 [DIRS 101596]) and where necessary, accounting for the change in the sign of "c."

The general retrieval equation for the apparent standard partial molar Gibbs free energy of a solid as a function of temperature T and pressure P is in Helgeson et al. (1978 [DIRS 101596], p. 28):

$$\Delta G_{f,T,P}^{o(app)} = \Delta G_{f,T_r,P_r}^o - S_{T_r,P_r}^o (T - T_r) + \int_{T_r}^T C_{P_r}^o dT - T \int_{T_r}^T C_{P_r}^o d \ln T + \int_{P_r}^P V_T^o dP$$
 (Eq. 6-3)

where T_r is the reference temperature of 298.15K (25°C), P_r is the reference pressure of 1 bar, $\Delta G_{f,T_r,P_r}^o$ is the actual standard partial molar Gibbs free energy of formation from the elements at the reference temperature and pressure, S_{T_r,P_r}^o is the corresponding standard molar entropy, V_T^o is the corresponding standard partial molar volume at temperature T (for many solids, this is closely approximated by V_{T_r,P_r}^o , thus simplifying the final integral in this equation), and $C_{P_r}^o$ is the standard partial molar heat capacity at the reference pressure. Similar retrieval equations exist for the apparent standard partial molar enthalpy, the standard partial molar entropy, and so forth. However, only the Gibbs free energy relation is immediately pertinent here and therefore Eq. 6-3 was used to retrieve log K data for the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]).

In the case of the Maier-Kelley formulation, the two heat capacity integrals appearing in the above equation are in Helgeson et al. (1978 [DIRS 101596], p. 29, corrected with regard to "c"):

$$\int_{T_r}^{T} C_{P_r}^o dT = a(T - T_r) + \frac{b(T^2 - T_r^2)}{2} - c\left(\frac{1}{T} - \frac{1}{T_r}\right)$$
 (Eq. 6-4)

and

$$\int_{T_r}^{T} C_{P_r}^o d \ln T = a \ln(T/T_r) + b(T - T_r) - \frac{c}{2} \left(\frac{1}{T^2} - \frac{1}{T_r^2} \right)$$
 (Eq. 6-5)

For purposes of qualifying the database (i.e., log K values for 0°C < T < 300°C), the Maier-Kelley equation is more than sufficient. However, heat capacity coefficients reported and tabulated in the literature often extend this equation by adding one or more additional terms. The purpose of this is to facilitate accurate representation of the heat capacity over a wider temperature range than that considered here. An example is the equation proposed in Haas and Fisher (1976 [DIRS 158983]):

$$C_{P_r}^o = a + 2bT + \frac{c}{T^2} + fT^2 + \frac{g}{\sqrt{T}}$$
 (Eq. 6-6)

(Note that b and c are subtly redefined here.)

Given the data in such extended forms, one must use all the coefficients in the integrations necessary to obtain the Gibbs free energy as a function of temperature. Alternatively, if one uses

the retrieval equations for the Gibbs free energy given previously assuming the Maier-Kelley format, one must refit the given data to the Maier-Kelley equation. One may not simply take "a," "b," and "c" from a larger set of coefficients and plug these into these retrieval equations, with or without corrections for the subtle redefinitions. In some cases, the coefficients obtained by fitting of heat capacity data using equations resembling that of Eq. 6-7 can be used in the Maier-Kelley equation if the coefficient for the terms are zero (i.e., Eq. 6-7 simplifies to the Maier-Kelley equation).

There are numerous examples of such extended Maier-Kelley equations. The following very general form is used in the database of the NEA-Thermodynamic Data Base project (Puigdomenech et al. 1997 [DIRS 159204], Chapter X, Eq. 8, p. 430):

$$C_{P_r}^o = a + bT + cT^2 + jT^3 + \frac{d}{T} + \frac{e}{T^2} + \frac{k}{T^3} + f \ln T + gT \ln T + h\sqrt{T} + \frac{i}{\sqrt{T}}$$
 (Eq. 6-7)

Although the right hand side of this equation contains 11 terms, each with its corresponding coefficient, typically no more than about five would actually be used in any given instance. This equation is merely intended to be all-inclusive in form, combining all the kinds of terms that one might expect to have to deal with in constructing a large database from numerous and varied sources. Frequently only the a, b, and e terms are actually used, which corresponds to the use of the Maier-Kelley equation (here "e" is the Maier-Kelley "c"), or those plus one other. Note that in a global sense, one cannot count on the letter used to represent a coefficient to match any given power in T.

Eq. 6-7 may also be written as:

$$C_{P_r}^o = a + bT + cT^2 + dT^3 + \frac{e}{T} + \frac{f}{T^2} + \frac{g}{T^3} + h\sqrt{T} + \frac{i}{\sqrt{T}} + j\ln T + kT\ln T$$
 (Eq. 6-8)

This group relates terms more closely together and emphasizes the fact that formulations containing terms in I and I in I are less commonly employed than terms in actual powers. Therefore,

$$\int_{T_r}^{T} C_{P_r}^o dT = a(T - T_r) + \frac{b(T^2 - T_r^2)}{2} + \frac{c(T^3 - T_r^3)}{3} + \frac{d(T^4 - T_r^4)}{4} + e \ln(T/T_r)$$

$$- f \left(\frac{1}{T} - \frac{1}{T_r}\right) - \frac{g}{2} \left(\frac{1}{T^2} - \frac{1}{T_r^2}\right) + \frac{2h}{3} \left(T^{3/2} - T_r^{3/2}\right) + 2i \left(\sqrt{T} - \sqrt{T_r}\right)$$

$$+ j \left[T(\ln T - 1) - T_r(\ln T_r - 1)\right] + \frac{k}{2} \left[T^2(\ln T - \frac{1}{2}) - T_r^2(\ln T_r - \frac{1}{2})\right]$$
(Eq. 6-9)

and

$$\int_{T_r}^{T} C_{P_r}^o d \ln T = a \ln(T/T_r) + b(T-T_r) + \frac{c(T^2 - T_r^2)}{2} + \frac{d(T^3 - T_r^3)}{3} - e \left(\frac{1}{T} - \frac{1}{T_r}\right) \\
- \frac{f}{2} \left(\frac{1}{T^2} - \frac{1}{T_r^2}\right) - \frac{g}{3} \left(\frac{1}{T^3} - \frac{1}{T_r^3}\right) + 2h \left(\sqrt{T} - \sqrt{T_r}\right) - 2i \left(\frac{1}{\sqrt{T}} - \frac{1}{\sqrt{T_r}}\right) \\
+ \frac{j}{2} \left(\ln T \ln T - \ln T_r \ln T_r\right) + k \left[T(\ln T - 1) - T_r(\ln T_r - 1)\right]$$
(Eq. 6-10)

Substitution of these results into the generalized retrieval equation then yields the apparent standard molar Gibbs free energy for solids whose heat capacities are described using extensions of the Maier-Kelley formalism.

6.1.2 SUPCRT92 Usage and Development of Log K-Temperature Grids

SUPCRT92 was used primarily in two ways to develop the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) (i.e., to develop changes from the previous data0.ymp.R0 database; DTN: MO0009THRMODYN.001 [DIRS 152576]). One application was to update the preexisting log K data for silicate mineral dissolution for consistency with the Rimstidt paradigm of quartz solubility, which differs from the older Fournier paradigm. The Rimstidt paradigm is characterized by a higher solubility of quartz at 25°C with the effect principally associated with a greater thermodynamic stability of the species SiO₂(aq). The rationale behind this change is discussed elsewhere in this report (see Section 6.1.5). The second application of SUPCRT92 was to provide "library" worksheets of thermodynamic data for basis and analog species for use in the specialized spreadsheets discussed below.

The basis species data consisted of the apparent Gibbs free energy of formation on the standard EQ3/6 temperature grid (0°C-25°C-60°C-100°C-150°C-200°C-250°C-300°C). These data were used to compute reaction properties for species whose individual thermodynamic properties are developed entirely in the spreadsheets. Analog species data are needed to facilitate temperature extrapolations using the isocoulombic/isoelectric method described below. The requisite data for analog species (which include many if not most basis species) are the standard Gibbs free energy of formation and standard entropy, both at 298.15K and 1 bar pressure.

SUPCRT92 produces various kinds of output files. All data were taken from the "plot" files, which have filename extensions of the form .?xy (e.g., Gibbs free energies on the .gxy file, entropies on the .sxy file, log K values on the .kxy file). The precision used in these files better matches that employed in EQ3/6 data files than that found on the SUPCRT92 "output" file. For example, the "output" file gives log K values to only three decimal places, whereas the .kxy file and the EQ3/6 data0 file use four decimal places. The plot files are also much more convenient as a source of data because the desired data are isolated in a special, smaller file, rather than mixed up with other data in the larger "output" file. Fairly modest editing of a plot file permits working it into the form of a *.csv (comma separated value) file, which can be opened by Excel.

Many of the data in data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]) were originally generated using SUPCRT92 in conjunction with an associated data file known as *slop98.dat* (DTN: MO0106MWDTDG01.035 [DIRS 161791]). The sources of data in this file were described in CRWMS M&O (2000 [DIRS 152575]). A problem with earlier SUPCRT92 data files is that they used a different set of conventions from EQ3/6 in handling species names. For example, these files have "Ca+2" instead of the EQ3/6 "Ca++," "FORMATE,AQ" in place of "Formate," "QUARTZ" instead of "Quartz," and "H2,g" in place of "H2(g)". To avoid lengthy and repeated exercises changing or matching species names, a new SUPCRT92 data file, *speq02.dat* (DTN: MO0303SPASPEQ2.000 [DIRS 162278]), was set up to use the EQ3/6 names. As noted elsewhere in the discussion of the Rimstidt vs. Fournier paradigms, the data were changed for quartz (very minor change) and SiO₂(aq) (significant change). Both data files are included in DTN: MO0302SPATHDYN.001 [DIRS 161886], which is input to, and qualified by, this report.

The thermodynamic data for steam (H₂O(g)) in all SUPCRT92 data files were known to be erroneous at the start of this qualification. They appear to have been constructed to match up with the gas phase properties calculable (in principle at least) from the equation of state model for H₂O that is built into SUPCRT92. Due to technical details in the implementation of the equation of state model in the software, that model can not be used to directly obtain the H₂O(g) properties and a data file species is required. However, the match in the current instance is calibrated for a temperature/pressure range that is outside that of interest to the YMP, and it does not extrapolate accurately into the needed range. This problem was not fixed in *speq02.dat* (DTN: MO0303SPASPEQ2.000 [DIRS 162278]). Rather, corrected data were obtained using the spreadsheet approach and incorporated into data0.ymp.R2 (DTN: MO0302SPATHDYN.001 [DIRS 161886]). That is, the properties for H₂O(g) were obtained from Barin and Platzki (1995 [DIRS 157865]) and the calculation is given in Spreadsheet *Gases_j_TJW_2.xls* (DTN: MO0302SPATHDYN.001 [DIRS 161886]).

6.1.3 Special Function Spreadsheets

Three types of special function spreadsheets were developed to facilitate the other calculations needed develop the log grids for the data0.vmp.R2 K (DTN: MO0302SPATHDYN.000 [DIRS 161756]). The term "generic" spreadsheet is used to describe the type, with the understanding that this actually is the template or general form that is applied to a particular type of calculation, without regard to the specific set of data treated. There are many specific applications of such "generic" spreadsheets (representing the work of various contributors). These spreadsheets use no macros, just formulas and built-in functions. used developing the data0.ymp.R2 All the spreadsheets in database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) included are in DTN: MO0302SPATHDYN.001 ([DIRS 161886]).

Some generic spreadsheets use calorie units, some joule units. The latter are more prominent today (the SI standard); however, it was thought expedient to allow some calculations in calorie units. SUPCRT92 still uses calorie units.

Most spreadsheets have a "Cover" worksheet of some type, a "Directions" worksheet, an "Example" worksheet (with a real example), and a "Template" worksheet, which can be copied

as needed. In general, the data for one species or reaction is worked up on a single worksheet, and multiple worksheets then appear for workups of multiple species or reactions. Many spreadsheets also have a "Results Summary" worksheet. This worksheet can be exported under Excel as a *.csv (comma separated value) file, which facilitates getting the data into EQ3/6 data blocks. Some spreadsheets also have "library" worksheets of data for basis and analog species to be copied and pasted as needed onto the worksheets for specific species or reactions.

One type of spreadsheet was used to reduce tabulated heat capacity values (heat capacities vs. temperature) to Maier-Kelley heat capacity coefficients (which are then used in another type of spreadsheet described below). The heat capacity-fitting spreadsheets exist in two generic forms, here termed $Cp_Solids_cal.xls$ (uses calorie units) and $Cp_Solids_j.xls$ (uses joule units). Specific instances of usage of these are represented by spreadsheets with more complex names, usually indicating the user and at least one other distinguishing characteristic. An earlier version of these spreadsheets allowed work in mixed calorie/joule units, and specific instances of that were also used in developing data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). The heat capacity coefficient regression spreadsheets utilize Excel's built-in regression tool. Directions for activating and using it are included in the spreadsheets themselves (in the generic templates, hence in every specific instance of usage). Regression to fit other types of heat capacity temperature functions (such as those described in Section 6.1.1) was not necessary and no generic spreadsheet development to support this was done.

The second type of spreadsheet was developed to compute log K values on the EQ3/6 temperature grid for mineral dissolution reactions (it is also applicable to, and was used in the case of gas species dissolution reactions). The four generic forms are here termed <code>Minerals_cal.xls</code>, <code>Minerals_j.xls</code>, <code>Solids_cal.xls</code>, and <code>Solids_j.xls</code>. The "Minerals" spreadsheets presume the Maier-Kelley formalism for the description of heat capacities, whereas the "Solids" spreadsheets allow a very generalized formalism for heat capacities. The "_cal" spreadsheets use calorie units, while the "_j" ones use joule units.

These spreadsheets operate by inputting the standard Gibbs free energy and standard entropy of a species at 298.15K and 1 bar pressure along with the heat capacity coefficients. The apparent Gibbs free energy (the same Gibbs free energy used in SUPCRT92) is then calculated on the EQ3/6 temperature grid (0°C–25°C–60°C–100°C–150°C–200°C–250°C–300°C). The retrieval equation for this is given in the heat capacity discussion (Section 6.1.1, Eq. 6-6). This Gibbs free energy grid was carried forward on the worksheet into an area in which the associated reaction properties were then calculated. The user must supply the reaction coefficients, negative for reactants, positive for products (the coefficient is always –1 for the associated species). The user must copy the parallel Gibbs free energy grids for the other species in the reaction (which must all be basis species) from "Basis Species" library worksheets. Standard thermodynamic relations are then used to compute the Gibbs free energy of reaction on the temperature grid and then the log K. The log K grids are the desired output and may be copied onto the "Results Summary" worksheet.

With very few exceptions (noted below), the "library" data for basis species were obtained from SUPCRT92 and *slop98.dat* (DTN: MO0106MWDTDG01.035 [DIRS 161791]). This set of library data grew during the update as additional needs were identified. The final collection, summarized in *BasisSpeciesLib_j_TJW_1p3.xls* in DTN: MO0302SPATHDYN.001

[DIRS 161886], contained data for 139 species (124 from SUPCRT92, 15 worked up in other spreadsheets described below) distributed over four worksheets. Not all specific instances of the "Mineral/Solid" log K spreadsheets contain the full set of final basis species data. In the course of work, data for two basis species, SiO₂(aq) and Ti(OH)₄(aq), were revised. Users were notified of the changes and directed to use the replacement worksheets provided. To avoid any possible confusion, the deprecated data were retained on the revised library worksheets along with the revised data. The deprecated data were marked as such, and a different background color was used to highlight them.

The third type of spreadsheet uses the isocoulombic/isoelectric method (Lindsay 1980 [DIRS 159038]; Murray and Cobble 1980 [DIRS 159200]; see also Fernandez-Prini et al. 1992 [DIRS 161651], Section 3-7, pp. 124-127; Puigdomenech et al. 1999 [DIRS 159205], p. 65) to obtain the apparent Gibbs free energy of a species (aqueous or mineral) on the temperature grid. The method is not exact but appears to give accurate results to 275°C to 300°C. It replaces the Criss-Cobble method and the "const-H" method that were both found unsuitable in CRWMS M&O (2000 [DIRS 152575], pp. 13–17). Comments on the Criss-Cobble method are provided by Puigdomenech et al. (1999 [DIRS 159205], pp. 64–65). The isocoulombic/isoelectric method also replaces the "DQUANT" method in Helgeson (1969 [DIRS 137246]) that was previously used in the case of neutral aqueous species but is only generally valid to about 150°C.

The isocoulombic/isoelectric method, like those it replaces, is a temperature extrapolation algorithm that requires for its primary input only the standard Gibbs free energy and standard entropy at 298.15K and 1 bar for the species in question as well as for other species (basis or analog) that appear in a chosen isocoulombic/isoelectric reaction. An isocoulombic reaction (the better of the two) is characterized by equal numbers of ions of a given charge type on both sides of the reaction (as an example, see Spreadsheet *BasisSpecies_j_TJW_4.xls* in DTN: MO0302SPATHDYN.001 [DIRS 161886]). Neutral species are commonly ignored. An example is:

$$PuO_2SO_4(aq) + UO_2^{++} = UO_2SO_4(aq) + PuO_2^{++}$$
 (Eq. 6-11)

As suggested by this example, most of the best isocoulombic reactions are exchange reactions. Here the properties of PuO₂SO₄(aq) could be extrapolated if sufficient data (entropies at 298.15K and full Gibbs free energy grids) were available for UO₂SO₄(aq) (an "analog" species) and two basis species, UO₂⁺⁺ and PuO₂⁺⁺. An isoelectric reaction only requires that the sums of charge types (positive and negative) be the same on both sides of the equation. An example is:

$$HSO_4^- + OH^- = SO_4^{--} + H_2O$$
 (Eq. 6-12)

Normally an isoelectric reaction is required to deal with very highly charged species for which there are few usable analogs. Note also that most EQ3/6 reactions are not isocoulombic/isoelectric (for example: $CdSO_4(aq) = SO_4^{--} + Cd^{++}$). Normally a distinct reaction is required to use the method.

The user must choose the reaction and provide the requisite data for the other species, normally from another set of "library" pages. In essence, the spreadsheet uses the input data to calculate the Gibbs free energy of reaction and entropy of reaction at 298.15K and 1 bar for the

isocoulombic or isoelectric reaction. The Gibbs free energy of reaction is then normally extrapolated up-temperature using the van't Hoff relation of thermodynamics along with the assumption of a zero heat capacity of reaction over the entire temperature range. The method allows the assumption of a constant non-zero heat capacity of reaction, but the usage of this is rare. The apparent Gibbs free energy grid for the species in question is then extracted from the Gibbs free energy of reaction grid in a calculation that resembles but partially inverts the process of calculating a Gibbs free energy of reaction grid from the Gibbs free energy grids for the species in the reaction. This requires copying Gibbs free energy grids for basis and analog species from library pages. The log K grid for the desired EQ3/6 reaction (which is normally different from the isocoulombic/isoelectric reaction) is then obtained using the same kind of operations as in the "Minerals/Solids" log K worksheets.

6.1.4 Algorithms, Procedures, and Parameters Used to Obtain Input Parameters for the Temperature Extrapolation Excel Templates

6.1.4.1 Estimation of the Coefficients of the Maier-Kelley Equation

The Spreadsheet *Minerals_cal.xls* (DTN: MO0302SPATHDYN.001 [DIRS 161886]) was used to extrapolate Gibbs free energies of solids at different temperatures, using the Maier-Kelley equation to represent the standard molal heat capacity of solids. The Maier-Kelley equation implemented in the spreadsheets is:

$$C_p^0 = a + bT + c/T^2$$
 (Eq. 6-13)

If the heat capacity data were not available for a mineral, an estimation method given in Helgeson et al. (1978 [DIRS 101596]) was used to obtain them. The method assumes that the standard molal heat capacity equals the summation of the heat capacity of its constituent oxides. If the Maier-Kelley coefficients (Eq. 6-13) of the constituent oxides of a solid were known, the Maier-Kelley coefficients (a_i, b_i, and c_i) of the standard molal heat capacity of the solid were developed using the following formulas:

$$a_i = \sum_j v_{j,i} a_j \tag{Eq. 6-14}$$

$$b_i = \sum_j v_{j,i} b_j \tag{Eq. 6-15}$$

$$c_i = \sum_j v_{j,i} c_j \tag{Eq. 6-16}$$

where $v_{i,i}$ is the number of moles of the jth oxide formula unit in one mole of the ith solid.

The Maier-Kelley coefficients of most oxides given in Table 2 in Helgeson et al. (1978 [DIRS 101596]) were used in the estimation. Note that the Maier-Kelley equation in Helgeson et al. (1978 [DIRS 101596]) differs from Eq. 4-1 in the sign for the third term. Thus, the sign for c_j in this discussion is opposite from Helgeson et al. (1978 [DIRS 101596]).

6.1.4.2 Estimation of Entropies

Eqs. 55, 56, and 57 in Helgeson et al. (1978 [DIRS 101596]) were used to estimate the standard molal entropies of solids. The molal entropy and volume data of oxides are also from Table 2 in Helgeson et al. (1978 [DIRS 101596]). The molal entropy of radionuclide solids were obtained from Grenthe et al. (1992 [DIRS 101671]), Barin and Platzki (1995 [DIRS 157865]) and Binnewies and Milke (1999 [DIRS 158955]). The molal volumes, when available, were from these sources plus those obtained from peer-reviewed journals, and data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]).

6.1.4.3 Obtaining Gibbs Free Energies of Formation at 25°C from Measurements at Other Temperatures

To obtain $\Delta G_f^o(T=298.15K)$ of a solid from solubility measurements at temperatures other than 25°C (say 30°C), $\Delta G_f^o(T=303.15K)$ has to be obtained first. This requires the $\Delta G_f^o(T=303.15K)$ data for involved species. Those $\Delta G_f^o(T=303.15K)$ data were obtained by running SUPCRT92 with the *slop98.dat* (DTN: MO0106MWDTDG01.035 [DIRS 161791]) or its modified version *speq02.dat* (DTN: MO0303SPASPEQ2.000 [DIRS 162278]).

The next step was to derive $\Delta G_f^o(T=298.15K)$ from $\Delta G_f^o(T=303.15K)$. The temperature extrapolation spreadsheet (*Minerals_cal.xls*) was used for this purpose. In order to do that, $\Delta G_f^o(T=298.15K)$ was adjusted iteratively until the $\Delta G_f^o(T=303.15K)$ value extrapolated using the spreadsheet was equal to the measured value. The final value of $\Delta G_f^o(T=298.15K)$ was the answer.

6.1.5 SUPCRT92 Silicate Mineral Revisions: Moving to the Rimstidt Paradigm

The original treatment of silicate mineral thermodynamics in SUPCRT92 (Helgeson et al. 1978 [DIRS 101596]) has long been a core part of EQ3/6 data files. The equilibrium constants for the dissolution reactions of the minerals in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) were calculated from a combination of the thermodynamic properties of the minerals themselves and those of the aqueous species participating in the reactions. In the vast majority of cases, the mineral properties described in Helgeson et al. (1978 [DIRS 101596]) were obtained directly from calorimetric ("third law") measurements, high-temperature (non-aqueous) phase equilibrium data in conjunction with calorimetric measurements for other minerals, or the use of predictive correlations. The equilibrium constants for the silicate mineral dissolution reactions are therefore "synthetic" in the sense that they are not based on measurements of aqueous solubility. In particular for the silicate minerals, such results depend on the assumed thermodynamic properties of aqueous silica [SiO₂(aq)]. These properties have long been somewhat controversial, particularly at temperatures near 25°C (Walther and Helgeson 1977 [DIRS 133240], pp. 1324-1328).

In general, the properties of SiO₂(aq) (or the alternative species H₄SiO₄(aq)) are derived from measurements of the aqueous solubilities of quartz or other silica polymorphs, combined with calorimetric measurements of the thermodynamic properties of these minerals. Helgeson et al.

(1978 [DIRS 101596]) followed the earlier analysis in Walther and Helgeson (1977 [DIRS 133240]). They in turn had recognized the disparity of reported measurements of the solubility of quartz especially at the lower temperatures, noting that sluggish reaction rates impede the attainment of equilibrium in experiments under these conditions. They chose the low-temperature solubility measurements in Morey et al. (1962 [DIRS 159198]) as a cornerstone of their analysis. These data, which are on the low end of the spectrum, are consistent with a 25°C solubility of 6 ppm SiO_2 or very nearly 1.00×10^{-4} molal. The higher reported measurements were ascribed to disequilibrium effects, such as abnormally high surface energies of mineral particle surfaces, due to grinding. To simplify further discussion, this interpretation of aqueous silica thermodynamics will be referred to as the Fournier paradigm, after the second author of Morey et al. (1962 [DIRS 159198]), who later reiterated this picture (Fournier and Potter 1982 [DIRS 160956]).

The issue was reopened by Rimstidt (1997 [DIRS 101709]) who performed a new set of quartz solubility experiments in the range of 21°C to 96°C. His results indicated a 25°C solubility of 11.0 ± 1.1 ppm SiO₂ (about 1.83×10^{-4} molal). As support for these higher results, he cites both a problem with Morey et al. (1962 [DIRS 159198]) data in relation to the solubility of amorphous silica and also the fact that the higher results seem in better accord with the dissolved silica concentrations in ancient groundwaters.

Rimstidt (1997 [DIRS 101709]) did not claim to have delivered a definitive case. However, his analysis gained increasing favor (e.g., Gunnarsson and Arnórsson 2000 [DIRS 160465]; Stefánsson 2001 [DIRS 159208]). The principal reason is that it provides an equilibrium model for silicate mineral/water interactions that better fits real groundwaters, including geothermal waters. This is true for silicate minerals in general, not just for SiO₂ phases.

Most research areas of the YMP (e.g., the waste form degradation) had used the previously qualified data file (data0.ymp.R0; DTN: MO0009THRMODYN.001 [DIRS 152576]) or its unqualified predecessors. These were all based on the Fournier paradigm. However, thermal-hydrologic-chemical reactive transport calculations using a modified database were among activities that were based on the Rimstidt paradigm. A key goal of the data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) development was to fold everything together so that all modeling activities within the YMP could use the same database.

The decision was made to move to the Rimstidt paradigm for data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). One expectation of doing this was that it would reduce the number of mineral suppressions needed in reaction-path and reactive transport calculations.

It was decided to adopt the SUPCRT92 data for $SiO_2(aq)$ and quartz, as documented in the report *Data Qualification for Thermodynamic Data Used to Support THC Calculations* (BSC 2004 [DIRS 170268], Section 6.3 and Table 6.4-1). These data are consistent with the Rimstidt paradigm and represent a substantial revision due to the shift in the updated silica thermodynamic properties. The changes in the data for quartz itself are in fact quite small, and only reflect a newer "best fit" to more recent thermodynamic data. The new data are consistent with, but not really reflective of, the change in silica solubility paradigm. Similar refinements

were calculated for the thermodynamic data for other silicate minerals, but not included in the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) as discussed below.

In implementing the Rimstidt paradigm in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), the following actions were taken. Updated thermodynamic data for SiO₂(aq) and quartz were put in the SUPCRT92 data file speq02.dat (DTN: MO0303SPASPEQ2.000 [DIRS 162278]). Gibbs free energy grids (values of the Gibbs free energies on the standard EQ3/6 temperature grid) were calculated using SUPCRT92 and placed in the library worksheets of the spreadsheets used for non-SUPCRT92 calculations. In both speq02.dat and the library worksheets, the updated data were labeled Rimstidt and the previous data were retained and marked "Fournier." The Fournier data on the library worksheets were also marked as "deprecated" and highlighted in a different color (gray instead of yellow). The Gibbs free energy grid as a function of temperature calculated for SiO₂(aq) in SUPCRT92 is very similar to the grid calculated from the data from Gunnarsson and Arnórsson (2000 [DIRS 160465], Table 3) with a maximum difference of 125 cal/mol at 200°C (Table 6-1). Such relatively small differences provide corroboration of the thermodynamic data used in data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]). Next, the log K grids for all SUPCRT92 minerals were recalculated using the Rimstidt data. This was done by extracting all the relevant minerals and reactions from data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]) onto a set of SUPCRT92 input (.rxn) files and running these through SUPCRT92 in conjunction with a modified SUPCRT92 data file (speq02.dat; DTN: MO0303SPASPEQ2.000 [DIRS 162278]). The log K values from the relevant SUPCRT92 "plot" (.kxy) files were then pasted into the relevant mineral data blocks for data0.vmp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]).

Table 6-1. Comparison of ΔG_f° Obtained from Data0.ymp.R2 with the ΔG_f° from Gunnarsson and Arnórsson for SiO₂(aq)

T (°C)	0.01	25	60	100	150	200	250	300	
bars	1.0133	1.0133	1.0133	1.0133	4.7572	15.5366	39.7366	85.8379	
K	273.16	298.15	333.15	373.15	423.15	473.15	523.15	573.15	
Source		ΔG _f ° (cal/mol)							
1	-199219.4	-199540.0	-199909.5	-200352.1	-200994.3	-201739.0	-202555.6	-203362.2	
2	-199337.7	-199546.4	-199912.5	-200411.4	-201115.1	-201864.1	-202617.1	-203337.1	
Difference	118.3	6.4	3.0	59.3	120.8	125.1	61.5	-25.1	

Sources: 1 Data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]).

2 Gunnarsson and Arnórsson 2000 [DIRS 160465].

In doing this SUPCRT92 silicate update, the log K grids for silica reactions involving only aqueous species (e.g., $HSiO_3^- + H^+ = SiO_2(aq) + H_2O$) were not updated, as the original constraining data were log K values. In theory, the SUPCRT92 data file properties for species like HSiO₃⁻ should have been reevaluated to produce the old log K values. data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), that was not carried out as it was not strictly necessary considering that the predominance of this particular silica species (HSiO₃⁻) is restricted to alkaline pH values greater than 9 to 10. The lack of such corrections significant impact qualification has no on of data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) because the predicted pH values for waters

of interest to YMP are lower (BSC 2004 [DIRS 169860]). Calculation of the appropriate log K values with the current SUPCRT92 data file (*speq02.dat*; DTN: MO0303SPASPEQ2.000 [DIRS 162278]) can be performed by specifying the "SiO2(aq)(Fournier)" species in the relevant reaction.

The revision as carried out for the silicate minerals assumed a calorimetric or equivalent origin of the constraining data. Thus the log K values were synthetic and somewhat different than those previously obtained using the Fournier data. However, the data for two minerals in the SUPCRT92 data set were derived in Helgeson et al. (1978 [DIRS 101596]) from low-temperature solubility (log K) data. These were amorphous silica (Helgeson et al. 1978 [DIRS 101596], p. 86; see also Walther and Helgeson 1977 [DIRS 133240], p. 1321 and pp. 1326-1328) and sepiolite (Helgeson et al. 1978 [DIRS 101596], p. 98 and Figure 34, p. 99). Therefore, the log K grids for these minerals were left consistent with previous results (as were those for aqueous species like HSiO₃⁻). The appropriate log K values can be calculated using the speq02.dat data file (DTN: MO0303SPASPEQ2.000 [DIRS 162278]) by specifying the "SiO2(aq) (Fournier)" species in the relevant reactions.

The status of a few other silicate minerals was questioned in the development of data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), but the necessity of further corrections in moving to the Rimstidt paradigm was not clear. This was in part due to uncertainty as to exactly how the constraining data were used in Helgeson et al. (1978 [DIRS 101596]) to obtain the reported values for the standard Gibbs free energies of formation (and by implication those for the standard enthalpies of formation). No further corrections were made. However, the cases are discussed here for possible future reference.

Solubility measurements appear to have been used in whole or in part in Helgeson et al. (1978) [DIRS 101596]) to determine the standard Gibbs free energies of formation of forsterite, chrysotile, and antigorite. In the case of forsterite, the solubility data in question were at temperatures in excess of 500°C (Helgeson et al. 1978 [DIRS 101596], p. 89 and p. 93, Figure 27), which are required for this phase to be stable. In the case of antigorite (Helgeson et al. 1978 [DIRS 101596], p. 89 and p. 94, Figure 28), solubility data at and above 300°C were employed. If the apparent Gibbs free energies of these minerals were obtained from the solubility data at high temperature (where the difference in paradigms is small) and then extrapolated down using the standard entropy and heat capacity data for each mineral, any further necessary correction would be rather small. If on the other hand the solubility data were extrapolated down to 298.15K and the Gibbs free energies of formation then extracted, a significant further correction would be necessary. However, the exact calculational path was not given in Helgeson et al. (1978 [DIRS 101596]). There may be a more definite problem with chrysotile (Helgeson et al. 1978 [DIRS 101596], p. 89 and p. 93, Figure 27) as some solubility data shown extend down to 100°C. Note that none of these minerals appears to have much if any relevance to YMP investigations.

The Gibbs free energy of formation of kaolinite was partially constrained by assuming equilibrium with some low-temperature groundwaters of known composition (Helgeson et al. 1978 [DIRS 101596], pp. 112–114 and p. 125, Footnote). No attempt was made to correct for this. The methodology used in Helgeson et al. (1978 [DIRS 101596]) was not fully compelling, and corrections also involving aluminum could be in order. More telling, the original Gibbs free

energy of formation (-905.614 kcal/mol or -3789.089 kJ/mol) was in line with expectations based on data for related minerals. This was shown by a very small residual of -0.009 kcal/mol in the final Gibbs free energy regression for sheet silicate minerals discussed in the "clay minerals" section of this report. Furthermore, this value is in reasonable accord with more recent calorimetric determinations of -3799.4 ± 6.4 kJ/mol (de Ligny and Navrotsky 1999 [DIRS 158973]) and -3793.9 ± 4.1 kJ/mol (Fialips et al. 2001 [DIRS 158975]), falling in the uncertainty band of the latter and slightly above that of the former. Barin and Platzki (1995 [DIRS 157865], p. 61) give a value of -3799.444 kJ/mol. This is probably based on calorimetric measurement, but the ultimate source could not be determined. The compilation of Wagman et al. (1982 [DIRS 159216]) was cited as the source, and they in turn do not identify sources.

The data for pyrophyllite appear to be partly tied to those of kaolinite (Helgeson et al. 1978 [DIRS 101596], p. 113, reaction 138 and p. 114, Figure 47). However, the mutual solubility data that may have been employed only extended down to 200°C. There may be similar concerns in the case of analcime (Helgeson et al. 1978 [DIRS 101596], pp. 149-150 and p. 150, Figure 72), as some relevant solubility data appear to extend down to about 150°C.

No other cases were found in which possible further corrections were a potential issue.

The effect of the move from the Fournier paradigm to the Rimstidt paradigm is illustrated by its effect on the log K grid for quartz as shown in Table 6-2. The Rimstidt data are taken from data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) and the Fournier data from data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]). The differences are largest at lower temperatures. A very small part of the differences shown is due to changes in the thermodynamic data for quartz itself. A much larger part is due to changes in the data for SiO₂(aq). Therefore, multiplying these differences by the number of SiO₂ units in the mineral formula of another silicate closely approximates the changes in the log K data for that silicate.

Table 6-2. Calculated Log K Grids for Quartz Showing the Effect of Changing from the Fournier Paradigm to the Rimstidt Paradigm

Temperature (°C)	Fournier	Rimstidt	Difference
0	-4.6319	-4.1605	0.4714
25	-3.9993	-3.7501	0.2492
60	-3.4734	-3.3553	0.1181
100	-3.0782	-3.0132	0.0650
150	-2.7191	-2.6679	0.0512
200	-2.4378	-2.3823	0.0555
250	-2.2058	-2.1490	0.0568
300	-2.0171	-1.9822	0.0349

NOTE: See Spreadsheet *silica.xls* (DTN: MO0302SPATHDYN.001 [DIRS 161886]).

A check of the modified SUPCRT92 data was made by comparing the present Rimstidt results for the log K for quartz with those obtained by evaluating a temperature function given in Rimstidt (1997 [DIRS 101709]). The comparison, on the EQ3/6 temperature grid, is shown in Table 6-3. Also shown for comparison are results obtained by evaluating a similar temperature function given in Gunnarsson and Arnórsson (2000 [DIRS 160465]), which also follows the Rimstidt paradigm (these temperature function evaluations were done in spreadsheet *Rimstidt_Silica_TJW.xls* as shown in DTN: MO0302SPATHDYN.001 [DIRS 161886]).

Table 6-3. Calculated Log K Grids for Quartz Comparing the Present Rimstidt Data (SUPCRT92 with Updated $SiO_2(aq)$) with Rimstidt Temperature Function and with Gunnarsson and Arnórsson Temperature Function

Temperature (°C)	Rimstidt (SUPCRT92 Calculation)	Rimstidt Temperature Function	Gunnarsson and Arnórsson Temperature Function
0	-4.1605	-4.0786	-4.0679
25	-3.7501	-3.7387	-3.7463
60	-3.3553	-3.3486	-3.3549
100	-3.0132	-2.9924	-2.9808
150	-2.6679	-2.6418	-2.6076
200	-2.3823	-2.3653	-2.3252
250	-2.1490	-2.1417	-2.1223
300	-1.9822	-1.9570	-1.9905

Sources: Rimstidt 1997 [DIRS 101709]; Gunnarsson and Arnórsson 2000 [DIRS 160465]. DTNs: MO0303SPASPEQ2.000 ([DIRS 162278], SUPCRT92 data file speq02.dat); MO0302SPATHDYN.001 ([DIRS 161886], spreadsheet calculation given in the Worksheet Rimstidt_Silica_TJW.xls).

Approximately 100 silicate solids were not corrected to the Rimstidt paradigm in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). These species generally do not occur in natural geologic systems but may be encountered in interactions with engineered materials. The resulting difference in log K is generally less than about one log unit, usually less than 0.5 units. The basic thermodynamic data are contained in the revised data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) for most of the species, so the Rimstidt calculation could be made for these species using the template spreadsheets included in the supplemental CD-ROM. A note to this effect was added in the Comments section of the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]). At the present time, the affected silicates can only be identified by comparing log K values for silicates in the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) with those in the data0.ymp.R0 database (DTN: MO0009THRMODYN.001 [DIRS 152576]).

6.1.6 Clarification of the Discrepancy in ΔG_f° Data for Ca-Bearing Silicates

In comparing thermodynamic parameters such as ΔG_f° for Ca-bearing silicates against their given source in the database (i.e., Helgeson et al. 1978 [DIRS 101596], Table 8, pp. 120-125), a discrepancy was found between these values and those listed in the former source. The ΔG_f° values are correct in the databases slop98.dat (DTN: MO0106MWDTDG01.035 [DIRS 161791]), speq02.dat (DTN: MO0303SPASPEQ2.000 [DIRS 162278]), and accordingly in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). Moreover, these ΔG_f° values for Ca-bearing silicates are also internally consistent with other species. It is not clear

why the values given by the source Helgeson et al. (1978 [DIRS 101596]) differ from those in the database and the goal of this section is to precisely clarify this discrepancy.

The Gibbs free energy of formation data for most of the minerals in the SUPCRT92 database (e.g., slop98.dat, DTN: MO0106MWDTDG01.035 [DIRS 161791]) and speq02.dat (DTN: MO0303SPASPEQ2.000 [DIRS 162278]) were regressed from high-temperature phase equilibrium experiments reported in the literature preceding the publication of Helgeson et al. (1978 [DIRS 101596]). These experiments represent the thermodynamic stabilities of assemblages of one or more minerals relative to other such assemblages. In order to utilize this approach, one must first establish a set of values for the Gibbs free energies of formation (i.e., ΔG_f°) of some "basis" set of minerals, commonly the simple oxides. The values for these minerals are determined purely from other kinds of data, principally calorimetric. calorimetric data (for all the minerals delineating the phase equilibrium reaction in the experiments) are used to make temperature and pressure corrections to the apparent Gibbs free energies of formation of the minerals, such that only the values at 298.15K and 1 bar pressure of certain minerals remain to be regressed from the experimental data. By this logic, one would use lime (CaO) as the "basis" mineral for Ca in regressing phase equilibrium data for other Ca minerals. However, the available phase equilibrium data did not permit this linkage, so calcite (CaCO₃, the stable form at 298.15K and 1 bar pressure) was used instead. The Gibbs free energy of formation at 298.15K and 1 bar pressure for calcite was itself regressed by Helgeson et al. (1978 [DIRS 101596], p. 87-88) from a solubility experiment. This required the assumption of values for the Gibbs free energies of formation of the Ca⁺⁺ and CO₃⁻⁻ ions at 298.15K and 1 bar pressure as detailed in Helgeson et al. (1978 [DIRS 101596]). Aragonite (a less stable form of CaCO₃ at ambient conditions) was treated in a similar manner, using solubility data from the same sources. The data for lime (CaO) and monticellite (CaMgSiO₄) were established purely from calorimetric data. The data for all remaining Ca minerals, however, were linked to the data for calcite. Sometime in the late 1980s, notification was received from an EQ3/6 user (to the code developer, Dr. T. J. Wolery) that saturation indices for calcite as computed from EQ3/6 and a largely SUPCRT92-derived database differed noticeably from values calculated using another code. This was initially puzzling, as the ultimate data source for calcite solubility in both cases was listed as the same given in Helgeson et al. (1978 [DIRS 101596]). The matter was referred to Professor H.C. Helgeson at the University of California, Berkeley. The problem, which has not heretofore been documented except for an informal written communication distributed thereafter by Professor Helgeson to known users of the SUPCRT92 database, was that changes in the Gibbs free energies of formation of the ions (including Ca⁺⁺ and CO₃⁻⁻) had occurred. In order to obtain the original equilibrium constant for calcite dissolution (and hence a consistent set of saturation indices), the Gibbs free energy of formation of calcite at 298.15K and 1 bar pressure needed to be recalculated. The corresponding Gibbs free energy of formation of every mineral linked to calcite (directly or indirectly) therefore also needed to be relcalculated (all Ca minerals except calcite itself, aragonite, lime, and monticellite). The Worksheet Ca Mineral Data Comparison in the Spreadsheet SUPCRT92 Ca Minerals Analysis.xls (output DTN: SN0410T0510404.001) shows that the Gibbs free energy of formation of calcite at 298.15K and 1 bar pressure was increased by 220 cal/mol. Then, that of each of the affected minerals was increased by 220 cal/mol for each calcium appearing in the molecular formula of the linked mineral. This correction precisely preserves the phase equilibrium relations in the original paper by Helgeson et al. (1978 [DIRS 101596]). The Worksheet Calcite Data

Correction the Spreadsheet SUPCRT92 Ca Minerals Analysis.xls in DTN: SN0410T0510404.001) shows the derivation of the 220 cal/mol per Ca correction. In this derivation, two factors must be kept in mind. First, the Gibbs free energies of formation of the ions at 298.15K and 1 bar pressure changed from the set of values adopted by Helgeson et al. (1978 [DIRS 101596]) to a set that is now documented by Shock et al. (1997 [DIRS 127953]). Second, the revised solubility data for calcite and aragonite are based on a later paper (Plummer and Busenberg, 1982 [DIRS 151737]). These newer solubility data account for the fact that the correction to the Gibbs free energy of formation of aragonite is 192 cal/mol, not 220 cal/mol. The affected Ca-bearing silicates along with the corrected Gibbs free energy values are listed in Table 6-4. Since these values are correct in the input data used to develop data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), no further qualification is necessary except to specify that Helgeson et al. (1978 [DIRS 101596]) is not the root source for the thermodynamic data of Ca silicates listed in Table 6-4.

Table 6-4. Differences in ΔG_f° of Ca-Bearing Minerals Due for Updated Ca⁺⁺ Thermodynamic Properties

Mineral	Formula	ΔG _f ° (cal/mol)	ΔG _f ° (cal/mol)	Difference per Ca in Formula (cal/mol)	Comment
Lime	CaO	-144366	-144366	0	NL
Calcite	CaCO ₃	-270100	-269880	220	L
Aragonite	CaCO₃	-269875	-269683	192	NS
Ordered Dolomite	CaMg(CO ₃) ₂	-517980	-517760	220	L
Disordered Dolomite	CaMg(CO ₃) ₂	-515873	-515653	220	L
Dolomite	CaMg(CO ₃) ₂	-517980	-517760	220	L
Gehlenite	Ca ₂ Al ₂ SiO ₇	-903588	-903148	220	L
Grossular	Ca ₃ Al ₂ Si ₃ O ₁₂	-1496967	-1496307	220	L
Andradite	Ca₃Fe₂Si₃O₁₂	-1297479	-1296819	220	L
Monticellite	CaMgSiO₄	-512829	-512829	0	NL
Merwinite	Ca₃Mg(SiO₄)₂	-1037186	-1036526	220	L
Akermanite	Ca ₂ MgSi ₂ O ₇	-879802	-879362	220	L
Clinozoisite	Ca ₂ Al ₃ Si ₃ O ₁₂ (OH)	-1549680	-1549240	220	L
Zoisite	Ca ₂ Al ₃ Si ₃ O ₁₂ (OH)	-1549619	-1549179	220	L
Ordered Epidote	Ca ₂ FeAl ₂ Si ₃ O ₁₂ (OH)	-1451346	-1450906	220	L
Epidote	Ca ₂ FeAl ₂ Si ₃ O ₁₂ (OH)	-1451346	-1450906	220	L
Lawsonite	CaAl ₂ Si ₂ O ₇ (OH) ₂ ·H ₂ O	-1073628	-1073408	220	L
Wollastonite	CaSiO₃	-369445	-369225	220	L
Ca-Al Pyroxene	CaAl₂SiO ₆	-742287	-742067	220	L
Diopside	CaMg(SiO ₃) ₂	-724000	-723780	220	L
Tremolite	Ca ₂ Mg ₅ Si ₈ O ₂₂ (OH) ₂	-2770685	-2770245	220	L
Pargasite	NaCa ₂ Mg ₄ Al(Al ₂ Si ₆ O ₂₂)(OH) ₂	-2847168	-2846728	220	L
Anorthite	CaAl ₂ Si ₂ O ₈	-954298	-954078	220	L
Wairakite	CaAl ₂ Si ₄ O ₁₂ ·2H ₂ O	-1477652	-1477432	220	L

Table 6-4. Differences in ΔG_f° of Ca-Bearing Minerals Due for Updated Ca⁺⁺ Thermodynamic Properties (Continued)

Mineral	Formula	ΔG _f ° (cal/mol)	ΔG _f ° (cal/mol)	Difference per Ca in Formula (cal/mol)	Comment
Laumontite	CaAl ₂ Si ₄ O ₁₂ ·4H ₂ O	-1597043	-1596823	220	L
Prehnite	Ca ₂ Al(AlSi ₃ O ₁₀)(OH) ₂	-1390537	-1390097	220	L
Margarite	CaAl ₂ (Al ₂ Si ₂ O ₁₀)(OH) ₂	-1394370	-1394150	220	L

Sources: Column 3: Helgeson et al. 1978 [DIRS 101596], Table 8, pp. 120-125. Column 4: slop98.dat (DTN: MO0106MWDTDG01.035 [DIRS 161791]); data0.ymp.R0

(DTN: MO0009THRMODYN.001 [DIRS 152576]).

NL = Not linked to the calcite correction; L = Linked to the calcite correction; NS = Value based on newer solubility data.

6.2 EVALUATION AND QUALIFICATION OF THERMODYNAMIC DATA FOR **AQUEOUS SPECIES**

In this section, qualified log K grids are presented for temperatures of 0.01°C, 25°C, 60°C, 100°C, 150°C, 200°C, 250°C, and 300°C as incorporated into the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) to model geochemical reactions for the YMP. These log K grids were derived from thermodynamic data gathered from the literature and presented in Section 4 using data reduction methods presented in Section 6.1.2.

6.2.1 **Evaluation and Qualification of Np and Pu Species**

The OECD/NEA recently published the results of an extensive peer review of thermodynamic data for neptunium and plutonium (Lemire 2001 [DIRS 159027]). This panel gathered a wide range of peer review publications, government publications, and previous compilations of data. Using the techniques of corroborating data, peer review, and technical assessment, details of which are documented in the published book, the panel of internationally recognized scientists reached consensus on the best available thermodynamic data for neptunium and plutonium. The data in this publication are accepted by the scientific community as "established fact" and therefore do not require further qualification per AP-SIII.2Q.

The thermodynamic data published in Lemire (2001 [DIRS 159027]) were then processed using the methods discussed in Section 6.1 to develop EQ3/6 log K grids. When possible, log K values were derived for the temperature range from 0.01°C to 300°C (273.16K to 573.15K) (the value of 0.01°C is used to represent 0°C, avoiding singularity in the Maier-Kelly heat capacity equation). In many instances, data were only available for 25°C, and temperature extrapolation was not possible. The resulting log K grids for neptunium and plutonium aqueous species are shown in Table 6-5.

Table 6-5. Log K EQ3/6 Grid for Neptunium and Plutonium Aqueous Species

Data0 Species Designation	Reaction	log K 0.01°C	log K 25°C	log K 60°C	log K 100°C	log K 150°C	log K 200°C	log K 250°C	log K 300°C
(NpO ₂) ₂ (OH) ₂ ⁺⁺	$(NpO_2)_2(OH)_2^{++} + 2H^+ = 2NpO_2^{++} + 2H_2O$	-	6.2700	-	-	-	-	-	ı
(NpO ₂) ₂ CO ₃ (OH) ₃ ⁻	$(NpO_2)_2CO_3(OH)_3^- + 4H^+ = 2NpO_2^{++} + HCO_3^- + 3H_2O$	-	13.2180	-	1	-	-	1	-
(NpO ₂) ₃ (CO ₃) ₆ ⁽⁻⁶⁾	$(NpO_2)_3(CO_3)_6^{(-6)} + 6H^+ = 3NpO_2^{++} + 6HCO_3^-$	-	12.2193	-	-	-	-	-	-
(NpO ₂) ₃ (OH) ₅ ⁺	$(NpO_2)_3(OH)_5^+ + 5H^+ = 3NpO_2^{++} + 5H_2O$	-	17.1200	-	-	-	-	-	-
(UO ₂) ₂ (NpO ₂)(CO ₃) ₆ ⁽⁻⁶⁾	$(UO_2)_2(NpO_2)(CO_3)_6^{(-6)} + 6H^+ = 2UO_2^{++} + NpO_2^{++} + 6HCO_3^{-}$	-	8.4965	-	1	-	-	1	-
Np(CO ₃) ₃	$Np(CO_3)_3^{} + 3H^+ = Np^{+++} + 3HCO_3^-$	-	15.3709	-	-	-	-	-	-
Np(CO ₃) ₄	$Np(CO_3)_4^{} + 4H^+ = Np^{++++} + 4HCO_3^-$	-	4.6879	-	-	-	-	-	-
Np(CO ₃) ₅ ⁽⁻⁶⁾	$Np(CO_3)_5^{(-6)} + 5H^+ = Np^{++++} + 5HCO_3^-$	-	16.1014	-	-	-	-	-	-
NpCI ⁺⁺⁺	NpCl ⁺⁺⁺ = Np ⁺⁺⁺⁺ + Cl ⁻	-	- 1.5000	-	-	-	-	-	-
NpF***	NpF*** = Np**** + F-	-8.9464	-8.9202	-9.0057	-9.1891	-9.5059	-9.9165	-10.4436	-11.1428
NpF ₂ ⁺⁺	$NpF_2^{++} = Np^{++++} + 2F^-$	-	- 15.7000	-	-	-	-	-	-
NpI ⁺⁺⁺	$NpI^{+++} = Np^{++++} + I^{-}$	-	- 1.5000	-	-	-	-	-	-
NpNO ₃ ⁺⁺⁺	$NpNO_3^{+++} = Np^{++++} + NO_3^-$	-	- 1.9000	-	-	-	-	-	-
NpO ₂ (CO ₃) ₂	$NpO_2(CO_3)_2^{} + 2H^+ = NpO_2^{++} + 2HCO_3^-$	-	4.1703	-	-	-	-	-	-
NpO ₂ (CO ₃) ₂	$NpO_2(CO_3)_2^{} + 2H^+ = NpO_2^+ + 2HCO_3^-$	-	14.1528	-	-	-	-	-	-
NpO ₂ (CO ₃) ₂ OH	$NpO_2(CO_3)_2OH^{} + 3H^+ = NpO_2^{++} + 2HCO_3^- + H_2O$	-	26.0003	-	-	-	-	-	-
NpO ₂ (CO ₃) ₃	$NpO_2(CO_3)_3^{} + 3H^+ = NpO_2^{++} + 3HCO_3^-$	11.7234	11.6593	11.6647	11.7893	12.0773	12.4781	12.9816	13.6214
NpO ₂ (CO ₃) ₃ ⁽⁻⁵⁾	$NpO_2(CO_3)_3^{(-5)} + 3H^+ = NpO_2^+ + 3HCO_3^-$	26.1033	25.5302	25.0683	24.8778	24.9913	25.3997	26.0739	27.0833

Table 6-5. Log K EQ3/6 Grid for Neptunium and Plutonium Aqueous Species (Continued)

Data0 Species Designation	Reaction	log K 0.01°C	log K 25°C	log K 60°C	log K 100°C	log K 150°C	log K 200°C	log K 250°C	log K 300°C
NpO ₂ (HPO ₄) ₂	$NpO_2(HPO_4)_2^{} = NpO_2^{++} + 2HPO_4^{}$	-	-9.5000	-	ı	-	-	ı	-
NpO ₂ (OH) ₂ ⁻	$NpO_2(OH)_2^- + 2H^+ = NpO_2^+ + 2H_2O$	25.5045	23.6147	21.4199	19.4099	17.4475	15.9411	14.7957	13.9864
NpO ₂ (SO ₄) ₂	$NpO_2(SO_4)_2^{} = NpO_2^{++} + 2SO_4^{}$	- 4.2153	-4.5406	- 5.1435	- 5.8895	- 6.8628	- 7.9061	- 9.0919	- 10.5738
NpO ₂ Cl ⁺	$NpO_2CI^+ = NpO2^{++} + CI^-$	-	-0.4000	-	ı	-	-	ı	-
NpO ₂ CO ₃ ⁻	$NpO_2CO_3^- + H^+ = NpO_2^+ + HCO_3^-$	-	5.3814	-	ı	-	-	ı	-
NpO ₂ CO ₃ (aq)	$NpO_2CO_3(aq) + H^+ = NpO_2^{++} + HCO_3^-$	-	1.0229	-	-	-	-	-	-
NpO ₂ F(aq)	$NpO_2F(aq) = NpO_2^+ + F^-$	-	-1.2000	-	-	-	-	-	-
NpO_2F^+	$NpO_2F^+ = NpO_2^{++} + F^-$	-	-4.5700	-	-	-	-	-	-
NpO ₂ F ₂ (aq)	$NpO_2F_2(aq) = NpO_2^{++} + 2F^{-}$	-	-7.6000	-	-	-	-	-	-
NpO ₂ H ₂ PO ₄ ⁺	$NpO_2H_2PO_4^+ = NpO_2^{++} + H^+ + HPO_4^{}$	-	-11.7320	-	-	-	-	-	-
NpO ₂ HPO ₄ ⁻	$NpO_2HPO_4^- = NpO_2^+ + HPO_4^{}$	-	-2.9500	-	-	-	-	-	-
NpO ₂ HPO ₄ (aq)	$NpO_2HPO_4(aq) = NpO_2^{++} + HPO_4^{}$	-	-6.2000	-	-	-	-	-	-
NpO ₂ IO ₃ (aq)	$NpO_2IO_3(aq) = NpO_2^+ + IO_3^-$	-	-0.5000	-	-	-	-	-	-
NpO ₂ IO ₃ ⁺	$NpO_2IO_3^+ = NpO_2^{++} + IO_3^-$	-	-1.2000	-	ı	-	-	ı	-
NpO ₂ OH(aq)	$NpO_2OH(aq) + H^+ = NpO_2^+ + H_2O$	12.3159	11.3072	10.0823	8.9121	7.7057	6.7012	5.8331	5.0502
NpO ₂ OH ⁺	$NpO_2OH^+ + H^+ = NpO_2^{++} + H_2O$	-	5.1000	-	-	-	-	-	-
NpO ₂ SO ₄ -	$NpO_2SO_4^- = NpO_2^+ + SO_4^{}$	- 0.0950	-0.3604	- 0.9237	- 1.6673	- 2.6546	- 3.6824	- 4.7698	- 5.9887
NpO ₂ SO ₄ (aq)	$NpO_2SO_4(aq) = NpO_2^{++} + SO_4^{}$	- 3.0004	-3.2004	- 3.6011	- 4.1338	- 4.8842	- 5.7501	- 6.7969	- 8.1732
Np(SO ₄) ₂ (aq)	$Np(SO_4)_2(aq) = Np^{++++} + 2SO_4^{}$	-10.1808	-10.8937	-12.1427	-13.6900	-15.7423	-17.9799	-20.5442	-23.7254
Np(SCN) ⁺⁺⁺	$Np(SCN)^{+++} = Np^{++++} + SCN^{-}$	-3.1668	-3.0031	-2.9306	-2.9697	-3.1445	-3.4432	-3.8796	-4.5041
Np(SCN)2 ⁺⁺	$Np(SCN)_2^{++} = Np^{++++} + 2SCN^{-}$	-4.3131	-4.1062	-4.0096	-4.0596	-4.3086	-4.7634	-5.4699	-6.5496
Np(SCN) ₃ ⁺	$Np(SCN)_3^+ = Np^{++++} + 3SCN^-$	-5.1615	-4.8091	-4.7234	-4.9336	-5.5376	-6.5209	-7.9941	-10.2561
NpOH ⁺⁺	$NpOH^{++} + H^{+} = Np^{+++} + H_2O$	-	6.8000	-	ı	-	-	ı	-
NpOH ⁺⁺⁺	$NpOH^{+++} + H^{+} = Np^{++++} + H_{2}O$	-	0.2900	-	-	-	-	-	-
NpSO ₄ ⁺⁺	$NpSO_4^{++} = Np^{++++} + SO_4^{}$	- 6.3493	- 6.7719	- 7.3983	- 8.1085	- 9.0072	- 9.9744	- 11.0953	- 12.5171
(PuO ₂) ₂ (OH) ₂ ⁺⁺	$(PuO_2)_2(OH)_2^{++} + 2H^+ = 2PuO_2^{++} + 2H_2O$	-	7.5000	-	-	-	-	-	-
(PuO ₂) ₃ (CO ₃) ₆ ⁽⁻⁶⁾	$(PuO_2)_3(CO_3)_6^{(-6)} + 6H^+ = 3PuO_2^{++} + 6HCO_3^-$	-	11.9600	-	-	-	-	-	-

Table 6-5. Log K EQ3/6 Grid for Neptunium and Plutonium Aqueous Species (Continued)

Data0 Species Designation	Reaction	log K 0.01°C	log K 25°C	log K 60°C	log K 100°C	log K 150°C	log K 200°C	log K 250°C	log K 300°C
(UO ₂) ₂ (PuO ₂)(CO ₃) ₆ ⁽⁻⁶⁾	$(UO_2)_2(PuO_2)(CO_3)_6^{(-6)} + 6H^+ = 2UO_2^{++} + PuO_2^{++} + 6HCO_3^-$	-	9.3821	-	-	-	-	-	-
Pu(SO ₄) ₂ -	$Pu(SO_4)_2^- = Pu^{+++} + 2SO_4^{}$	- 5.4444	- 5.5436	- 5.8876	- 6.4087	- 7.2038	- 8.1883	- 9.4577	- 11.2236
Pu(SO ₄) ₂ (aq)	$Pu(SO_4)_2(aq) = Pu^{++++} + 2SO_4^{}$	-	- 10.9837	-	-	-	-	-	-
PuBr ⁺⁺⁺	PuBr ⁺⁺⁺ = Pu ⁺⁺⁺⁺ + Br ⁻	-	- 1.6000	-	-	-	-	-	-
PuCl ⁺⁺	PuCl ⁺⁺ = Pu ⁺⁺⁺ + Cl ⁻	-	- 1.2000	-	-	-	-	-	-
PuCI ⁺⁺⁺	PuCl ⁺⁺⁺ = Pu ⁺⁺⁺⁺ + Cl ⁻	-	- 1.8000	-	-	-	-	-	-
PuF ⁺⁺⁺	PuF*** = Pu**** + F-	- 8.7046	- 8.8002	- 9.0256	- 9.3367	- 9.7792	- 10.2890	- 10.8962	- 11.6616
PuF ₂ ⁺⁺	$PuF_{2}^{++} = Pu^{++++} + 2F^{-}$	- 15.5043	- 15.6206	- 15.8952	- 16.2842	- 16.8667	- 17.5846	- 18.5039	- 19.7593
PuH ₃ PO ₄ ++++	$PuH_3PO_4^{++++} = Pu^{++++} + HPO_4^{} + 2H^+$	-	- 12.9512	-	-	-	-	-	-
Pul ⁺⁺	PuI ⁺⁺ = Pu ⁺⁺⁺ + I ⁻	-	- 1.1000	-	-	-	-	-	-
PuNO ₃ ⁺⁺⁺	PuNO ₃ ⁺⁺⁺ = Pu ⁺⁺⁺⁺ + NO ₃ ⁻	-	- 1.9500	-	-	-	-	-	-
PuO ₂ (CO ₃) ₂	$PuO_2(CO_3)_2^{} + 2H^+ = PuO_2^{++} + 2HCO_3^-$	6.2444	6.1866	6.1725	6.2329	6.3787	6.5629	6.7540	6.9248
PuO ₂ (CO ₃) ₃	$PuO_2(CO_3)_3^{} + 3H^+ = PuO_2^{+++} + 3HCO_3^-$	13.4332	13.3301	13.2568	13.2671	13.3616	13.4842	13.5686	13.5195
PuO ₂ (CO ₃) ₃ ⁽⁻⁵⁾	$PuO_2(CO_3)_3^{(-5)} + 3H^+ = PuO_2^+ + 3HCO_3^-$	26.4092	26.0048	25.5405	25.1164	24.6992	24.3701	24.1039	23.8841
PuO ₂ (OH) ₂ (aq)	$PuO_2(OH)_2(aq) + 2H^+ = PuO_2^{++} + 2H_2O$	-	13.2000	-	-	-	-	-	-
PuO ₂ (SO ₄) ₂	$PuO_2(SO_4)_2^{} = PuO_2^{++} + 2SO_4^{}$	- 3.6429	- 4.2407	- 5.1565	- 6.1882	- 7.4427	- 8.7078	- 10.0728	- 11.7028
PuO ₂ Cl ⁺	$PuO_2CI^+ = PuO_2^{++} + CI^-$	-	- 0.7000	-	-	-	-	-	-
PuO ₂ Cl ₂ (aq)	$PuO_2Cl_2(aq) = PuO_2^{++} + 2Cl^-$	-	0.6000	-	-	-	-	-	-
PuO ₂ CO ₃ -	$PuO_2CO_3^- + H^+ = PuO_2^+ + HCO_3^-$	-	5.2234	-	-	-	-	-	-
PuO ₂ CO ₃ (aq)	$PuO_2CO_3(aq) + H^+ = PuO_2^{++} + HCO_3^-$	-	- 1.2567	-	-	-	-	-	-
PuO ₂ F ⁺	$PuO_2F^+ = PuO_2^{++} + F^-$	-	- 4.5600	-	-	-	-	-	-
PuO ₂ F ₂ (aq)	$PuO_2F_2(aq) = PuO_2^{++} + 2F^-$	-	- 7.2500	-	-	-	-	-	-
PuO ₂ OH(aq)	$PuO_2OH(aq) + H^+ = PuO_2^+ + H_2O$	-	9.7300	-	_	-	-	-	-
PuO₂OH ⁺	$PuO_2OH^+ + H^+ = PuO_2^{++} + H_2O$	5.9780	5.5073	5.0185	4.6203	4.2718	4.0208	3.8200	3.6358
PuO ₂ SO ₄ (aq)	$PuO_2SO_4(aq) = PuO_2^{++} + SO_4^{}$	- 3.0878	- 3.3003	- 3.6596	- 4.0955	- 4.6821	- 5.3562	- 6.1948	- 7.3529

Table 6-5. Log K EQ3/6 Grid for Neptunium and Plutonium Species (Continued)

		log K							
Data0 Species Designation	Reaction	0.01°C	25°C	60°C	100°C	150°C	200°C	250°C	300°C
PuOH ⁺⁺	$PuOH^{++} + H^{+} = Pu^{+++} + H_{2}O$	-	6.9000	-	-	-	ı	-	-
PuOH ⁺⁺⁺	$PuOH^{+++} + H^{+} = Pu^{++++} + H_{2}O$	1.3638	0.7872	0.1266	- 0.4703	- 1.0585	- 1.5380	- 1.9561	- 2.3367
PuSCN ⁺⁺	PuSCN ⁺⁺ = Pu ⁺⁺⁺ + SCN ⁻	-	- 1.3000	-	ı	-	ı	-	-
PuSO ₄ ⁺	$PuSO_4^+ = Pu^{+++} + SO_4^{}$	- 3.6010	- 3.8318	- 4.2121	- 4.6676	- 5.2743	- 5.9659	- 6.8203	- 7.9921
PuSO ₄ ⁺⁺	PuSO ₄ ⁺⁺ = Pu ⁺⁺⁺⁺ + SO ₄	-	- 6.8119	-	-	-	-	-	-

DTN: MO0302SPATHDYN.001 ([DIRS 161886], Spreadsheets Np_25C_aquSpeRXN.xls, AqueousSpecies_j_TJW_1.xls, Pu_25C_aquSpeRXN.xls, and AqueousSpecies_j_YC_Pu.xls).

NOTE: For information about specific spreadsheets used to generate these calculations, see the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]).

6.2.2 Evaluation and Qualification of Other Species

Based on isocoulombic/isoelectric spreadsheet calculations, the log K grid for EQ3/6 input for secondary (redox) species for actinides was calculated (Table 6-5). The Am data were taken from Silva et al. (1995 [DIRS 102087]) and the Np and Pu data were taken from the OECD/NEA Np and Pu volume (Lemire 2001 [DIRS 159027]). Log K grids were also calculated for titanium hydrolysis species using data taken from Knauss et al. (2001 [DIRS 158998]). The results summarized in Knauss et al. (2001 [DIRS 158998]) for Ti(OH)₃⁺ and Ti(OH)₅⁻ were not all mutually consistent, thus these species were treated as follows. The primary results were log K values for TiO₂ (rutile) solubility (in three pH ranges corresponding to dominance by each of the three aqueous species) at 100°C, 150°C, 200°C, 250°C, and 300°C. Also provided were three-parameter temperature functions for the log Ks and two-parameter or constant enthalpy extrapolations of reaction properties at 298.15K. The authors warned that the three-parameter temperature functions were over-fits (fitting function detail not fully supported by the discrete The approach taken for data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) was to use the grid of log K values for each species, create a solubility reaction that was isocoulombic/isoelectric, and use the Excel Regression Tool to fit the requisite 298.15K reaction properties (Gibbs free energy of reaction, entropy of reaction) to fit that log K grid. The desired species properties at 298.15K were then extracted and used in a normal isocoulombic/isoelectric temperature extrapolation to obtain the needed apparent Gibbs free energy grid for the species. Then, the log K grid (Table 6-6) for the EQ3/6 reaction is obtained as described in Section 6.1.1.

Knauss et al. (2001 [DIRS 158998]) also provided calculation of reference state thermodynamic data at 25°C of several reactions representing the equilibria between Ti-hydroxy complexes and rutile solubility. These values are based on thermodynamic data developed from experimental studies and from other rutile solubility investigations (e.g., Ziemniak et al. 1993 [DIRS 172325]). Stefánsson (2001 [DIRS 159208]) evaluated thermodynamic data for Ti-hydroxy complexes from hydrolysis constants given by Baes and Mesmer (1976 [DIRS 157860]) in combination with thermodynamic properties of rutile given by Robie and Hemingway (1995 [DIRS 153683]) and thermodynamic data for H₂O equivalent to that present in *speq02.dat* (DTN: MO0303SPASPEQ2.000 [DIRS 162278]) or data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). All these data comparisons at reference state for given reactions are given in Table 6-7.

Notice that the differences in the estimates for the log K of reaction $Ti(OH)_3^+ + H_2O = Ti(OH)_4(aq) + H^+$ at 25°C are in good agreement with values obtained using thermodynamic data from other sources (e.g., Ziemniak et al. 1993 [DIRS 172325]); Stefánsson 2001 [DIRS 159208]) establishing confidence in the adopted source Knauss et al. (2001 [DIRS 158998]) through data corroboration. The extrapolation to 298.15K (25°C) for this reaction as described above generates a log K value of -1.2859 (Table 6-6) which is larger than those listed in Table 6-7. The range of estimated Gibbs free energies of formation for these complexes reported by various sources (see discussion by Stefánsson 2001 [DIRS 159208], p. 235) can produce differences in log K values of approximately 0.6 to 1.1 log K units.

Therefore, the extrapolation obtained using the isocoulombic/isoelectric method can be considered within the overall uncertainty bounds of the data. The experimental data of Knauss

et al. (2001 [DIRS 158998]) were produced by workers recognized in the field of experimental geochemistry using laboratory techniques (analytical and experimental) that are considered highly appropriate for the retrieval of accurate solubility data at high temperatures and pressures.

Rutile (TiO₂)thermodynamic data were also updated data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) to be consistent with thermodynamic properties of the Ti aqueous species used in this report. The calculations for the log K grid of the rutile solubility reaction $(TiO_2(s) + 2H_2O = Ti(OH)_4(aq))$ (see Table 6-6) were computed in the Spreadsheet Minerals_j_ERP_rutile.xls (DTN: MO0302SPATHDYN.001 [DIRS 161886]). The thermodynamic properties of this phase are consistent with those reported by Robie and Hemingway (1995 [DIRS 153683], p. 222) and those adopted by Stefánsson (2001 [DIRS 159208], p. 235), therefore qualifying the data for use in the YMP. However, the log K values for same rutile solubility reaction present in data0.ymp.R0 the (DTN: MO0009THRMODYN.001 [DIRS 152576]) are different from those in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). A possible reason for this discrepancy is the thermodynamic property values for Ti(OH)₄(aq) that were adopted in data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]).

Table 6-6. Log K EQ3/6 Grids for Actinide Redox Species and Titanium Species

					Tempera	ture (°C)			
Species	Reaction	0.01	25	60	100	150	200	250	300
Secondary B	asis Species (Redox)								
Am ⁺⁺ a	$Am^{++} + H^{+} + 0.25O_2(g) = Am^{+++} + 0.5H_2O$	66.1230	59.6550	52.1783	45.3165	38.5253	33.1271	28.7110	25.0128
Am ⁺⁺⁺⁺ a	$Am^{+++} + 0.5H_2O = Am^{+++} + H^+ + 0.25O_2(g)$	24.4899	23.4320	22.1496	20.9176	19.6484	18.6122	17.7614	17.0643
AmO ₂ ^{+ a}	$AmO_2^+ + 2H^+ = Am^{+++} + 0.5O_2(g) + H_2O$	18.4277	16.8332	15.0507	13.4700	11.9471	10.7457	9.7386	8.8443
AmO ₂ ^{++ a}	$AmO_2^{++} + H^+ = Am^{+++} + 0.75O_2(g) + 0.5H_2O$	24.7620	23.0358	21.0145	19.1413	17.2626	15.7368	14.4484	13.3263
Np ⁺⁺⁺ b	$Np^{+++} + H_2O + 0.5O_2(g) = NpO_2^+ + 2H^+$	30.2579	27.6311	24.5634	21.7116	18.8682	16.6225	14.8388	13.4272
Np ⁺⁺⁺⁺ b	$Np^{++++} + 1.5H_2O + 0.25O_2(g) = NpO_2^+ + 3H^+$	10.3964	10.5500	10.6102	10.5572	10.4156	10.2690	10.1733	10.1622
NpO ₂ ⁺⁺ b	$NpO_2^{++} + 0.5H_2O = NpO_2^{+} + H^{+} + 0.25O_2(g)$	-1.6314	-1.1851	-0.7603	-0.4470	-0.2064	-0.0606	0.0386	0.1247
Pu ⁺⁺⁺ c	$Pu^{+++} + H_2O + 0.5O_2(g) = PuO_2^+ + 2H^+$	6.8918	6.3912	5.7651	5.1429	4.4937	3.9785	3.5945	3.3384
Pu ⁺⁺⁺⁺ c	$Pu^{++++} + 1.5H_2O + 0.25O_2(g) = PuO_2^+ + 3H^+$	2.3229	3.3087	4.3247	5.1444	5.8616	6.3924	6.8445	7.2858
PuO ₂ ⁺⁺ c	$PuO_2^{++} + 0.5H_2O = PuO_2^{+} + H^{+} + 0.25O_2(g)$	-5.8743	-4.9576	-3.9924	-3.1857	-2.4595	-1.9308	-1.5218	-1.1800
Titanium Spe	ecies								
Ti(OH) ₃ ^{+ d}	$Ti(OH)_3^+ + H_2O = Ti(OH)_4(aq) + H^+$	-1.0332	-1.2859	-1.6528	-2.0061	-2.3452	-2.5995	-2.8028	-2.9964
Ti(OH) ₅ - d	$Ti(OH)_5^- + H^+ = Ti(OH)_4(aq) + H_2O$	14.9337	13.4810	11.8506	10.4623	9.2533	8.4703	8.0123	7.8416
TiO ₂ (s) (rutile) e	$TiO_2(s) + 2H_2O = Ti(OH)_4(aq)$	-7.4295	-7.4282	-7.5034	-7.5904	-7.6674	-7.7149	-7.7510	-7.8065
Molybdenum	Species								
H ₂ MoO ₄ (aq) ^f	$H_2MoO_4(aq) = 2H^+ + MoO_4^{}$	-8.9145	-8.2400	-7.8007	-7.7233	-8.0273	-8.6485	-9.5498	-10.8062
HMoO ₄ - f	$HMoO_4^- = H^+ + MoO_4^{}$	-4.0079	-4.2400	-4.6473	-5.1536	-5.8146	-6.5084	-7.2615	-8.1413

DTN: MO0302SPATHDYN.001 [DIRS 161886].

^a Spreadsheet: BasisSpecies_j_TJW_2_Rev1.xls.

^b Spreadsheet: BasisSpecies_j_TJW_3.xls.

^c Spreadsheet: BasisSpecies_j_TJW_4.xls.

^d Spreadsheet: AqueousSpecies_j_TJW_2.xls.

^e Spreadsheet: Minerals_j_ERP_rutile.xls.

^f Spreadsheet: AqueousReactions_j_TJW_MoW1.xls.

Table 6-7. Thermodynamic Data for Titanium-Hydroxy Species and Associated Reactions

Reaction	ΔG _r ° (25°C) (kJ/mol)	log K (25°C)	Source	
$Ti(OH)_3^+ + H_2O = Ti(OH)_4(aq) + H^+$	10.4	-1.8220	Knauss et al. 2001 [DIRS 158998], Table 5	
$Ti(OH)_3^+ + H_2O = Ti(OH)_4(aq) + H^+$	11.3	-1.9797	Knauss et al. 2001 [DIRS 158998], Table 5; based on data from Vasil'ev et al. (1974 [DIRS 150836])	
$Ti(OH)_3^+ + H_2O = Ti(OH)_4(aq) + H^+$	10.9	-1.9096	Knauss et al. 2001 [DIRS 158998], Table 5; based on data from Ziemniak et al. (1993 [DIRS 172325])	
$Ti(OH)_3^+ + H_2O = Ti(OH)_4(aq) + H^+$	11.421	-2.0010	Calculated with data given in Stefánsson (2001 [DIRS 159208]); Spreadsheet AqueousSpecies_j_TJW_2_CFJC.xls (output DTN: SN0410T0510404.001)	
$Ti(OH)_5^- + H^+ = Ti(OH)_4(aq) + H_2O$	-68.4	11.9832	Knauss et al. 2001 [DIRS 158998], Table 5	
$Ti(OH)_4(aq) + H_2O = Ti(OH)_5^- + H^+$	-70.46	12.3336	Ziemniak et al. 1993 [DIRS 172325]; also in Knauss et al. (2001 [DIRS 158998], Table 5) but for inverted reaction	
$Ti(OH)_5^- + H^+ = Ti(OH)_4(aq) + H_2O$	-70.441	12.3409	Calculated with data given in Stefánsson (2001 [DIRS 159208]); Spreadsheet AqueousSpecies_j_TJW_2_CFJC.xls (output DTN: SN0410T0510404.001)	
$H_2O = H^+ + OH^-$	-	-13.9951	data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576])	
	ΔG _f ° (25°C)			
Species	(kJ/mol)		Source	
Ti(OH) ₃ ⁺	-1086.7	Stefánsson 2	2001 [DIRS 159208], p. 235	
Ti(OH) ₃ ⁺	-1086.21	Ziemniak et	al. 1993 [DIRS 172325], Table V, p. 617	
Ti(OH) ₄ (aq) ^a	-1312.48		2001 [DIRS 159208], Table 3, p. 229	
Ti(OH)₄(aq) ^b	-1309.0		2001 [DIRS 159208], p. 235	
Ti(OH) ₄ (aq)	-1322.7		t AqueousSpecies_j_TJW_2.xls 302SPATHDYN.001 [DIRS 161886])	
Ti(OH) ₅ ^{-a}	-1479.2	Stefánsson 2	2001 [DIRS 159208], p. 235	
Ti(OH)₅⁻	-1482.9		: AqueousSpecies_j_TJW_2.xls 302SPATHDYN.001 [DIRS 161886])	
TiO ₂ (rutile)	-890.7	Robie et al. 1979 [DIRS 107109]; Spreadsheet Minerals_j_ERP_rutile.xls (DTN: MO0302SPATHDYN.001 [DIRS 161886])		
TiO ₂ (rutile)	-888.8	Robie and H	emingway 1995 [DIRS 153683], p. 222	
H ₂ O	-237.181	Spreadsheet AqueousSpecies_j_TJW_2_CFJC.xls (output DTN: SN0410T0510404.001)		
H⁺	0.0		t AqueousSpecies_j_TJW_2_CFJC.xls (output 10T0510404.001)	

Output DTN: SN0410T0510404.001 (Log K values calculated in Spreadsheet AqueousSpecies_j_TJW_2_CFJC.xls).

 $^{^{\}rm a}$ Original data reported in Ziemniak et al. (1993 [DIRS 172325]). For Ti(OH)4(aq), Ziemniak et al. (1993 [DIRS 172325], Table V, p. 617) reports a value of -1312.48 kJ/mol.

^b Calculated from hydrolysis constants given in Baes and Mesmer (1976 [DIRS 157860]), rutile ΔG_f° from Robie and Hemingway (1995 [DIRS 153683]), and ΔG_f° for H₂O equivalent to that in *speq02.dat* (DTN: MO0303SPASPEQ2.000 [DIRS 162278]).

6.3 EVALUATION AND QUALIFICATION OF THERMODYNAMIC DATA FOR SOLID PHASES

6.3.1 Evaluation and Qualification of Thermodynamic Data for Clays

Wolery (1978 [DIRS 151346], pp. 230-251, Appendix A) provided estimates of the thermodynamic data for a number of sheet silicates, including various important clay minerals. These data were intended to supplement the data provided in Helgeson et al. (1978 [DIRS 101596]). In some cases, these estimates were needed to fill out the data sets for sheet silicates treated at least in part in Helgeson et al. (1978 [DIRS 101596]). The missing data in such cases consisted of the Gibbs free energy of formation and the enthalpy of formation, both at 298.15K and 1 bar pressure. In other cases, the minerals were ignored in Helgeson et al. (1978 [DIRS 101596]) and all requisite thermodynamic functions had to be estimated. These minerals were chosen because of their general relevance to geochemical processes or specific relevance to hydrothermal alteration of oceanic crust at mid-ocean ridges, the principal topic addressed by Wolery (1978 [DIRS 151346]).

The following terms and groupings are used to provide some context for the aspects of the data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) development related to clays. There is no intent to provide a formal classification of such minerals, which may exhibit greater breadth than described here. The sheet silicates as are comprised of two main groups, the "micas" (including chlorites and "brittle" micas) and the clays. Both groups include examples of nearly constant stoichiometry (e.g., micas: muscovite; clays: kaolinite) and highly variable composition (e.g., micas: chlorites; clays: smectites). The clays of variable composition consist of two main groups: illites and smectites. These are distinguished for the present purposes by their ion exchange properties. Smectites (and the similar mineral group, the vermiculites) contain a significant proportion of readily exchangeable mono and divalent cations, whereas illites (and the similar mineral group, the celadonites) do not.

The smectites can be further divided into various characteristic groups. Montmorillonites and beidellites can be thought of as derivatives of the stoichiometric clay mineral pyrophyllite ($Al_2Si_4O_{10}(OH)_2$). In pyrophyllite, the aluminum is octahedrally coordinated in a layer sandwiched between layers of tetrahedrally coordinated silicon. An idealized montmorillonite (e.g., $Na_{0.33}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2$) can be obtained by replacing some of the octahedral aluminum with Mg and balancing the missing electrical charge by putting exchangeable cations (here Na^+) in a new, adjacent exchange layer. Changing the exchangeable cation can create other idealized montmorillonites. An idealized beidellite (e.g., $Na_{0.33}Al_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$) is created by bringing in more aluminum and substituting it for some of the tetrahedral silicon. This creates charge imbalance that is countered by the addition of exchangeable cations. Natural smectite compositions usually contain a mix of exchangeable cations, including Na^+ , K^+ , Ca^{++} , and Mg^{++} .

Two other smectite groups are important. The saponites are related to talc $(Mg_3Si_4O_{10}(OH)_2)$ in somewhat the same way that the beidellites are related to pyrophyllite. An idealized saponite $(Na_{0.33}Mg_3Al_{0.33}Si_{3.67}O_{10}(OH)_2)$ is created by substituting aluminum for tetrahedral silicon and balancing the resulting charge by adding exchangeable cation. The nontronites are similar to the beidellites, except that ferric iron replaces the octahedral aluminum. This suggests a parent

mineral of composition $Fe_2Si_4O_{10}(OH)_2$ analogous to pyrophyllite; however, no such phase is known to exist.

Wolery (1978 [DIRS 151346]) estimated thermodynamic data for some chlorite compositions and all illite and smectite compositions of interest. The actual compositions for which data were estimated were in most instances idealized as indicated in the preceding paragraphs. These included beidellites, saponites, and nontronites (montmorillonites as defined here were not addressed). In addition, some actual reported compositions were treated (e.g., "Reykjanes" smectite, "low Fe–Mg" smectite, and "high Fe–Mg" smectite).

Several empirical methods have been proposed to estimate the thermodynamic properties of minerals including sheet silicates. Although a general review of such methods is tempting, this has been eschewed because it is doubtful that any methods would produce inarguably superior results. Nevertheless, some alternative approaches and results therefrom are discussed at the end of this section.

Wolery (1978 [DIRS 151346], Appendix A) estimated the Gibbs free energy of formation (ΔG_f°) at 298.15K and 1 bar pressure using an algorithm proposed in Tardy and Garrels (1974) [DIRS 159209]). This is a linear approach that assumes that the Gibbs free energy of a sheet silicate is the sum of the product of the Gibbs free energies of "silicated" oxide and hydroxide components and the stoichiometric coefficient in the clay. Tardy and Garrels (1974 [DIRS 159209]) analyzed the (Gibbs) free energy of silication (in sheet silicates), defined by them as the difference between the Gibbs energy of a "silicated" oxide component (as determined in their regression) and the Gibbs energy of the corresponding stable oxide phase. They found that the Gibbs energy of silicated SiO₂ was identical to that of quartz. This result was dependent on their usage of data for a sepiolite of composition Mg₂Si₃O₆(OH)₄ in conjunction with data for talc and chrysotile to regress the Gibbs free energies of silicated Mg(OH)₂, MgO, and SiO₂. The present regressions use data from Helgeson et al. (1978) [DIRS 101596]). They included data (p. 124) for a sepiolite composition of "Mg₄Si₆O₁₅(OH)₂·6H₂O." Because of the presence of water of hydration in this formulation, data for this sepiolite could not be used in the regression for data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). Absent the inclusion of sepiolite, the linear system in the regression is nearly singular. Quartz was included in the regression to stabilize it. This can be justified by the zero Gibbs energy of silication found by Tardy and Garrels. Because the Gibbs energies of formation for both chrysotile and talc are identical to the precision presented in both the Tardy and Garrels and Helgeson et al. data sets, this usage of quartz is equivalent to using the Tardy-Garrels sepiolite in the regression.

Insufficient data were available to regress values for any form of silicated Fe₂O₃ for the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]). The Tardy-Garrels analysis yielded a bilinear relationship between the Gibbs energy of silication and the electronegativity of the cation in the silicated oxide components. From this, Tardy and Garrels deduced that silicated Fe₂O₃ should have a Gibbs free energy very close to that of hematite. Hematite was used for the data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) development to fix the Gibbs free energies of both octahedral and tetrahedral silicated Fe₂O₃. Tardy and Garrels did not distinguish between octahedral and tetrahedral Al₂O₃. An attempt to distinguish the latter pair obtained a difference of only 608 cal/mol. In the estimations for

data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), the distinction between octahedral and tetrahedral forms of both Al₂O₃ and Fe₂O₃ was ignored. Nothing in this work addressed the Gibbs energies of silication of SiO₂ and Fe₂O₃ in other kinds of silicates. Silicated Mg(OH)₂ is the only hydroxide component, and any OH in a mineral was first assigned to it. Any remaining OH was assigned to silicated H₂O. The Gibbs free energies of these silicated components were derived from a regression of known Gibbs free energy of formation for relevant (related) minerals (including pyrophyllite, talc, muscovite, phlogopite, and the 7Å and 14Å clinochlores) against their known stoichiometries. Wolery (1978 [DIRS 151346]) took all such data in his regression from Helgeson et al. (1978 [DIRS 101596]) with the aim of maintaining consistency with the associated SUPCRT92 data set.

The regression did not give values for the exchangeable cation oxide components. Such components (e.g., CaO(ex) vs. CaO) are required to deal with readily exchangeable cations from the "exchange" layers of smectites and vermiculites. No data for examples of such phases were available to include in the regressions. The necessary data were extracted (Tardy and Garrels 1974 [DIRS 159209]) from reported exchange equilibrium measurements. The data were initially for reactions exemplified by:

$$CaO(ex) + 2Na^{+} = Na_{2}O(ex) + Ca^{++}$$
 (Eq. 6-17)

They were then adjusted as recommended in Tardy and Garrels (1974 [DIRS 159209]) so that the silicated $K_2O(ex)$ had the same Gibbs free energy as silicated K_2O (Wolery 1978 [DIRS 151346], pp. 236-237).

The method of Tardy and Garrels (1974 [DIRS 159209]) does not directly give values for exchangeable cation oxide components. Such components (e.g., CaO(ex) vs. CaO) are required to deal with readily exchangeable cations from the exchange layers of smectites and vermiculites. The original ΔG_f° for these exchangeable oxide components (Table 6-8) was calculated by Wolery (1978 [DIRS 151346], Table 3b, p. 236). These data were corrected for data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) by calculating $\Delta G_f^{\circ}(K_2O(ex)) - \Delta G_f^{\circ}(K_2O)$ and adding this difference to each of the original ΔG_f° values in Table 4-5 (see Spreadsheet *Clays_TJW_1_Rev1b.xls*, Worksheet *G matrix*; DTN: MO0302SPATHDYN.001 [DIRS 161886]).

	Original	Corrected*
Silicated Component	ΔG_f° (cal/mol)	ΔG _f ° (cal/mol)
CaO(ex)	-180200	-180062.7
H ₂ O(ex)	-56000	-55862.7
K ₂ O(ex)	-185440	-185302.7
Li ₂ O(ex)	-188000	-187862.7
MgO(ex)	-156900	-156762.7
Na ₂ O(ex)	-172800	-172662.7

Table 6-8. ΔG_f° of Silicated Exchangeable Components Used by Wolery

Sources: Column 2: Wolery 1978 [DIRS 151346], Table 3b, p. 236.

Column 3: DTN: MO0302SPATHDYN.001 ([DIRS 161886], the computation of corrected values is given in Spreadsheet *Clays_TJW_1_Rev1b.xls*, Worksheet *G Calc A*).

^{*} See p. 237 and Footnote e of Table 3b to make the Gibbs free energy of formation the same for the K₂O and K₂O(ex) components consistent with the original assumptions of Wolery (1978 [DIRS 151346]).

Wolery (1978 [DIRS 151346], Appendix B) used an analogous method (with more minerals in the regression set) to estimate molar volumes. However, a separate set of silicated exchangeable cation oxide components was not employed. This was equivalent to assuming that the molar volume of a silicated exchangeable oxide component was the same as that of the corresponding "regular" silicated oxide component.

The entropy at 298.15K and 1 bar pressure was obtained using a method described by Helgeson et al. (1978 [DIRS 101596], pp. 43-52). First, a molar volume (V°) was calculated from the silicated oxide components of the clay (e.g., Worksheet V Calc in Spreadsheet $Clays_TJW_1_Rev1b.xls$; DTN: MO0302SPATHDYN.001 [DIRS 161886]). Next, for a reference reaction involving a similar mineral (Eq. 6-18), the changes in the entropy (ΔS_s°) and molar volume (ΔV_s°) were calculated assuming that the entropies and molar volumes for the reaction are zero (e.g., Worksheets Delta Ss Calc and Delta Vs Calc, respectively, in the Spreadsheet $Clays_TJW_1_Rev1b.xls$; DTN: MO0302SPATHDYN.001 [DIRS 161886]). The entropy for the clay (S°) was then calculated by:

$$S^{\circ} = \Delta S_s (\Delta V_S^{\circ} + V^{\circ}) / \Delta V_S^{\circ} - 2 \upsilon_{Fe(III)}$$
 (Eq. 6-18)

where $v_{Fe(III)}$ is the stoichiometric coefficient of ferric iron in the chemical formula for the clay. The heat capacity coefficients were obtained by a simple linear method (Helgeson et al. 1978 [DIRS 101596], pp. 52-66) that used mostly real oxide components. In both the entropy and heat capacity coefficient estimation schemes, a "structural H₂O" component was used in addition to the real oxide components. Helgeson et al. (1978 [DIRS 101596]) also employed a "zeolitic" H₂O component, though this has no relevance to sheet silicates.

The enthalpy of formation at 298.15K and 1 bar pressure (ΔH_f^o) was calculated from the corresponding Gibbs free energy and entropy. First, the entropy of formation (ΔS_f^o) was calculated from the entropy and the entropies of the elements in their standard reference states. Then the following standard thermodynamic relation was applied:

$$\Delta H_f^o = \Delta G_f^o + T \Delta S_f^o$$
 (Eq. 6-19)

The data estimated by Wolery (1978 [DIRS 151346], Appendix A) have long been a staple of EQ3/6 thermodynamic data files. The estimation was revisited for the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) because the SUPCRT92 data for some of the minerals in the original Gibbs free energy regression set had changed over the years, and there was concern that some of the data for other thermodynamic functions might have changed as well. There was also an intent to take better account of mixing effects (e.g., regressing on Gibbs free energies with any mixing effects taken out, then when estimating Gibbs free energies for other minerals, adding any such effects back in at the end of the process). But mixing implemented corrections were not in the reestimation data0.ymp.R2 for (DTN: MO0302SPATHDYN.000 [DIRS 161756]) for several reasons. First, the choice of mixing entities is not always straightforward. Second, such corrections appear to be comparable

or of lesser magnitude than differences due to structural effects. The Gibbs free energy of mixing (assumed ideal in the site mixing sense and that enthalpic mixing terms are negligible) on the *j*-th site is given by:

$$\Delta G_j^{mixing} = n_j RT \sum_i x_i \ln x_i$$
 (Eq. 6-20)

where n_j is the stoichiometric number of the site in the mineral's chemical formula, R is the gas constant, T is the absolute temperature, and x_i is the mole fraction of the i-th entity on the j-th site. Consider the case of muscovite [KAl₂AlSi₃O₁₀(OH)₂] in which an aluminum substitutes for one of what would be four tetrahedral silicons. Assuming that the mixing entities are just Al⁺⁺⁺ and Si⁺⁺⁺⁺ (ignoring vacancies and any potential pairing/ordering effects), the Gibbs free energies of mixing on the tetrahedral site would be:

$$\Delta G_j^{mixing} = 4RT \left[\frac{1}{4} \ln \left(\frac{1}{4} \right) + \frac{3}{4} \ln \left(\frac{3}{4} \right) \right]$$
 (Eq. 6-21)

Taking *R* to be 1.9872 cal/mol-K (Weast and Astle 1979 [DIRS 102865], p. F-108) and *T* to be 298.15K, this Gibbs free energy of mixing evaluates to –1,333 cal/mol (–5,577 joule/mol). In contrast, the difference in Gibbs free energies of 7Å and 14Å clinochlores as given in Helgeson et al. (1978 [DIRS 101596], p. 124) is 4,602 cal/mol (19,255 joule/mol). This illustrates that a subtle structural difference can be more significant than mixing. Furthermore, the magnitude of mixing corrections will be matched or exceeded by the uncertainties in the Gibbs free energies of the minerals used in the regression. Uncertainties in calorimetric determinations of the Gibbs free energies of formation of kaolinite and dickite, for example, are on the order of 4,000 to 7,000 joule/mol (roughly 960 to 1,670 cal/mol) (de Ligny and Navrotsky 1999 [DIRS 158973]; Fialips et al. 2001 [DIRS 158975]). From such considerations, it must be concluded that there is little likelihood of reducing the error in the regression by introducing mixing corrections. (Note that dickite is not included in this version of the database.)

The first step in the reestimation was to prepare a spreadsheet (*Clays_TJW_0_Rev1b.xls*; DTN: MO0302SPATHDYN.001 [DIRS 161886]) to re-create the original calculations. The purpose of this spreadsheet was to confirm the original calculations and to provide a template for the updated calculations; no data from this were carried forward into the database update. This re-creation included the modification by Wolery (1978 [DIRS 151346]) of the Tardy-Garrels method in which the silicated Al₂O₃ component was split into separate octahedral and tetrahedral forms. The values obtained in Wolery (1978 [DIRS 151346], p. 236, Table 3b) for these two components were almost identical: –380.08 kcal/mol for Al₂O_{3tetr}, –380.69 kcal/mol for Al₂O_{3oct}). Another modification from the original Tardy-Garrels method had been the use of quartz and hematite in the regression suite, though these are not sheet silicates. That was justified by arguments given in Tardy and Garrels (1974 [DIRS 159209]) that the Gibbs free energies of silication of these oxides should be negligible (see previous discussion in p. 6-29). The use of quartz in the regression was found in Wolery (1978 [DIRS 151346]) to be necessary to stabilize the regression. In the original Tardy-Garrels work, the inclusion of a sepiolite in the regression had apparently played a stabilizing role. However, Helgeson et al. (1978

[DIRS 101596]) used a sepiolite of a different composition, and Wolery (1978 [DIRS 151346]) reported that this failed to have the necessary stabilizing effect.

Excel's Regression Tool (part of the Analysis Tool Pak) was used for data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) development, to perform multiple linear regression of the known ΔG_f° for a suite of minerals against the stoichiometric coefficients of the component oxides. The fitted parameters were the ΔG_f° for the silicated oxided components. As there was no guarantee that the fitting criteria would be identical to those employed in the original calculations (which were unknown at the start of the work), there was a possibility that the results might differ. However, the re-created Gibbs free energy regression (Worksheet *G matrix 0* in Spreadsheet *Clays_TJW_0_Rev1b.xls*; DTN: MO0302SPATHDYN.001 [DIRS 161886]) exactly duplicated that reported in Wolery (1978 [DIRS 151346], p. 235, Table 3a) to the precision reported in the original work.

The molar volume calculations were done in analogous manner with a larger suite of minerals in the regression set. The original regression (Wolery 1978 [DIRS 151346], p. 247, Table 5a) could not be duplicated (the attempt is documented in Worksheet V matrix 0. Spreadsheet Clays_TJW_0_Rev1b.xls; DTN: MO0302SPATHDYN.001 [DIRS 161886]). The calculated molar volumes for the minerals used in the regression and hence the regression errors were identical in the original work and the attempted re-creation; only the values for the components The standard errors of the component values in the Excel output in Worksheet differed. Clays_TJW_0_Rev1b.xls; Spreadsheet (DTN: MO0302SPATHDYN.001 V matrix 0, [DIRS 161886]) were large and only one of the 11 fitted parameters was significantly different from zero. Therefore, the nature of the problem was that the regression matrix was insufficient to produce a unique set of values for the component volumes. In order to resolve this problem and provide a usable template, it was necessary to modify the original volume calculations.

Three possibilities for extending the suite of minerals in the regression matrix were evaluated in the data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) development. The first involved adding two sheet silicates (antigorite and sepiolite) for which SUPCRT92 data were readily available but which, for unknown reasons, were not used in the original regression. It was found that including these minerals (Spreadsheet Clays_TJW_0_Rev1b.xls, Worksheet V matrix 1; DTN: MO0302SPATHDYN.001 [DIRS 161886]) yielded parameters with reasonably small standard errors, and that were significantly different from zero. These results for the component volumes were notably different from either the original results in Wolery (1978 [DIRS 151346]) or the first attempted re-creation described above. A second attempt (Spreadsheet Clays_TJW_0_Rev1b.xls, Worksheet V matrix 2; DTN: MO0302SPATHDYN.001 [DIRS 161886]) adding instead quartz and hematite (which are not sheet silicates, but which were included in the Gibbs free energy regression) also gave regression parameters significantly different from zero with results for the components that were very close to those obtained by adding antigorite and sepiolite. Consequently, it was decided to do yet another regression (Worksheet V matrix 3, Spreadsheet Clays_TJW_0_Rev1b.xls; DTN: MO0302SPATHDYN.001 [DIRS 161886]) that included all four additional minerals.

The old molar volume regression (Wolery 1978 [DIRS 151346], p. 247, Table 5b) had yielded a large difference in the molar volumes of silicated octahedral and tetrahedral Al₂O₃ components (37.629 cm³/mol for Al₂O_{3tetr}, 4.099 cm³/mol for Al₂O_{3oct}). This result had been used to justify a

proportionally large difference for analogous Fe₂O₃ components (only a value for a "mean" Fe₂O₃ component could be obtained from the regression itself). In the first attempt to re-create the original regression (Worksheet *V matrix 0*, Spreadsheet *Clays_TJW_0_Rev1b.xls*; DTN: MO0302SPATHDYN.001 [DIRS 161886])), an even larger difference between the values for the two Al₂O₃ components was obtained; however, as noted above, the results of this regression in general failed to match those reported by Wolery (1978 [DIRS 151346]). Adding antigorite and sepiolite (Worksheet *V matrix 1*, Spreadsheet *Clays_TJW_0_Rev1b.xls*; DTN: MO0302SPATHDYN.001 [DIRS 161886])) as previously discussed resulted in notably different results. In particular, the values obtained for the two Al₂O₃ components were very close (26.461 ±4.443 cm³/mol for Al₂O_{3tetr}, 25.030 ±2.802 cm³/mol for Al₂O_{3oct}), where the uncertainty is the standard error of the fitted volume. Very similar results were obtained by adding instead quartz and hematite (Worksheet *V matrix 2*) and by using all four additional minerals together (Worksheet *V matrix 3*).

The re-creation of the entropy and heat capacity coefficient calculations proceeded in a more straightforward manner. The entropy calculations (Spreadsheet *Clays_TJW_0_Rev1b.xls*, Worksheets *Delta Ss Calc*, *Delta Vs Calc*, and *S calc*; DTN: MO0302SPATHDYN.001 [DIRS 161886]) were changed somewhat in that the algorithm for obtaining them depended on the corresponding molar volumes. Since the volumes were estimated in many instances, and the values so obtained were not identical to those previously described, somewhat modified results for the corresponding entropies were obtained as well. No such complication was encountered in dealing with the heat capacity coefficients (Spreadsheet *Clays_TJW_0_Rev1b.xls*, Worksheets *Cp a Calc*, *Cp b Calc*, and *Cp c Calc*; DTN: MO0302SPATHDYN.001 [DIRS 161886]).

Instead of using a straightforward summation of the contributions of the components, in many instances a difference calculation (based on a reference reaction involving a similar or related mineral with a known thermodynamic function) was employed for data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) development, in an attempt to reduce relative errors (Helgeson et al. 1978 [DIRS 101596]). Such a reference reaction is exemplified by that for Na-beidellite:

$$Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 0.33 SiO_2 =$$

 $Al_2Si_4O_{10}(OH)_2 + 0.165 Na_2O(ex) + 0.165 Al_2O_3$ (Eq. 6-22)

This reaction emphasizes the role of pyrophyllite as a conceptual "parent" mineral. Such reference reactions were employed to estimate the entropies (linear portion of the algorithm) and the heat capacity coefficients of all minerals for which estimates are made. They were also employed to estimate the Gibbs free energies of the beidellites, the saponites, greenalite, minnesotaite, and all the chlorite minerals for which such estimations were necessary. A few errors were discovered in the original documented set of reference reactions, none of which appeared to have affected the actual calculations. The reference reactions used for data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) are documented on the appropriate worksheets (where these reactions are used) in the spreadsheet.

In general, the re-creation of Wolery's (1978 [DIRS 151346], Appendix A) estimates of the free energy of formation of the clays, in the development of data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), did not produce very different results from

the original ones. The elimination of distinct octahedral and tetrahedral forms of the Al_2O_3 component in the Gibbs free energy had almost no effect, as expected, as the values for those two components were nearly identical. The approach used for volume estimation produced more significant changes (the elimination of distinct octahedral and tetrahedral forms of the Al_2O_3 and Fe_2O_3 components, and significant changes to the regressed values for the volumes of the components). However, the molar volume estimates for various minerals were not significantly impacted as indicated in Table 6-9. Changes for the beidellites, illite, and high Fe-Mg smectite were basically insignificant. Changes for saponites were larger but still small. Only the changes for the nontronites were potentially significant. These changes were associated with the removal of distinct octahedral and tetrahedral Fe_2O_3 components. In the original estimates, there was a large difference between the values for the nontronite minerals.

Table 6-9. Estimated Molar Volumes (cm³/mol) for the Minerals of Interest: Modified Re-Creation Versus Original Calculations

Mineral	Original	Modified Re-Creation: Worksheet V Calc	Change
Na-beidellite	130.54	130.73	0.19
Ca-beidellite	129.53	129.77	0.24
K-beidellite	133.70	134.15	0.45
Mg-beidellite	128.19	128.73	0.54
Na-saponite	136.69	135.32	-1.37
Ca-saponite	135.68	134.36	-1.32
Na-nontronite	132.11	136.81	4.70
Ca-nontronite	131.10	135.85	4.75
Illite	138.94	139.35	0.41
High Fe-Mg smectite	139.07	139.51	0.44

Sources: Column 2: Wolery 1978 [DIRS 151346], p. 231, Table 1.

Column 3: DTN: MO0302SPATHDYN.001 ([DIRS 161886], Spreadsheet

Clays_TJW_1_Rev1b.xls, Worksheet V Calc).

Because the entropy estimation algorithm depends on molar volumes, the changes in estimated volumes for some minerals caused a corresponding change in the estimated entropies. However, as the volume changes were small, so were the entropy changes. For comparison, however, some cases are shown in Table 6-10. Only the changes for the nontronites were significant, but they are still relatively small. To give some perspective, the effect of a 1 cal/mol-K change on the entropy changes the apparent molal Gibbs free energy at 300°C by only 275 cal/mol (1,151 joule/mol), which in turn would change a log K value by 0.241 unit. At 200°C those changes would be 175 cal/mol (732 joule/mol) in the Gibbs free energy and 0.186 in the log K value. For minerals with large chemical formulas such as these, such changes are relatively small. They are overwhelmed by larger uncertainties in experimental determinations (solubility or calorimetric).

Table 6-10. Estimated Standard Entropies (cal/mol-K) for the Minerals of Interest: Modified Re-Creation Versus Original Calculations

Mineral	Original	Modified Re-Creation	Change
Na-beidellite	59.62	59.664	0.04
Ca-beidellite	58.30	58.353	0.05
Na-saponite	63.95	63.631	-0.32
Ca-saponite	62.64	62.336	-0.30
Na-nontronite	67.64	68.860	1.20
Ca-nontronite	66.35	67.557	1.21
Illite	63.59	63.688	0.10
High Fe-Mg smectite	68.30	68.408	0.11

Sources: Column 2: Wolery 1978 [DIRS 151346], p. 231, Table 1.

Column 3: DTN: MO0302SPATHDYN.001 ([DIRS 161886], Spreadsheet Clays TJW_1_Rev1b.xls, Worksheet S Calc).

Wolery (1978 [DIRS 151346]) had noted that the estimated Gibbs free energies for 7Å and 14Å ripidolites were greater than the corresponding physical mixtures of clinochlores and daphnites, a condition that seemed unreasonable. He adjusted the Gibbs free energies of the ripidolites to the physical mixture values and then applied a correction for the ideal Gibbs free energy of mixing. In the re-creation, the situation was identical, and the same strategy was employed. However, the mixing correction applied by Wolery (1978 [DIRS 151346]) did not account for a site stoichiometry factor of five. This was accounted for in the re-creation, resulting in a mixing correction with a magnitude larger by this factor.

The entropies of the ripidolites were treated in a similar manner to ensure that the Gibbs free energy of mixing relation given previously holds at all temperatures, another consideration not included in Wolery (1978 [DIRS 151346]). The appropriate mixing correction is given by:

$$\Delta S_j^{mixing} = -n_j R \sum_i x_i \ln x_i$$
 (Eq. 6-23)

For a ripidolite (formed by mixing 3/5 clinochlore and 2/5 daphnite), this correction is 6.687 cal/mol-K. At 300°C, the entropy correction results in a change of -1,839 cal/mol in the apparent molar Gibbs free energy of a ripidolite. This is close to the Gibbs free energy of mixing at 25°C (-1,994 cal/mol). From another perspective, the entropy correction would decrease the log K by 1.615 units at 300°C, and by 1.245 unit at 200°C.

In theory, the molar volumes and heat capacity coefficients are unaffected by mixing corrections. Thus, there are no issues to resolve here with regard to those properties.

The results of the modified "re-creation" of the calculations in Wolery (1978 [DIRS 151346]) are summarized on the Worksheet *Results Summary* of the Spreadsheet *Clays_TJW_0_Rev1b.xls* (DTN: MO0302SPATHDYN.001 [DIRS 161886]). As has been discussed, the re-created molar volume regression does not match the original reported one, and is thereby improved. Furthermore, distinctions among octahedral vs. tetrahedral silicated oxide components (Al₂O₃ in the Gibbs free energy regression, Al₂O₃ and Fe₂O₃ in the molar volume regression) were found

to be statistically unsupported and were removed from the final regressions. This resulted in no sensible change in the Gibbs free energy method, as the Gibbs free energies for the two distinct Al₂O₃ components in the original method were virtually identical. Despite the reevaluation of the molar volume regression, the estimated values in most cases matched quite well with those reported in the original work. The principal exception concerned the nontronite clays, which exhibited molar volumes larger by roughly 3–4 percent. Although the changes in estimated molar volumes were carried through to those in the corresponding entropy estimates, the differences were increasingly insignificant. It was found that some of the reference reactions documented in Wolery (1978 [DIRS 151346]) were in error; however, it appeared that these errors were only in the documentation, not the actual calculations. In making some final adjustments for ripidolite chlorites, it was discovered that the entropy of mixing correction should have been larger than in the work in Wolery (1978 [DIRS 151346]) to accommodate a non-unit site stoichiometric factor. Also, the entropy itself should have received a mixing correction.

The "re-creation" of the calculations in Wolery (1978 [DIRS 151346]) in Spreadsheet Clays_TJW_0_Rev1b.xls, DTN: MO0302SPATHDYN.001 [DIRS 161886]) was then used as the basis for a second set of calculations. These are given in Spreadsheet Clays_TJW_1_Rev1b.xls, in DTN: MO0302SPATHDYN.001 [DIRS 161886]). Here the effects of updates to the SUPCRT92 data used in the regressions were taken into account. This second spreadsheet does not contain the extra worksheets with alternate regressions for the Gibbs free energies and molar volumes, as in the first spreadsheet. Thus, there is only a G matrix worksheet corresponding to the G matrix 1 worksheet in the first spreadsheet, and a V matrix corresponding to the V matrix 4. There is again a similar regression on enthalpies on an H matrix worksheet, but again this was not used to make any actual enthalpy estimates.

The final "reestimation" calculations conducted for data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) differed from the "re-creation" calculations described above, in that a few of the thermodynamic data used to calibrate the method were changed from those originally reported in Helgeson et al. (1978 [DIRS 101596]). included the Gibbs free energy, enthalpy, and entropy for quartz and the Gibbs free energy and enthalpy for margarite. These changes were the only ones found by comparing the data from the SUPCRT92 data speq02.dat (DTN: MO0303SPASPEQ2.000 [DIRS 162278]) with the data given in Helgeson et al. (1978 [DIRS 101596], pp. 120-125, Table 8). The changes for quartz are discussed elsewhere in this report and are related to the change to the Rimstidt paradigm in which quartz is more soluble at low temperature than in the Walther and Helgeson (1977 [DIRS 133240]) method adopted in Helgeson et al. (1978 [DIRS 101596]). (Note: this increase in solubility is due more to changes in the stability of SiO₂(aq) than of quartz itself.) The changes for margarite were part of an overall correction for calcium-bearing minerals that was required in response to a change in aqueous species properties in SUPCRT92 that occurred several years after the publication of Helgeson et al. (1978 [DIRS 101596]). This change in the Gibbs free energy of margarite resulted in changes in the log K grid for margarite (Table 6-11). More details on the Ca correction for Ca-bearing silicated are provided in Section 6.1.6.

Table 6-11. Comparison of Log K Grid for Margarite Between Original ΔG_f° and the Recalculated ΔG_f° Value

				Temperature (°C)						
	∆G _f ° (cal/mol)	Source	0.01	25	60	100	150	200	250	300
Original	-1394370	Helgeson et al. 1978 [DIRS 101596], Table 8, p. 124	46.7189	38.6793	29.1917	20.4123	11.6081	4.3707	-1.9478	-7.8367
Recalculated	-1394150	Recalculated	46.895	38.840	29.336	20.541	11.722	4.472	-1.856	-7.753
Difference			-0.176	-0.161	-0.144	-0.129	-0.114	-0.101	-0.092	-0.084

DTN: MO0302SPATHDYN.001 ([DIRS 161886], Recalculated log K values in SUPCRT92 output file *supmins2.out*).

Using these new data, the ΔG_f° values for the silicated oxide components were recalculated in the Excel worksheet G matrix in $Clays_TJW_1_Rev1b.xls$ (DTN: MO0302SPATHDYN.001 [DIRS 161886]). These ΔG_f° values were similar to those originally calculated by Tardy and Garrels (1974 [DIRS 159209]) with the largest difference (4124.4 cal/mol) being between the Na₂O values (see Table 6-12). The ΔV_f° of the silicated oxide components were recalculated in the Excel worksheet V matrix in $Clays_TJW_1_Rev1b.xls$ (DTN: MO0302SPATHDYN.001 [DIRS 161886]). The calculated values (Table 6-13) were all significantly greater than zero as indicated by the very small probability values.

Table 6-12. Calculated ΔG_f° Values for the Silicated Oxide Components that Are Used to Calculate the ΔG_f° of the Clay Phases

Oxide	Calculated Silicated ∆G _f ° (cal/mol)	Reported Silicated ∆G _f ° (cal/mol)	Difference (cal/mol)
Al_2O_3	-380339.5	-382400	2060.5
CaO	-166129.9	-	-
Fe ₂ O ₃	-178155.0	-177700	-455.0
FeO	-64098.1	-64100	1.9
H ₂ O	-57942.1	-59200	1257.9
K ₂ O	-185302.7	-188000	2697.3
Mg(OH) ₂	-204224.2	-203300	-924.2
MgO	-148071.6	-149200	1128.4
Na ₂ O	-166924.4	-162800	-4124.4
SiO ₂	-204699.4	-204600	-99.4

Sources: Column 2: DTN: MO0302SPATHDYN.001 ([DIRS 161886], Spreadsheet Clays_TJW_1_Rev1b.xls, Worksheet G matrix).

Column 3: Tardy and Garrels 1974 [DIRS 159209], Table 2, p. 1105.

Table 6-13. Calculated ΔV_f° Values for the Silicated Oxide Components that Will Be Used to Calculate the ΔG_f° of the Clavs

Oxide	Calculated Silicated ∆V° (cm³/mol)
Al ₂ O ₃	25.483
CaO	19.228
Fe ₂ O ₃	31.567
FeO	13.677
H ₂ O	14.056
K ₂ O	45.809
Mg(OH) ₂	26.975
MgO	8.578
Na ₂ O	25.050
SiO ₂	22.575

DTN: MO0302SPATHDYN.001 ([DIRS 161886], Spreadsheet Clays_TJW_1_Rev1b.xls, Worksheet

The changes in the affected quartz properties, in the development of data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), were quite small. Also, the inclusion of margarite in the regression basically served only to constrain the Gibbs free energy of a non-exchangeable CaO component that was not actually used in any of the further estimations. The effect of these changes with respect to the "re-creation" calculations was therefore virtually negligible with regard to Gibbs free energies of formation and associated thermodynamic properties. Changes in the Gibbs free energy are shown for representative cases in Table 6-14. These are on the order of several calories at most, far less than any associated uncertainties. However, in moving to the Rimstidt paradigm, the significant changes to the thermodynamic properties of SiO₂(aq) introduced more significant changes to the log K values for the associated reactions. Comparison of final calculated values with corresponding values from data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]) (Table 6-15) show a typical change of about one log K unit.

Table 6-14. Estimated Gibbs Free Energies of Formation (cal/mol) for the Minerals of Interest: Original Wolery Estimates, "Re-Creation" Estimates, and Final "Reestimation" Estimates

Mineral	Original: Wolery 1978 [DIRS 151346], Table 1, p. 231	"Re-Creation"	Final "Reestimation"
Na-beidellite	-1279688	-1279691.9	-1279691.6
Ca-beidellite	-1280909	-1280912.9	-1280912.6
K-beidellite	-1281773	-1281777.5	-1281777.2
Mg-beidellite	-1277064	-1277068.4	-1277068.1
Na-saponite	-1343879	-1343882.9	-1343882.6
Ca-saponite	-1345100	-1345103.9	-1345103.6
Na-nontronite	-1078271	-1078585.1	-1078589.5
Ca-nontronite	-1079492	-1079806.1	-1079810.5
Illite	-1303971	-1303939.6	-1303942.0
High Fe-Mg smectite	-1262121	-1262121.7	-1262124. 8

DTN: MO0302SPATHDYN.001 ([DIRS 161886]; Column 3 is from Spreadsheet Clays_TJW_0_Rev1b.xls; Column 4 is from Spreadsheet Clays_TJW_1_Rev1b.xls).

Table 6-15. Estimated Log K Values at 25° C for Dissolution Reactions of Some Minerals: Values from Data0.ymp.R0 Versus Revised Values for Data0.ymp.R2 Based on the Current Final "Reestimation" of Gibbs Free Energies in Conjunction with the Rimstidt Paradigm for $SiO_2(aq)$ Properties

Mineral	Old: Data0.ymp.R0	New: Data0.ymp.R2
Na-beidellite	4.0521	4.9911
Ca-beidellite	3.9962	4.9352
K-beidellite	3.7136	4.6522
Mg-beidellite	3.9585	4.8971
Na-saponite	26.1200	27.0591
Ca-saponite	26.0641	27.0032
Na-nontronite	-11.7523	-11.0442
Ca-nontronite	-11.8082	-11.1001
Illite	7.4514	8.3706
High Fe-Mg smectite	16.5642	17.4595

Sources: Column 2: DTN: MO0009THRMODYN.001 [DIRS 152576]. Column 3: DTN: MO0302SPATHDYN.001 [DIRS 161886].

In making these estimations, some additional minerals were added to data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). A set of idealized montmorillonites was added to complement the other groups of idealized smectites (beidellites, saponites, and nontronites). The montmorillonites had been included on some earlier EQ3/6 data files, but owing to uncertainty over the origin of the corresponding data, they were excluded from data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]). Two additional minerals from the celadonite group were also added, ferroceladonite ($K_2Fe^{++}_2Fe^{+++}_2Si_8O_{20}(OH)_4$) and ferroaluminoceladonite ($K_2Fe^{++}_2Al_2Si_8O_{20}(OH)_4$). These minerals were recently described by Li et al. (1997 [DIRS 159034]). The authors described the archetypal celadonite by the formula $K_2Mg_2Al_2Si_8O_{20}(OH)_4$.

The "reestimated" thermodynamic properties (ΔG_f° , S° , ΔV_f° , and the heat capacity coefficients "a," "b," and "c") were summarized in the Worksheet Results Summary of the Spreadsheet Clays_TJW_1_Rev1b.xls (DTN: MO0302SPATHDYN.001 [DIRS 161886]), and are presented in Table 6-16. The "reestimated" ΔG_f° for several additional clay minerals are shown in Table 6-17. The requisite entropies and heat capacity coefficients for these clays are those in the SUPCRT92 database are from Helgeson et al. (1978 [DIRS 101596]) and were included in the qualified slop98.dat database (DTN: MO0106MWDTDG01.035 [DIRS 161791]). thermodynamic data were used in the Spreadsheet *Minerals_cal_sea_clays1a.xls* (DTN: MO0302SPATHDYN.001 [DIRS 161886]) to calculate the log K for each reaction for the EO3/6 temperature grid from 0.01 up to 300°C. These results are summarized in Table 6-18.

Table 6-16. Summary of "Reestimated" Thermodynamic Properties of Clay Minerals

					Heat Capacity Coefficients*		
		ΔG_f°	S°	V°	а	b x 10 ³	c x 10 ⁻⁵
Phase	Formula	(cal/mol)	(cal/mol-K)	(cm³/mol)	(cal/mol-K)	(cal/mol-K ²)	(cal-K/mol)
14A-Ripidolite	$Mg_3Fe_2Al_2Si_3O_{10}(OH)_8$	-1798613.01	130.407	209.634	170.38	42.76	36.01
7A-Ripidolite	$Mg_3Fe_2Al_2Si_3O_{10}(OH)_8$	-1794011.01	126.147	215.380	166.7	51.28	39.42
Ca-Beidellite	Ca _{0.165} Al _{2.33} Si _{3.67} O ₁₀ (OH) ₂	-1280912.557	58.345	129.766	82.1908	37.1515	18.0311
Ca-Montmorillonite	Ca _{0.165} Mg _{0.33} Al _{1.67} Si ₄ O ₁₀ (OH) ₂	-1272306.883	59.845	133.070	80.1811	39.5011	16.6451
Ca-Nontronite	Ca _{0.165} Fe ₂ Al _{0.33} Si _{3.67} O ₁₀ (OH) ₂	-1079810.475	67.549	135.850	78.1908	52.9315	13.2011
Ca-Saponite	Ca _{0.165} Mg ₃ Al _{0.33} Si _{3.67} O ₁₀ (OH) ₂	-1345103.557	62.328	134.359	85.2388	39.5475	14.0891
Ferroaluminoceladonite	KFeAlSi ₄ O ₁₀ (OH) ₂	-1223659.186	76.901	153.678	87.062	44.199	14.282
Ferroceladonite	KFeFeSi ₄ O ₁₀ (OH) ₂	-1122566.912	81.552	156.720	85.062	52.089	11.867
H-Beidellite	H _{0.33} Al _{2.33} Si _{3.67} O ₁₀ (OH) ₂	-1260419.557	58.286	128.913	81.4384	38.3329	17.7737
High Fe-Mg Smectite	$Na_{0.1}K_{0.2}Ca_{0.025}(Mg_{1.15}Fe^{+++}_{0.2}Fe^{++}_{0.5}Al_{0.75})$ $(Al_{0.5}Si_{3.5})O_{10}(OH)_2$	-1262124.787	68.395	139.510	86.6845	40.089	15.493
H-Montmorillonite	H _{0.33} Mg _{0.33} Al _{1.67} Si ₄ O ₁₀ (OH) ₂	-1251813.883	59.786	132.216	79.4287	40.6825	16.3877
H-Nontronite	H _{0.33} Fe ₂ Al _{0.33} Si _{3.67} O ₁₀ (OH) ₂	-1059317.475	67.482	134.996	77.4384	54.1129	12.9437
H-Saponite	H _{0.33} Mg ₃ Al _{0.33} Si _{3.67} O ₁₀ (OH) ₂	-1324610.557	62.263	133.506	84.4864	40.7289	13.8317
Illite	K _{0.6} Mg _{0.25} Al _{2.3} Si _{3.5} O ₁₀ (OH) ₂	-1303942.016	63.676	139.346	86.0435	38.567	17.823
K-Beidellite	K _{0.33} Al _{2.33} Si _{3.67} O ₁₀ (OH) ₂	-1281777.157	60.608	134.152	83.3194	38.40055	17.9189
K-Montmorillonite	K _{0.33} Mg _{0.33} Al _{1.67} Si ₄ O ₁₀ (OH) ₂	-1273171.483	62.108	137.455	81.3097	40.75015	16.5329
K-Nontronite	K _{0.33} Fe ₂ Al _{0.33} Si _{3.67} O ₁₀ (OH) ₂	-1080675.075	69.821	140.235	79.3194	54.18055	13.0889
K-Saponite	K _{0.33} Mg ₃ Al _{0.33} Si _{3.67} O ₁₀ (OH) ₂	-1345968.157	64.585	138.745	86.3674	40.79655	13.9769
Low Fe-Mg Smectite	$Na_{0.15}K_{0.2}Ca_{0.02}(Mg_{0.9}Fe^{+++}_{0.16}Fe^{++}_{0.29}AI)$ $(AI_{0.25}Si_{3.75})O_{10}(OH)_2$	-1262853.251	66.515	139.602	84.3274	41.01415	15.63395
Mg-Beidellite	Mg _{0.165} Al _{2.33} Si _{3.67} O ₁₀ (OH) ₂	-1277068.057	57.809	128.725	81.94495	37.2604	18.0179
Mg-Montmorillonite	Mg _{0.495} Al _{1.67} Si ₄ O ₁₀ (OH) ₂	-1268462.383	59.309	132.029	79.93525	39.61	16.6319
Mg-Nontronite	Mg _{0.165} Fe ₂ Al _{0.33} Si _{3.67} O ₁₀ (OH) ₂	-1075965.975	67.010	134.809	77.94495	53.0404	13.1879
Mg-Saponite	Mg _{3.165} Al _{0.33} Si _{3.67} O ₁₀ (OH) ₂	-1341259.057	61.629	132.602	84.99295	39.6564	14.0759
Na-Beidellite	Na _{0.33} Al _{2.33} Si _{3.67} O ₁₀ (OH) ₂	-1279691.557	59.656	130.727	83.2765	37.78015	18.25055

Table 6-16. Summary of "Reestimated" Thermodynamic Properties of Clay Minerals (Continued)

					Heat Capacity Coefficients*			
		ΔG_f°	S°	V°	а	b x 10 ³	c x 10 ⁻⁵	
Name	Formula	(cal/mol)	(cal/mol-K)	(cm³/mol)	(cal/mol-K)	(cal/mol-K ²)	(cal-K/mol)	
Na-Montmorillonite	Na _{0.33} Mg _{0.33} Al _{1.67} Si ₄ O ₁₀ (OH) ₂	-1271085.883	61.157	134.030	81.2668	40.12975	16.86455	
Na-Nontronite	Na _{0.33} Fe ₂ Al _{0.33} Si _{3.67} O ₁₀ (OH) ₂	-1078589.475	68.852	136.810	79.2765	53.56015	13.42055	
Na-Saponite	Na _{0.33} Mg ₃ Al _{0.33} Si _{3.67} O ₁₀ (OH) ₂	-1343882.557	63.623	135.320	86.3245	40.17615	14.30855	
Reykjanes Smectite	$\begin{array}{c} Na_{0.33}K_{0.03}Ca_{0.66}(Mg_{1.29}Fe^{+++}_{0.35}Fe^{++}_{0.33}Mn_{0.01}\\ Al_{0.28})(Al_{0.83}Si_{3.17})O_{10}(OH)_2 \end{array}$	-1310547.875	71.115	142.853	90.2311	39.0046	15.6183	

DTN: MO0302SPATHDYN.001 ([DIRS 161886], Spreadsheet Clays_TJW_1_Rev1b.xls, Worksheet Results Summary).

^{*} Coefficients defined in Eq. 4-1.

Table 6-17. △G_f° Data for Additional Clay Minerals

Phase	Formula	ΔG _f ° (cal/mol)
14A-Amesite	$Mg_4AI_4Si_2O_{10}(OH)_8$	-1991568.2
14A-Daphnite	$Fe_5Al_2Si_3O_{10}(OH)_8$	-1548993.7
7A-Amesite	$Mg_2Al_2SiO_5(OH)_4$	-991182.1
7A-Chamosite	Fe ₂ Al ₂ SiO ₅ (OH) ₄	-826814.2
7A-Cronstedtite	Fe ₂ Fe ₂ SiO ₅ (OH) ₄	-624629.6
7A-Daphnite	$Fe_5Al_2Si_3O_{10}(OH)_8$	-1544391.7
Celadonite	KMgAlSi ₄ O ₁₀ (OH) ₂	-1305843.2
Greenalite	$Fe_3Si_2O_5(OH)_4$	-716529.6
Minnesotaite	Fe ₃ Si ₄ O ₁₀ (OH) ₂	-1070057.2

DTN: MO0302SPATHDYN.001 ([DIRS 161886], Spreadsheet Clays_TJW_1_Rev1b.xls, Worksheet Results Summary).

NOTE: The requisite entropies and heat capacity coefficients in the SUPCRT92 database speq02.dat (DTN: MO0303SPASPEQ2.000 [DIRS 162278]) are from Helgeson et al. (1978 [DIRS 101596]) and were included in the qualified slop98.dat database (DTN: MO0106MWDTDG01.035 [DIRS 161791]).

Some additional comments are appropriate concerning the accuracy of the estimated values presented here. These are primarily directed toward values for Gibbs free energy and molar volume, for which regressions were made. The Excel regression tool computes standard errors for regressed parameters. It might be tempting to use these to estimate uncertainties in estimated properties for minerals outside the regression set. However, these standard errors tend to be strongly correlated, so using them in this way would tend to overestimate uncertainties. That was clearly shown in the attempt to re-create the original molar volume regression discussed above.

The regression errors themselves largely underestimate the likely uncertainties in estimated parameter values for minerals outside the regression set. The number of minerals used in the regressions is not large compared to the number of regression components. Thus in the Gibbs free energy regression, the regression error in the case of margarite is zero. That is because only margarite contains the CaO component. Clearly, the uncertainty in the Gibbs free energy of margarite itself is not zero.

A minimum measure of uncertainty in estimated Gibbs free energies is suggested by the general level of uncertainty in experimental determinations. This would be best represented by the uncertainty in calorimetric measurements as this avoids problems of error correlation associated with phase equilibrium or solubility measurements. It was mentioned earlier that such uncertainties for the Gibbs free energies of formation of kaolinite and dickite are roughly 960 to 1,670 cal/mol (de Ligny and Navrotsky 1999 [DIRS 158973]; Fialips et al. 2001 [DIRS 158975]). To extrapolate such results, it is necessary to use some kind of normalization to account for the size of the molecular formula. For sheet silicates, a reasonable normalizing factor is the number of cations (Si⁺⁺⁺⁺, Al⁺⁺⁺⁺) in the tetrahedral layers. For kaolinite and dickite that factor would be 2. So a minimal uncertainty for sheet silicates is in the range of 500 to 800 cal/mol per tetrahedral cation. The number of tetrahedral cations for most of the compositions for which Gibbs free energies were estimated is four. The minimum uncertainty in such a "typical" case is about 2,000 to 3,200 cal/mol.

Table 6-18. Log K Matrix for Clay Minerals

		Temperature (°C)							
Mineral	Reaction	0.01	25	60	100	150	200	250	300
Celadonite	Celadonite + $6H^+$ = $K^+ + AI^{+++} + 4H_2O + Mg^{++} + 4SiO_2(aq)$	9.3867	7.8372	5.7794	3.8829	2.0909	0.7097	-0.4913	-1.7540
7A-Chamosite	7A-Chamosite + $10H^{+}$ = $2AI^{+++}$ + $7H_{2}O$ + $2Fe^{++}$ + $SiO_{2}(aq)$	38.3852	32.6174	25.8845	19.7095	13.5709	8.5699	4.2401	0.2323
7A-Cronstedtite	7A-Cronstedtite + $10H^{+}$ = $2Fe^{+++} + 7H_{2}O + 2Fe^{++} + SiO_{2}(aq)$	21.4814	17.3756	12.5812	8.2074	3.8785	0.3407	-2.7751	-5.7609
7A-Amesite	7A-Amesite + $10H^{+}$ = $2AI^{+++} + 7H_{2}O + 2Mg^{++} + SiO_{2}(aq)$	45.5694	39.1427	31.6777	24.8682	18.1455	12.7178	8.0675	3.8149
14A-Amesite	14A-Amesite + 20H ⁺ = 4AI ⁺⁺⁺ + 14H ₂ O + 4Mg ⁺⁺ + 2SiO ₂ (aq)	83.8687	71.5387	57.1989	44.1066	31.1666	20.6994	11.7058	3.4494
H-Beidellite	H-Beidellite + $6.99H^+$ = $2.33AI^{+++}$ + $4.66H_2O$ + $3.67SiO_2(aq)$	6.5291	3.9773	0.6217	-2.6329	-5.9722	-8.7737	-11.3044	-13.8242
Na-Beidellite	Na-Beidellite + $7.32H^{+}$ = $0.33Na^{+} + 2.33Al^{+++} + 4.66H_{2}O + 3.67SiO_{2}(aq)$	7.5710	4.9911	1.6049	-1.6729	-5.0287	-7.8389	-10.3752	-12.9025
K-Beidellite	K-Beidellite + $7.32H^+$ = $0.33K^+ + 2.33AI^{+++} + 4.66H_2O + 3.67SiO_2(aq)$	7.1513	4.6522	1.3538	-1.8507	-5.1429	-7.9101	-10.4166	-12.9220
Ca-Beidellite	Ca-Beidellite + $7.32H^{+}$ = 0.165 Ca ⁺⁺ + 2.33Al ⁺⁺⁺ + 4.66H ₂ O + 3.67SiO ₂ (aq)	7.6185	4.9352	1.4241	-1.9769	-5.4668	-8.3955	-11.0397	-13.6677
Mg-Beidellite	Mg-Beidellite + $7.32H^{+}$ = 0.165 Mg ⁺⁺ + $2.33AI^{+++}$ + $4.66H_{2}O$ + $3.67SiO_{2}(aq)$	7.6307	4.8971	1.3296	-2.1202	-5.6543	-8.6151	-11.2835	-13.9303
7A-Daphnite	7A-Daphnite + $16H^{+}$ = $2AI^{+++}$ + $12H_{2}O$ + $5Fe^{++}$ + $3SiO_{2}(aq)$	63.6316	55.0117	44.8770	35.6047	26.4563	19.0674	12.6966	6.7515
14A-Daphnite	14A-Daphnite + $16H^{+}$ = $2AI^{+++}$ + $12H_{2}O$ + $5Fe^{++}$ + $3SiO_{2}(aq)$	60.0171	51.6383	41.7694	32.7295	23.8005	16.5785	10.3389	4.4998
Ferroalumino- celadonite	Ferroaluminoceladonite + $6H^+$ = $K^+ + AI^{+++} + 4H_2O + Fe^{++} + 4SiO_2(aq)$	5.6657	4.5745	2.9253	1.2797	-0.3933	-1.7825	-3.0649	-4.4541
Ferroceladonite	Ferroceladonite + $6H^+$ = K^+ + Fe^{+++} + $4H_2O$ + Fe^{++} + $4SiO_2(aq)$	-2.7737	-3.0464	-3.7219	-4.4443	-5.1715	-5.7824	-6.4098	-7.2406

Table 6-18. Log K Matrix for Clay Minerals (Continued)

		Temperature (°C)								
Mineral	Reaction	0.01	25	60	100	150	200	250	300	
Greenalite	Greenalite + $6H^+$ = $5H_2O + 3Fe^{++} + 2SiO_2(aq)$	26.0534	23.1624	19.7179	16.5850	13.5453	11.1388	9.0868	7.1439	
Illite	Illite + $8H^+$ = 2.3Al ⁺⁺⁺ + 0.25Mg ⁺⁺ + $5H_2O$ + 0.6 K ⁺ +3.5SiO ₂ (aq)	11.1913	8.3706	4.7199	1.2042	-2.3885	-5.3930	-8.0973	-10.7757	
Minnesotaite	Minnesotaite + $6H^+$ = $4H_2O + 3Fe^{++} + 4SiO_2(aq)$	17.1553	15.0002	12.2222	9.6380	7.1347	5.1629	3.4582	1.7440	
H-Montmo- rillonite	H-Montmorillonite + $5.67H^{+}$ = 0.33 Mg ⁺⁺ + $1.67AI^{+++}$ + $4H_{2}O$ + $4SiO_{2}(aq)$	3.1333	1.4445	-0.9146	-3.2347	-5.6069	-7.5864	-9.3859	-11.2358	
Na-Montmo- rillonite	Na-Montmorillonite + $6H^{+}$ = 0.33 Na ⁺ + 0.33 Mg ⁺⁺ + 1.67Al ⁺⁺⁺ + $4H_{2}O$ + $4SiO_{2}(aq)$	4.1752	2.4583	0.0686	-2.2746	-4.6636	-6.6516	-8.4568	-10.3142	
K-Montmo- rillonite	K-Montmorillonite + $6H^{+}$ = 0.33 K ⁺ + 0.33 Mg ⁺⁺ + 1.67Al ⁺⁺⁺ + $4H_{2}O$ + $4SiO_{2}(aq)$	3.7554	2.1194	-0.1824	-2.4524	-4.7777	-6.7228	-8.4982	-10.3337	
Ca-Montmo- rillonite	Ca-Montmorillonite + $6H^+$ = 0.165 Ca ⁺⁺ + 0.33 Mg ⁺⁺ + 1.67Al ⁺⁺⁺ + $4H_2O$ + $4SiO_2(aq)$	4.2226	2.4024	-0.1121	-2.5786	-5.1015	-7.2081	-9.1212	-11.0793	
Mg-Montmo- rillonite	Mg-Montmorillonite + $6H^{+}$ = 0.495 Mg ⁺⁺ + 1.67Al ⁺⁺⁺ + $4H_{2}O$ + $4SiO_{2}(aq)$	4.2348	2.3643	-0.2067	-2.7218	-5.2890	-7.4277	-9.3650	-11.3418	
H-Nontronite	H-Nontronite + $6.99H^+$ = $2Fe^{+++} + 0.33AI^{+++} + 4.66H_2O + 3.67SiO_2(aq)$	-11.2178	-12.0580	-13.3804	-14.7103	-16.0807	-17.2650	-18.4365	-19.7989	
Na-Nontronite	Na-Nontronite + $7.32H^{+}$ = $0.33Na^{+} + 2Fe^{+++} + 0.33Al^{+++} + 4.66H_{2}O + 3.67SiO_{2}(aq)$	-10.1759	-11.0442	-12.3972	-13.7502	-15.1373	-16.3301	-17.5073	-18.8772	
K-Nontronite	K-Nontronite + $7.32H^+$ = $0.33K^+ + 2Fe^{+++} + 0.33AI^{+++} + 4.66H_2O + 3.67SiO_2(aq)$	-10.5953	-11.3831	-12.6486	-13.9288	-15.2526	-16.4027	-17.5503	-18.8986	
Ca-Nontronite	Ca-Nontronite + $7.32H^{+}$ = 0.165 Ca ⁺⁺ + $2Fe^{+++}$ + 0.33AI ⁺⁺⁺ + 4.66H ₂ O + 3.67SiO ₂ (aq)	-10.1283	-11.1001	-12.5781	-14.0546	-15.5758	-16.8873	-18.1725	-19.6432	

Table 6-18. Log K Matrix for Clay Minerals (Continued)

Temperature (°C)									
Mineral	Reaction	0.01	25	60	100	150	200	250	300
Mg-Nontronite	Mg-Nontronite + $7.32H^{+}$ = 0.165 Mg ⁺⁺ + $2Fe^{+++}$ + 0.33Al ⁺⁺⁺ + 4.66H ₂ O + 3.67SiO ₂ (aq)	-10.1162	-11.1382	-12.6726	-14.1977	-15.7631	-17.1067	-18.4161	-19.9055
Ripidolite-7A	Ripidolite-7A + $16H^{+}$ = $2AI^{+++} + 3Mg^{++} + 12H_{2}O + 2 Fe^{++} + 3SiO_{2}(aq)$	71.9986	62.5511	51.3031	40.8781	30.4819	22.0378	14.7716	8.0641
Ripidolite-14A	Ripidolite-14A + 16H ⁺ = $2AI^{+++} + 3Mg^{++} + 12H_2O + 2 Fe^{++} + 3SiO_2(aq)$	68.4043	59.1778	48.1896	38.0078	27.8567	19.6105	12.5078	5.9378
H-Saponite	H-Saponite + $6.99H^+$ = $3 Mg^{++} + 0.33AI^{+++} + 4.66H_2O + 3.67SiO_2(aq)$	29.6074	26.0453	21.6364	17.5487	13.5495	10.3777	7.6756	5.1115
Na-Saponite	Na-Saponite + $7.32H^{+}$ = $0.33Na^{+} + 3 Mg^{++} + 0.33Al^{+++} + 4.66H_{2}O + 3.67SiO_{2}(aq)$	30.6491	27.0591	22.6199	18.5093	14.4935	11.3133	8.6058	6.0343
K-Saponite	K-Saponite + $7.32H^{+}$ = $0.33K^{+} + 3 Mg^{++} + 0.33AI^{+++} + 4.66H_{2}O + 3.67SiO_{2}(aq)$	30.2295	26.7202	22.3686	18.3310	14.3787	11.2413	8.5634	6.0136
Ca-Saponite	Ca-Saponite + $7.32H^{+}$ = $0.165Ca^{++} + 3 Mg^{++} + 0.33Al^{+++} + 4.66H_{2}O + 3.67SiO_{2}(aq)$	30.6968	27.0032	22.4387	18.2045	14.0545	10.7554	7.9397	5.2674
Mg-Saponite	Mg-Saponite + $7.32H^{+}$ = $3.165 \text{ Mg}^{++} + 0.33\text{Al}^{+++} + 4.66H_{2}\text{O} + 3.67\text{SiO}_{2}(\text{aq})$	30.7058	26.9651	22.3479	18.0685	13.8775	10.5490	7.7110	5.0214
Low Fe-Mg Smectite	Low Fe-Mg Smectite + $7H^+$ = $0.15Na^+ + 0.2K^+ + 0.02Ca^{++} + 0.9 Mg^{++} + 0.16Fe^{+++} + 0.29Fe^{++} + 1.25AI^{+++} + 4.5H_2O + 3.75SiO_2(aq)$	13.7198	11.1541	7.8261	4.6537	1.4698	-1.1361	-3.4437	-5.7296
High Fe-Mg Smectite	High Fe-Mg Smectite + 8H ⁺ = 0.1Na ⁺ + 0.2K ⁺ + 0.025Ca ⁺⁺ + 1.15 Mg ⁺⁺ + 0.2Fe ⁺⁺⁺ + 0.5Fe ⁺⁺ + 1.25Al ⁺⁺⁺ + 5H ₂ O + 3.5SiO ₂ (aq)	20.8773	17.4595	13.1723	9.1326	5.0925	1.7976	-1.0908	-3.8865
Reykjanes Smectite	Reykjanes Smectite + 9.32H ⁺ = 0.33Na ⁺ + 0.03K ⁺ + 0.66Ca ⁺⁺ + 1.29 Mg ⁺⁺ + 0.35Fe ⁺⁺⁺ + 0.33Fe ⁺⁺ + 0.01Mn ⁺⁺ + 1.11Al ⁺⁺⁺ + 5.66 H ₂ O + 3.17SiO ₂ (aq)	26.1136	22.1615	17.2950	12.7445	8.2070	4.5112	1.2779	-1.8342

DTN: MO0302SPATHDYN.001 ([DIRS 161886], Spreadsheet Minerals_cal_sea_clays1a.xls).

Actual uncertainties in estimated Gibbs free energy values for minerals not in the regression set are difficult to quantify due to correlated errors and other factors (some of which are noted below). It is likely that they are about 2 to 3 times greater than the minimal values suggested by uncertainties in calorimetric measurements. Thus in "typical" cases with four tetrahedral cations in the molecular formula, the uncertainties are approximately 4,000 to 9,600 cal/mol.

In the case of the molar volume regression, more minerals were included and the regression error (2 to 4 cm³/mol for formulas with four tetrahedral cations, or 1 to 2.5 percent) probably gives a fair estimation of the actual uncertainty in estimating molar volumes for minerals not in the regression matrix. Uncertainties of this magnitude are acceptable for two reasons. First, molar volume values do not significantly affect log K values in the temperature-pressure range of interest to the YMP. Second, with regard to pure volumetric calculations (e.g., in calculating gain or loss of permeability), uncertainties at this level tend to be insignificant in relation to natural variation in real minerals.

With regard to errors in estimating entropies and heat capacity coefficients, refer to Helgeson et al. (1978 [DIRS 101596], pp. 43-52 for entropies, pp. 52-66 for heat capacity coefficients). Unlike molar volumes, these properties are basically of interest only when they affect Gibbs free energies or log K values at elevated temperature. Generally the uncertainty in the Gibbs free energy at 25°C is a significantly larger factor in the 25°C to 200°C range of principal interest to the YMP.

The estimation methods used here have some uncertainties that should be discussed. First, the mineral compositions tend to be idealized. Even when formulas are comprised on the basis of detailed chemical analyses, the true amount of interlayer water in smectites and some other clay minerals is not represented. This is in part due to a lack of reliable means of determining the amount of interlayer water in real clays. Second, the temperature dependence of the Gibbs free energies of the exchangeable oxide components is approximate. It is assumed that the entropy and heat capacity coefficients of, say, exchangeable CaO(ex) are identical to those of non-exchangeable CaO. It would be better to assume that this is true only for K₂O(ex) and non-exchangeable K₂O, following the assumption of equality of Gibbs free energies for these components at 25°C. This problem is due to a paucity of exchange data at elevated temperature.

An issue unique to the Gibbs free energy and molar volume regressions concerns the use of a silicated $Mg(OH)_2$ component in addition to silicated MgO and H_2O components. The justification for this should be reconsidered on a statistical basis. The use of this component in a sense "de-linearizes" the method (because of the arbitrary rule of assigning Mg to this component first as the amount of OH permits). This applies to the situation in which ripidolites are found to be less stable than the equivalent mixtures of corresponding clinochlores and daphnites.

Vieillard (1994 [DIRS 159213], 1994 [DIRS 159214]) has developed more complex techniques for estimating the enthalpies of formation of silicates, including sheet silicates. These appear not to have been applied to smectite but rather only to some micas, some chlorites, an illite of different composition $[(K_{0.65}Na_{0.03})(Al_{1.83}Fe_{0.03}^{+++}Fe_{0.04}^{++}Mg_{0.1}Mn)(Si_{3.59}Al_{0.41})O_{10}(OH)_{1.8}F_{0.07}]$ than the one used here, and a few other sheet silicates. Although Vieillard (1994 [DIRS 159214], Table A14) gives simplified compositions for all the considered phases in this

work, the author makes it clear that the calculated enthalpies mostly pertain to more detailed actual compositions such as that given for the specified illite composition in his study. A comparison between the final reestimated values and the calculated and predicted values given in Vieillard (2000 [DIRS 171586]) (Table 6-19) show only small differences than these values and provides corroboration that the computed values are reasonable.

Ransom and Helgeson (1994 [DIRS 159207]) discussed estimation of heat capacities, entropies, and volumes of the 2:1 (Si:Al) clay minerals (which include smectites, illites, and vermiculites). As they did not estimate Gibbs free energies (or enthalpies), quantitative comparisons are not possible. The methods of estimation were largely similar if not identical to those used here. They discussed the problem of variable interlayer water content in clay minerals, and suggested ways in which the estimation method used for data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) might be improved by accounting for additional water.

Table 6-19. Estimated Gibbs Free Energies of Formation (cal/mol) for the Minerals of Interest: Original Wolery Estimates, "Re-Creation" Estimates, and Final "Reestimation" Estimates

Mineral	Original	Re-Creation	Final "Reestimation"	Calculated (cal/mol)	Predicted (cal/mol)
Na-beidellite	-1,279,688	-1,279,692	-1,279,692	-1,278,601	-1,279,177
Ca-beidellite	-1,280,909	-1,280,913	-1,280,913	-1,279,827	-1,280,420
K-beidellite	-1,281,773	-1,281,778	-1,281,777	-1,280,675	-1,281,134
Mg-beidellite	-1,277,064	-1,277,068	-1,277,068	-1,275,955	-1,277,346
Na-saponite	-1,343,879	-1,343,883	-1,343,883	-1,343,056	-1,335,182
Ca-saponite	-1,345,100	-1,345,104	-1,345,104	-1,341,553	-1,336,424
Na-nontronite	-1,078,271	-1,078,585	-1,078,590	-1,077,664	-1,077,439
Ca-nontronite	-1,079,492	-1,079,806	-1,079,811	-1,078,888	-1,078,682
Illite	-1,303,971	-1,303,940	-1,303,942	_*	_*
High Fe-Mg smectite	-1,262,121	-1,262,122	-1,262,125	-1,263,411	-1,263,344

Sources: Column 2: Wolery 1978 [DIRS 151346], p. 231, Table 1.

Column 3: DTN: MO0302SPATHDYN.001 ([DIRS 161886], Spreadsheet

Clays_TJW_0_Rev1b.xls, Worksheet Results Summary).
Column 4: DTN: MO0302SPATHDYN.001 ([DIRS 161886], Spreadsheet

Clays_TJW_1_Rev1b.xls, Worksheet Results Summary).

Columns 5 and 6: Vieillard 2000 [DIRS 171586], Table 5, p. 462-463.

Other estimation schemes for the Gibbs free energies of sheet silicates can be found in older literature dating back around the time of Tardy and Garrels (1974 [DIRS 159209]). These include methods proposed in Mattigod and Sposito (1978 [DIRS 159197]) and Kashik et al. (1979 [DIRS 158992]). Other more recent methods such as that used in Vieillard (2000 [DIRS 171586]) are based mainly on that of Tardy and Garrels (1974 [DIRS 159209]) but with further refinements. When the likely uncertainties are considered, these other methods produce results that are basically similar to the ones presented here. This is shown by the reasonable similarities between the values predicted by Vieillard (2000 [DIRS 171586]; see previous discussion section) and those determined data0.ymp.R2 in this for (DTN: MO0302SPATHDYN.000 [DIRS 161756]). This comparison of corroborative

^{*} No equivalent mineral in Vieillard (2000 [DIRS 171586]).

information demonstrates confidence in the data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) estimates of thermodynamic quantities for clay phases even when some differences exist between the various methods.

6.3.2 Evaluation and Qualification of Thermodynamic Data for Zeolites

The previous data0.ymp.R0 database (DTN: MO0009THRMODYN.001 [DIRS 152576]) contained 16 zeolite mineral phases with thermodynamic data taken from work reported by Viani and Bruton (1992 [DIRS 101407], Tables 1 and 2; Appendix E, Tables 1 and 2). Log K values were not calculated beyond 100°C. The requisite thermodynamic data for extending this temperature range are available in Viani and Bruton (1992 [DIRS 101407]), and these data were entered into spreadsheets to establish the log K grid beyond 100°C.

The heat capacity data given by Viani and Bruton (1992 [DIRS 101407]) allow for extrapolation of Gibbs energies to temperatures beyond 100°C in most cases. For the clinoptilolite phases, the maximum temperature limit given for heat capacity as a function of temperature is 500K (226.85°C). Only Cs-clinoptilolite has a lower temperature limit for heat capacity of 350K (76.85°C). For the other zeolites described by this source the upper temperature limits for heat capacity data range from 470K to 1,000K (196.85°C to 726.85°C) depending on the zeolite phase. The report *Data Qualification Report for Thermodynamic Data File, Data0.ympR0 for Geochemical Code, EQ3/6* (CRWMS M&O 2000 [DIRS 152575]) that qualified data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]) also qualified the Viani and Bruton (1992 [DIRS 101407]) data up to 100°C. However, this temperature cutoff was imposed on the entire data0.ymp.R0 database (DTN: MO0009THRMODYN.001 [DIRS 152576]) on the basis of what was considered relevant for the YMP repository environment at that time.

The basic methodology utilized in the retrieval of zeolite thermodynamic data by Viani and Bruton (1992 [DIRS 101407]) was qualified (CRWMS M&O 2000 [DIRS 152575]), and is applicable to higher temperatures (greater than 100°C) in aqueous systems. The original source (Viani and Bruton 1992 [DIRS 101407]) provides experimental and analytical results for temperatures greater than 100°C. Accordingly, defensible zeolite thermodynamic data can be estimated for temperatures greater than 100°C, and this was performed for the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]). Given the intended use of these data in the YMP and the adequacy of the methodology in providing a temperature extrapolation of thermodynamic parameters (e.g., ΔG°_f) for the zeolites, the extrapolated ΔG°_f values above 100°C are qualified up to the upper temperature limits given by the authors Viani and Bruton (1992 [DIRS 101407]). Any extrapolation beyond these temperature limits should be further justified. Since nearly all the heat capacity data for the zeolites considered by Viani and Bruton (1992 [DIRS 101407]) are based on experimental calorimetric work, the temperature bounds given by the authors provide realistic stability limits for these zeolite phases.

Thermodynamic data for an additional five zeolite minerals were taken from Table 1 of Chipera et al. (1995 [DIRS 100025]), included in a recent book on natural zeolites published by the International Committee on Natural Zeolites. The thermodynamic data presented in the study by Chipera et al. (1995 [DIRS 100025]) were estimated using a methodology similar to that used for determination of thermodynamic properties of clays in data0.ymp.R2

(DTN: MO0302SPATHDYN.000 [DIRS 161756]) (see Section 6.3.1). In general, these methods use an additive approach to represent the thermodynamic contributions of framework components of the mineral phase. The accuracy of these methods has been discussed in the geochemistry literature, and the most common way of validating the methods is by comparison experimental important for the data0.vmp.R2 with data. More (DTN: MO0302SPATHDYN.000 [DIRS 161756]), is that the thermodynamic data retrieved using these methods are consistent with the basic conventions defining thermodynamic parameters. The estimation methods used in the work of Chipera et al. (1995 [DIRS 100025]) are consistent with these conventions and have been applied to the retrieval of reference-state thermodynamic data for various rock-forming minerals. These are combined with extrapolation to elevated temperatures to assess the description of mineral phase equilibria in various geologic environments.

Modeling results using these data (BSC 2004 [DIRS 170031]) suggest that the data represent the behavior of known zeolite phases at Yucca Mountain. The data were entered into Excel spreadsheets (Zeolite Solids_j.xls, Zeolite #2 Solids_cal.xls, and Zeolite #3 Solids_j.xls; DTN: MO0302SPATHDYN.001 [DIRS 161886]), and the log K grid was developed using the updated quartz solubility data as discussed in Section 6.1.5. Qualified log K values are shown in Table 6-20. It should be pointed-out that the Maier-Kelley coefficients from the source were incorrectly implemented in the calculation spreadsheets for the phases analcime, laumontite, philipsite, Na-clinoptilolite, chabazite, erionite, and stellerite. These errors are documented in Spreadsheets Zeolite_Solids_j_CFJC_fix.xls, Zeolite_2_Solids_cal_CFJC_fix.xls, Zeolite_3_Solids_j_CFJC_fix.xls (output DTN: SN0410T0510404.001). An insignificant error was found for mesolite that did not change the computed log K values, and the corrected values (DTN: SN0410T0510404.001; Table 6-20 are the same as in Zeolite_Solids_j_CFJC_fix.xls). The log K values for the dissociation reactions that need to be corrected for the temperature extrapolations are given in Table 6-20. The log K values at 25°C for these phases in Table 6-20 are correct as is. All the above-mentioned corrections in extrapolated log K values are updated into data0.ymp.R4 (output DTN: SN0410T0510404.002). Therefore, only the corrected log K values (see Table 6-21) at temperatures other than 25°C and present in data0.ymp.R4 (output DTN: SN0410T0510404.002) are qualified for use at extrapolated temperatures. Given the large discrepancies produced by this transcription error in the heat capacity coefficients (see Table 6-22), only the affected zeolite data for temperatures below 100°C in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) should be considered for use in the YMP. Since the differences in log K (i.e., Δ Log K) increase markedly with temperature above 100°C (see Table 6-22), the user should use data0.ymp.R4 (output DTN: SN0410T0510404.002) to perform qualified calculations.

Qualification of thermodynamic data listed in Table 6-23 is mainly done through data comparisons with experimental data and/or tabulated data in handbook sources. Overall, the differences in Gibbs free energies of formation at the reference state of 25°C extracted from calorimetric or solubility experiments are considered reasonable given the uncertainties involved in the experimental determinations coupled with those related to the extraction of data used to generate reference-state thermodynamic data and associated parameter extrapolations as a function of pressure and temperature. Because the compositions for many of the zeolites reported by Chipera et al. (1995 [DIRS 100025]) do not generally resemble those of end-members, their reported thermodynamic values are in most cases different from those

reported in the literature. These differences in composition, even if they appear to be negligible, could contribute to the aforementioned discrepancies in the values for standard thermodynamic data. For the zeolites listed in Table 6-23, the largest discrepancies for which data comparisons were conducted are observed for Na-clinoptilolite and stellerite. These discrepancies ranged from approximately 72 kJ/mol for stellerite to 175 kJ/mol for Na-clinoptilolite. When the corroborative data for Na-clinoptilolite from Wilkin and Barnes (1998 [DIRS 172351]) are corrected for the amount of water of hydration (see Footnote g of Table 6-23), the difference is reduced from approximately 175 to 74.5 kJ/mol. Even with this simplistic correction that doesn't account for Gibbs energies of hydration attached to "zeolitic" H₂O in the mineral structure, the overall differences in estimated and measured Gibbs free energies due to thermodynamic contributions for a given zeolite composition are within the general uncertainty of the experimental measurements and the methodology, and are therefore reasonable.

There are few experimental data assessing the thermodynamic properties of erionite and phillipsite for the compositions adopted in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). Therefore, no comparison with other data sources was attempted for this report. These data are qualified on the basis that the authors used an estimation approach that generally provides values of standard thermodynamic data (e.g., ΔG_f° and ΔH_f°) for various zeolite phases that are reasonably close to those obtained using experimental methods. This is shown in Figure 2 of Chipera and Apps (2001 [DIRS 171017], Figure 2, p. 124), which depicts the percent difference between estimated and experimental values for a suite of zeolites all within approximately 0.4% (2 σ) for Gibbs free energies and enthalpies of formation. Given this reasonable difference in the predictive capability of the model, this establishes confidence in the thermodynamic values retrieved from their work and for the intended use by the YMP. Pages 121 through 124 of Chipera and Apps (2001 [DIRS 171017], pp. 121-124) provide further discussion of the model comparisons with reported thermodynamic data on zeolites. stellerite, a comparison was done with data retrieved from Fridriksson et al. (2001 [DIRS 160460]), Table 4, p. 4002) and from Kiseleva et al. (2001 [DIRS 172352], Table 5, p. 174). The difference in Gibbs free energies between the values given by Chipera et al. (1995) [DIRS 100025]) and those given in these two studies are approximately 44 kJ/mol and 72 kJ/mol, for Kiseleva et al. (2001 [DIRS 172352]) and Fridriksson et al. (2001 [DIRS 160460]), respectively. These differences can be considered within the overall uncertainty of the model prediction of Chipera et al. (1995 [DIRS 100025]) and that of Fridriksson et al. (2001 [DIRS 160460]) for the estimates of Gibbs free energies. Therefore, as with other zeolites, these differences are deemed reasonable for use by the YMP.

Table 6-20. Log K EQ3/6 Grid for Zeolite Minerals

Mineral	log K 0.01°C	log K 25°C	log K 60°C	log K 100°C	log K 150°C	log K 200°C	log K 250°C	log K 300°C
Analcime	7.5960	6.0057	4.7307	4.4496	5.3841	7.2915	9.8175	12.6819
Analcime-dehy	14.3700	12.3685	9.9558	7.7943	5.7799	4.2869	3.1077	2.0570
Clinoptilolite	-6.7954	-8.4187	-11.3963	-14.3663	-17.2881	-19.7134	-22.1498	-25.2382
Clinoptilolite- dehy	32.8947	27.2165	19.4921	12.1056	4.7793	-1.1392	-6.3869	-11.7610
Clinoptilolite-Ca	-3.3234	-5.6428	-9.8999	-14.7214	-20.4488	-26.1649	-32.3164	-39.4939
Clinoptilolite-Cs	-12.1520	-11.6912	-12.8071	-14.7666	-17.6478	-21.0608	-25.2702	-30.7396
Clinoptilolite-K	-9.5409	-9.5819	-11.2158	-13.6232	-16.9382	-20.6995	-25.2043	-30.9401
Clinoptilolite-NH ₄	-	-41.1127	-	-	-	-	-	-
Clinoptilolite-Na	-4.6606	-5.7696	-8.5627	-11.9415	-16.1074	-20.4506	-25.3610	-31.3903
Clinoptilolite-Sr	-3.6061	-5.7825	-9.8870	-14.5695	-20.1523	-25.7427	-31.7793	-38.8489
Heulandite	5.7184	3.6220	0.6905	-2.0963	-4.8363	-7.0706	-9.1445	-11.4378
Mesolite	16.0131	13.0290	9.3709	5.9953	2.6630	-0.0574	-2.4907	-4.9270
Mordenite	-4.3249	-4.5423	-5.1668	-5.8036	-6.3837	-6.8167	-7.2523	-7.8972
Natrolite	21.0240	17.9209	14.1477	10.7013	7.3511	4.6742	2.3348	0.0358
Scolecite	18.6599	15.2772	11.1522	7.3339	3.5403	0.4265	-2.3557	-5.1117
Stilbite	3.1884	1.3118	-1.3340	-3.8211	-6.2218	-8.1485	-9.9375	-11.9568
Chabazite	14.7333	10.3714	4.2602	-1.9440	-8.5835	-14.3739	-19.7583	-25.2283
Erionite	-2.7178	-4.8296	-8.9463	-13.5913	-18.8201	-23.5713	-28.2226	-33.3381
Laumontite	19.2830	14.2657	7.4233	0.5631	-6.7243	-13.0442	-18.8908	-24.7894
Phillipsite	-5.0381	-6.7617	-10.2599	-14.2541	-18.7801	-22.9139	-26.9789	-31.4706
Stellerite	-6.4688	-8.7844	-13.1698	-18.0986	-23.6535	-28.7068	-33.6443	-39.0401

DTN: MO0302SPATHDYN.001 ([DIRS 161886], Spreadsheets Zeolite Solids_j.xls, Zeolite #2 Solids_cal.xls, and Zeolite #3 Solids_j.xls).

Table 6-21. Log K EQ3/6 Grid for Corrected Zeolite Minerals

Mineral	log K 0.01°C	log K 25°C	log K 60°C	log K 100°C	log K 150°C	log K 200°C	log K 250°C	log K 300°C
Analcime	7.3411	6.0057	4.3207	2.7687	1.2666	0.0739	-0.9734	-2.0317
Clinoptilolite-Na	-4.6593	-5.7696	-8.5612	-11.9362	-16.0971	-20.4363	-25.3442	-31.3726
Chabazite	14.9395	10.3714	4.5581	-0.7982	-5.9745	-10.0955	-13.7420	-17.4773
Erionite	-2.4264	-4.8296	-8.5254	-11.9726	-15.1353	-17.5303	-19.7298	-22.3994
Laumontite	19.4704	14.2657	7.6939	1.6028	-4.3587	-9.1673	-13.4421	-17.7733
Phillipsite	-4.7708	-6.7617	-9.8737	-12.7688	-15.3984	-17.3689	-19.1824	-21.4273
Stellerite	-6.1718	-8.7844	-12.7407	-16.4486	-19.8970	-22.5474	-24.9839	-27.8839

Output DTN: SN0410T0510404.001 (Spreadsheets Zeolite_Solids_j_CFJC_fix.xls, Zeolite_2_Solids_cal_CFJC_fix.xls, and Zeolite_3_Solids_j_CFJC_fix.xls).

Table 6-22. △ Log K (Difference Between Incorrect and Corrected Values) for Zeolite Minerals in Table 6-21

Mineral	∆ log K 0.01°C	∆ log K 25°C	Δ log K 60°C	∆ log K 100°C	∆ log K 150°C	∆ log K 200°C	∆ log K 250°C	∆ log K 300°C
Analcime	-0.2549	0.0000	-0.4100	-1.6809	-4.1175	-7.2176	-10.7909	-14.7136
Clinoptilolite-Na	0.0013	0.0000	0.0016	0.0053	0.0103	0.0143	0.0168	0.0177
Chabazite	0.2062	0.0000	0.2980	1.1458	2.6090	4.2784	6.0163	7.7509
Erionite	0.2914	0.0000	0.4210	1.6187	3.6848	6.0411	8.4928	10.9387
Laumontite	0.1874	0.0000	0.2705	1.0397	2.3657	3.8769	5.4487	7.0162
Phillipsite	0.2673	0.0000	0.3862	1.4853	3.3817	5.5450	7.7966	10.0433
Stellerite	0.2970	0.0000	0.4291	1.6500	3.7565	6.1594	8.6604	11.1563

Output DTN: SN0410T0510404.001 (Spreadsheets Zeolite_Solids_j_CFJC_fix.xls, Zeolite_2_Solids_cal_CFJC_fix.xls, and Zeolite_3_Solids_j_CFJC_fix.xls).

6.3.3 Evaluation and Qualification of Thermodynamic Data for Cement Phases

For the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), a review of the literature on geochemical modeling of cement was conducted to support possible investigation of the effects from cement grouts on the Engineered Barrier System chemical environment. Thermodynamic modeling based on chemical equilibria has been advanced as a useful tool for modeling cement-water interactions (Gartner and Jennings 1987 [DIRS 144879]; Reardon 1990 [DIRS 100821]).

Given the compositional complexity of common cement phases, the compilation of data was restricted to cement phases for which solubility and/or thermodynamic data were well-constrained. For example, thermodynamic data for some cement phases are represented by their pure end-member compositions. Nevertheless, these data are useful in establishing a modeling framework even with all inherent limitations on data availability, uncertainties, and compositional variability of cement. The minerals shown in bold-italics in Table 6-24 were added to the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) for this reason.

The data selected for use are qualified for inclusion in the database by technical assessment. A number of sources were reviewed (Taylor 1990 [DIRS 120495]; Reardon 1992 [DIRS 100822]; Bruton et al. 1993 [DIRS 100710]; Atkins et al. 1992 [DIRS 100700]; Neall 1996 [DIRS 144784]; Batchelor and Wu 1993 [DIRS 156182]; Sarkar et al. 1982 [DIRS 119581]; Atkins et al. 1993 [DIRS 131758]; Shaw et al. 2000 [DIRS 158028]; Glasser et al. 1987 [DIRS 118111]; Damidot et al. 1994 [DIRS 144866]; Bennett et al. 1992 [DIRS 116990]; Babushkin et al. 1985 [DIRS 116981]; Greenberg and Chang 1965 [DIRS 144989]; Fujii and Kondo 1983 [DIRS 144876]; Harvie et al. 1984 [DIRS 118163]; MacPhee et al. 1989 [DIRS 145004]; Berner 1987 [DIRS 116991], 1990 [DIRS 100707]; Greenberg and Moller 1989 DIRS 152684]; and Perkins and Palmer 1999 [DIRS 152703]) to develop a list of applicable mineral phases (Table 6-24). These sources include not only the discussion from Taylor (1990 [DIRS 120495]), but also previous modeling studies from U.S. and international nuclear waste management projects. The minerals listed formed the basis for an additional literature search for the pertinent data required for generating the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]). The minerals listed are those that are common to the hydration of Portland cements and are generally limited to the Ca-Al-Si-S-Mg-H₂O system. When available the common mineral names are used. However, some cement chemical nomenclature is used (see Taylor 1990 [DIRS 120495], Section 1.1.3, for a description of this nomenclature).

Thermodynamic data for cement phases were evaluated based on the data obtained in the thermodynamic compilation of Babushkin et al. (1985 [DIRS 116981]). Data extracted from this source are included in Table 4-11. As a cross-check on the quality of thermodynamic data, the data for several cement minerals that were previously included in the data0.ymp.R0 database file (DTN: MO0009THRMODYN.001 [DIRS 152576]) were found to be the same. The data in Table 4-11 were entered into Spreadsheet Minerals_cal_DJ_Cement.xls (DTN: MO0302SPATHDYN.001 [DIRS 161886]) for the temperature dependent derivation of inclusion into the data0.ymp.R2 the formation constants and direct database (DTN: MO0302SPATHDYN.000 [DIRS 161756]).

Sarkar et al. (1982 [DIRS 119581]) provides a compilation of thermodynamic data from various sources in the literature. They evaluated and selected the best values for heats, entropies, and free energies of formation for calcium silicates, aluminates, and ferrites. They also presented data for other cement phases including CSH gel and Friedl salt. Sarkar et al. (1982 [DIRS 119581]) indicate that the best data source for most of the minerals of interest is a 1972 edition of a volume translated from Russian entitled Thermodynamics of Silicates. This book was revised and published in English in 1985 and is the current edition of Babushkin et al. (1985 [DIRS 116981]). Heat capacity data for most of the cement phases were extracted from Babushkin et al. (1985 [DIRS 116981]). However, heat capacity data did not exist for CSH, therefore, these values needed to be estimated. They were processed in the same manner as the values found in Section 6.3.1 using a simple linear model (Helgeson et al. 1978 [DIRS 101596], pp. 52-66). For more details, see Sections 6.3.3.1 and 6.3.3.4. The log K grid generated for the mineral phases and included in the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) is summarized in Table 6-25.

It is noted that cement phases CSH:1.7, Friedl salt, and hydrogarnet are inactive in the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]). These phases remain inactive in the data0.ymp.R4 database (output DTN: SN0410T0510404.002). However, these phases are discussed in detail and qualified in this report as possible additions to future calculations.

Table 6-23. Thermodynamic Data for Additional Zeolite Minerals Included in Data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756])

						Empirical Coefficients for the Heat Capacity Equation ^a						
Phase	ΔG _f ° (J/mol)	ΔH _f ° (J/mol)	S° (J/mol-K)	V° (cm³/mol)	C _p ° (J/mol-K)	T (J/mol-K ²)	T ² (J/mol-K ³)	T ³ (J/mol-K ⁴)	T ⁻² (J-K ² /mol)	T ⁻³ (J-K ⁴ /mol)	T ^{-0.5} (J-K ^{0.5} /mol)	Source
Analcime	-3,077,200	-3,296,900	226.75	-	237.6	-4.743	1.663E-03	-1.236E-06	-	-	-	1
Analcime ^b	-3,097,959	-3,317,277	226.98	97.37	115.87	0.28741	-	-	2073027	-	-	3
Analcime ^c	-3,082,900	-3,301,800	233.60	96.95	108.77	0.29689	-	-	1341599	-	-	3
Analcime ^d	-3,080,700	-	-	ı	-	-	-	-	-	-	-	4
Clinoptilolite-Nae	-18,978,314	-	1,507.16	632.050	77.62	6.365	4.616E-03	-	-	-	-	1
Clinoptilolite-Naf	-18,803,700	-	-	ı	-	-	-	-	-	-	-	5
Clinoptilolite-Na ⁹	-18,903,791	-	-	ı	-	-	-	-	-	-	-	5
Chabazite	-13,850,300	-15,047,400	1,194.30	499.400	2,023	-	-	-	-3.016E-03	4.195E-05	-1.385E+00	2
Chabazite ^h	-14,366,000	15,716,000	1195.5	1	-	-	-	-	-	-	-	6
Chabazite ⁱ	-13,780,159 ⁱ	-	-	ı	-	-	-	-	-	-	-	6
Erionite	-19,813,000	-21,497,500	1,640.50	672.000	2,853	-	-	-	-4.704E-03	6.723E-05	-1.923E+00	2
Phillipsite	-17,817,700	-19,375,100	1,491.90	609.200	2,609	-	-	-	-4.158E-03	5.918E-05	-1.778E+00	2
Stellerite	-19,996,800	-21,751,300	1,611.70	665.500	2,887	-	-	-	-4.478E-03	6.259E-05	-1.983E+00	2
Stellerite ^j	-19,924,358	-21,656,237.6	1,604.73	666.5	-	1.7875E+03	6.3296E-01	-	-3.5756E+07	-	-	7
Stellerite ^k	-20,040,400	-21,774,800.0	1,600.6	-	-	-	-	-	-	-	-	8

Qualification of Thermodynamic Data for Geochemical Modeling of Mineral-Water Interactions in Dilute Systems

Sources: 1 Viani and Bruton 1992 [DIRS 101407], Tables 1 and 2; Appendix E, Tables E.1 and E.2, p. 59-60.

- 2 Chipera et al. 1995 [DIRS 100025], Table 1, p. 569.
- 3 Neuhoff et al. 2004 [DIRS 172354], Table 7, p. 44.
- 4 Mattigod and McGrail 1999 [DIRS 172343]. Table 3, p. 44.
- 5 Wilkin and Barnes 1998 [DIRS 172351], Table 7, p. 753.
- 6 Ogorodova et al. 2004 [DIRS 172353], Table 3, p. 193.
- 7 Fridriksson et al. 2001 [DIRS 160460], Table 4, p. 4002.
- 8 Kiseleva et al. 2001 [DIRS 172352], Table 5, p. 174.

a Empirical coefficients based on the equation given by Viani and Bruton (1992 [DIRS 101407], Table E.2, Footnote 1). Also the equation given by Chipera et al. (1995 [DIRS 100025], Table 1, p. 569, Footnote 4).

Chemical formula for this analcime phase as tabulated in Neuhoff et al. (2004 [DIRS 172354], Tables 6 and 7, p. 40 and 44): (NaAl)_{1.05}Si_{1.95}O₆•0.975H₂O.

^c Chemical formula for this analcime phase as tabulated in Neuhoff et al. (2004 [DIRS 172354], Tables 6 and 7, p. 40 and 44): (NaAl)_{1.05}Si_{1.95}O₆•0.975H₂O.

d Chemical formula for this analcime phase as tabulated in Mattigod and McGrail (1999 [DIRS 172343], Table 3, p. 44): (NaAl)_{0.96}Si_{2.04}O₆•H₂O, multiplied by 0.5 for ΔG_f comparison with other sources.

^e Units for partial molal thermodynamic properties originally given in cal/mol basis in the source. Converted to J/mol basis in this table.

Chemical formula for Na-clinoptilolite as given in Wilkin and Barnes (1998 DIRS 172351], Table 7, p. 753): Na_{1.1}Al_{1.1}Si_{4.9}O_{1.2*}3.48H₂O. The ΔG_f° value listed above for this phase was obtained by multiplying the value given in the source at 25°C of -6267.9 kJ/mol (for 3.48 moles H₂O per fractional formula unit) by 3 for comparison with the phase stoichiometry adopted in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]).

⁹ Value corrected by adding the equivalent ΔG_f° of 0.422 moles of H₂O using data from data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). This is done for comparison with the Na-clinoptilolite composition adopted in this database: -18.803.700 J/mol + (0.422)*(-237182.6) J/mol = -18.903.791.1 J/mol.

Table 6-23. Thermodynamic Data for Additional Zeolite Minerals Included in Data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) (Continued)

Thermodynamic data for the chemical formula of stellerite as given in Fridriksson et al. (2001 [DIRS 160460], Table 4, p. 4002): Ca₂Al₄Si₁₄O₃₆•14H₂O. Values in the source given in cal/mol units and converted in J/mol in this table.

^h Thermodynamic data for the chemical formula of chabazite as given in Ogorodova et al. (2004 [DIRS 172353], Table 3, p. 193): (Ca_{1.65}Na_{0.24}K_{0.10})[Al_{3.79}Si_{8.25}O₂₄]• 12.47H₂O.

Value corrected by substracting the equivalent ΔG_f° of 2.47 moles of H₂O using data from data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). This is done for comparison with the chabazite composition adopted in this database: $-14,366,000 \text{ J/mol} - (2.47)^*(-237182.6 \text{ J/mol}) = -13,780,159 \text{ J/mol}$.

Thermodynamic data for the chemical formula of stellerite as given in Kiseleva et al. (2001 [DIRS 172352], Table 5, p. 174): Ca₂Al₄Si₁₄O₃₆•14H₂O. In the source, the stoichiometry of the chemical formula is half of that presented in this table. Therefore, the thermodynamic values were multiplied by two so it can be compared to the stellerite composition adopted in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]).

Table 6-24. Minerals Commonly Associated with Cements and Grouts Along with Sources

Mineral	Taylor 1990 [DIRS 120495]	Reardon 1992 [DIRS 100822]	Bruton et al. 1993 [DIRS 100710]	Atkins et al. 1992 [DIRS 100700]	Neall 1996 [DIRS 144784]	Batchelor and Wu 1993 [DIRS 156182]	Sarkar et al. 1982 [DIRS 119581]	Atkins et al. 1993 [DIRS 131758]	Harvie et al. 1984 [DIRS 118163]	Bennett et al. 1992 [DIRS 116990]	Included in R2 Database?
Afwillite	Х		х				Х	Х			у
Allite (C ₃ S)	х	Х					Х				у
Anhydrite	x	Х							Х		у
Bellite (C ₂ S)	x	Х					Х				у
Brucite	х	Х		Х					Х		у
C ₁₂ A ₇	x						Х				у
C ₂ AH ₈	х					Х	Х				у
C ₃ A	х	Х					Х				у
C ₄ AF	х	Х									у
C ₄ AH ₁₃	х	Х		Х		х	х	х			у
C ₄ AH ₁₉	х						Х				у
CA	х						Х				у
CA ₂	х						Х				у
CAH ₁₀	х						Х				у
CSH ^a	х	Х		Х	Х	Х	Х	Х		Х	у
Ettringite	х	Х		Х	Х	Х	Х	Х			у
Ferrite-Ca	Х						Х				у
Ferrite-Dicalcium	х						х				у
Foshagite			Х				Х				у
Friedl Salt ^b	х					х	Х	х			у
Gehlenite Hydrate ^c	х			Х				Х		Х	25 ^d
Gibbsite	х	Х		Х							у
Gismondine-Na								Х			25 ^d
Gismondine-Ca								Х			25 ^d
Gypsum	х			х					х		у
Gyrolite	х		х				Х				у
Hillebrandite	х		х				Х				у
Hydrogarnet	х	х		х	х		х	х		х	у
Hydrotalcite ^e	х	х		х	х			х		х	25 ^d
Jennite	х							х			
Monocarboaluminate		Х				Х		Х			25 ^d

Table 6-24. Minerals Commonly Associated with Cements and Grouts Along with Sources (Continued)

Mineral	Taylor 1990 [DIRS 120495]	Reardon 1992 [DIRS 100822]	Bruton et al. 1993 [DIRS 100710]	Atkins et al. 1992 [DIRS 100700]	Neall 1996 [DIRS 144784]	Batchelor and Wu 1993 [DIRS 156182]	Sarkar et al. 1982 [DIRS 119581]	Atkins et al. 1993 [DIRS 131758]	Harvie et al. 1984 [DIRS 118163]	Bennett et al. 1992 [DIRS 116990]	Included in R2 Database?
Monosulphate	x	х		x		x	x	Х			у
Nekoite			Х								
Okenite			Х				х				у
Periclase	х	Х									у
Plombierite ^f	х		х				Х				у
Portlandite	х	х		х	х				х		у
Reyerite			х								
Riversideite ⁹			х				х				у
Syngenite	х	х				х			х		25 ^d
Thaumasite	х										
Tobermorite-11A ^h	х		х	х			х	х			у
Truscottite	х		х								
Xonotlite	х		Х				х				у
CaSO ₄ ·0.5H ₂ O (beta)											у
Hemicarboaluminate											25 ^d
Tricarboaluminate ⁱ											

 ^a CSH can be a solid solution. Note that Glasser et al. (1987 [DIRS 118111], p. 338) indicates that Portland cement generally hydrates to give a CSH with a Ca/Si ratio close to 1.7.
 ^b Often listed as C₃AlCaCl₂·10H₂O or called calcium chloroaluminate hydrate (Taylor 1990 [DIRS 120495]). The

NOTE: Listing includes minerals used in modeling studies. Also shown are YMP databases that contain cement phase minerals. Bold italics signify species added to the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) (see text).

Often listed as C₃AlCaCl₂·10H₂O or called calcium chloroaluminate hydrate (Taylor 1990 [DIRS 120495]). The reported name for this phase in the cement literature is "Friedel's salt," not "Friedl Salt."

^c Also known as stratlingite (Taylor 1990 [DIRS 120495]).

^d The annotation "25" indicates 25°C data only.

^e Hydrotalcite referred to here is the formulation of Bennett et al. (1992 [DIRS 116990]), not the natural hydrotalcite mineral with a formula of (Mg_{0.75}Al_{0.25}[OH]₂)](CO₃)_{0.125}(H₂O)_{0.5}.

f 1.4A Tobermorite is also known as Plombierite (Shaw et al. 2000 [DIRS 158028], p. 143).

⁹ 9A Tobermorite is known as Riversideite (Shaw et al. 2000 [DIRS 158028], p. 143).

^h This is "normal" Tobermorite.

Never reported to occur in cement pastes submitted to intensive carbonation (Damidot et al. 1994 [DIRS 144866], p. 563).

Table 6-25. Calculated Log K Grid for Cement Mineral Phases

		Temperature (°C)							
Mineral	Reaction	0.01	25	60	100	150	200	250	300
(C ₁₂ A ₇) ^a	$(C_{12}A_7) + 66H^+ =$ 12Ca ⁺⁺ + 33H ₂ O + 14AI ⁺⁺⁺	550.4886	487.2030	414.0713	346.9265	280.0183	225.8021	179.8050	138.9111
(C ₂ AH ₈) ^a	$(C_2AH_8) + 10H^{+} = 2Ca^{++} + 2AI^{+++} + 13H_2O$	66.1489	59.2699	51.4645	44.4608	37.6368	32.1948	27.5826	23.4125
(C ₃ A) ^a	$(C_3A) + 12H^{+} = 3Ca^{++} + 6H_2O + 2AI^{+++}$	130.3127	116.7717	101.1568	86.8476	72.6344	61.1837	51.5545	43.0912
(C ₄ AF) ^a	$(C_4AF) + 20H^+ = 4Ca^{++} + 2AI^{+++} + 10H_2O + 2Fe^{+++}$	157.6612	139.8695	119.3314	100.5049	81.7809	66.6349	53.7907	42.3452
(C ₄ AH ₁₃) ^a	$(C_4AH_{13}) + 14H^{+} = 4Ca^{++} + 2AI^{+++} + 20H_2O$	110.8317	100.6293	89.1050	78.8149	68.8522	60.9746	54.3629	48.4368
(C ₄ AH ₁₉) ^a	(C ₄ AH ₁₉) + 14H ⁺ = 4Ca ⁺⁺ + 2AI ⁺⁺⁺ + 26H ₂ O	109.9718	100.6045	90.1529	80.9597	72.1928	65.3429	59.6128	54.4408
(CA) ^a	(CA) + 8H ⁺ = Ca ⁺⁺ + 4H ₂ O + 2AI ⁺⁺⁺	52.4679	45.7317	37.9299	30.7511	23.5715	17.7179	12.7075	8.2047
(CA ₂) ^a	$(CA_2) + 14H^{+} = Ca^{++} + 7H_2O + 4AI^{+++}$	72.3522	61.7708	49.4921	38.1739	26.8205	17.5151	9.4887	2.2092
(CAH ₁₀) ^a	$(CAH_{10}) + 8H^{+} = $ $Ca^{++} + 2Al^{+++} + 14H_{2}O$	43.6796	39.0445	33.8558	29.2831	24.9053	21.4541	18.5237	15.8339
Afwillite	Afwillite + $6H^{+}$ = $3Ca^{++} + 2SiO_{2}(aq) + 6H_{2}O$	65.8852	60.5586	54.3512	48.7177	43.2335	38.9119	35.3174	32.0963
Allite (C ₃ S)	Allite + $6H^{+}$ = $SiO_{2}(aq) + 3Ca^{++} + 3H_{2}O$	80.7463	73.6625	65.4520	57.9399	50.5253	44.6084	39.6786	35.3514
Bellite (C ₂ S) ^a	Bellite + $4H+ =$ $2Ca++ + 2H_2O + SiO_2(aq)$	42.5902	38.8242	34.4238	30.3903	26.4097	23.2289	20.5608	18.1770
CSH:1.7 ^{1, a}	$CSH + 3.4H^{+} =$ 1.7Ca ⁺⁺ + SiO ₂ (aq) + 4.317H ₂ O	31.9548	29.5255	26.7220	24.2206	21.8439	20.0241	18.5492	17.2455
Ettringite	Ettringite (B) + $12H^+$ = $6Ca^{++} + 2AI^{+++} + 38H_2O + 3SO_4^{}$	62.1144	56.8823	50.7600	45.1311	39.3132	34.0737	28.7003	22.3823
Cr-ettringite	Cr-ettringite + $12H^{+}$ = $6Ca^{++} + 2Al^{+++} + 3CrO_{4}^{2-} + 38H_{2}O$	_b	59.0000	_b	b '	_b	p .	_b	_b
Foshagite	Foshagite + 8H ⁺ = 4Ca ⁺⁺ + 3SiO ₂ (aq)+ 5.5H ₂ O	72.8341	66.6910	59.4664	52.8906	46.4921	41.4558	37.2600	33.4631

Table 6-25. Calculated Log K Grid for Cement Mineral Phases (Continued)

		Temperature (°C)							
Mineral	Reaction	0.01	25	60	100	150	200	250	300
Friedl Salt ^a	Friedl Salt + 6H ⁺ = 4Ca ⁺⁺ + 2Cl ⁻ + 19H ₂ O	-178.8322	-160.3061	-138.9735	-119.3986	-100.0899	-84.9403	-72.9462	-63.5893
Gehlenite Hydrate ²	$Ca_2Al_2SiO_7 \cdot 8H_2O + 10H^{+} = 2Ca^{++} + 2Al^{+++} + SiO_2 + 13H_2O$	_b	49.2204	_b	_b	_b	_b	_b	_b
Gismondine-Ca	$CaAl_2Si_2O_8 \ 4H_2O \ +8H^+ = Ca^{++} \ + 2Al^{+++} \ + 2SiO_2 \ + 8H_2O$	_b	20.8686	_b	_b	_b	_b	_b	_b
Gismondine-Na	$Na_2Al_2Si_2O_8 4H_2O +8H^+ = 2Na^+ + 2Al^{+++} + 2SiO_2 + 8H_2O$	_b	21.8596	_b	_b	_b	_b	_b	_b
Gyrolite	Gyrolite + 4H+ = $2Ca^{++} + 3SiO_2(aq) + 4.5H_2O$	25.3869	23.6797	21.5505	19.6199	17.7964	16.4002	15.2205	14.0407
Hemicarbo- aluminate ³	Hemicarboaluminate + $13.5H^{+}$ = $4Ca^{++}$ + $2AI^{+++}$ + $0.5HCO_{3}^{-}$ + $17.5H_{2}O$	_b	88.3235	_b	_b	_b	_b	_b	_b
Hillebrandite	Hillebrandite + $4H^{+}$ = $2Ca^{++}$ + $SiO_{2}(aq)$ + $3.17H_{2}O$	40.4592	37.0757	33.1420	29.5650	26.0671	23.2950	20.9782	18.9002
Hydrogarnet ^a	Hydrogarnet + $12H^{+}$ = $3Ca^{++} + 2AI^{+++} + 6H_{2}O$	-180.8116	-169.1024	-155.8511	-143.9549	-132.5681	-124.0078	-117.6057	-112.9719
Hydrotalcite ⁴	$4MgO \cdot Al_2O_3 \cdot 10H_2O + 14H^+ = $ $4Mg^{++} + 2Al^{+++} + 17H_2O$	_b	73.7800	_b	_b	_b	_b	_b	_b
Monocarbo- aluminate ³	$3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 10H_2O + 13H^{\dagger} = 4Ca^{\dagger \dagger} + 2Al^{\dagger \dagger \dagger} + HCO_3^{-} + 16H_2O$	_b	77.3538	_b	_b	_b	_b	_b	_b
Monosulphate	Monosulphate + $12H^{+}$ = $4Ca^{++} + 2AI^{+++} + 18H_{2}O + SO_{4}^{}$	80.7137	72.4704	62.9530	54.2551	45.5660	38.3842	31.9936	25.7834
Okenite	Okenite + $2H^+$ = Ca^{++} + $2SiO_2(aq)$ + $3H_2O$	11.4698	10.8948	10.1470	9.5024	8.9579	8.5978	8.3158	7.9937
Plombierite	Plombierite + $10H^{+}$ = $5Ca^{++}$ + $6SiO_{2}(aq)$ + $15.5H_{2}O$	69.8789	65.3842	59.9716	55.1602	50.6830	47.3017	44.4797	41.6996
Riversideite	Riversideite + $10H^{+}$ = $5Ca^{++}$ + $6SiO_{2}(aq)$ + $8H_{2}O$	76.6335	70.6194	63.3144	56.6105	50.0934	44.9615	40.6267	36.5343
Syngenite ⁵	$K_2Ca(SO_4)_2 \cdot H_2O = Ca^{++} + 2K^+ + 2SO_4^{} + H_2O$	_b	-7.6001 ^c	_b	_b	_b	_b	_b	b

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Table 6-25. Calculated Log K Grid for Cement Mineral Phases (Continued)

		Temperature (°C)							
Mineral	Reaction	0.01	25	60	100	150	200	250	300
Syngenite ^d	$K_2Ca(SO_4)_2 \cdot H_2O = Ca^{++} + 2K^+ + 2SO_4^{} + H_2O$	-7.5463	-7.2618	-7.1520	-7.2929	-7.7579	-8.6663	-10.6136	_b
Tobermorite	Tobermorite + $10H^+$ = $5Ca^{++}$ + $6SiO_2(aq)$ + $10.5H_2O$	72.5004	67.1518	60.6578	54.7498	49.0777	44.6609	40.9360	37.3654
Xonotlite	Xonotlite + $12H^{+}$ = $6Ca^{++} + 6SiO_{2}(aq) + 7H_{2}O$	102.0247	93.3664	82.9922	73.4523	64.0988	56.6744	50.4171	44.6471

Sources: DTN: MO0302SPATHDYN.001 ([DIRS 161886], Spreadsheet Minerals_cal_DJ_Cement.xls), except as noted.

- 1 DTN: MO0302SPATHDYN.001 ([DIRS 161886], Spreadsheet Minerals i DJ CSH.xls).
- 2 DTN: MO0302SPATHDYN.001 ([DIRS 161886], Spreadsheet Solids j. DJ. Cement.xls).
- 3 Damidot et al. 1994 [DIRS 144866], Appendix 1.
- 4 Bennett et al. 1992 [DIRS 116990].
- 5 Harvie et al. 1984 [DIRS 118163].

^a Phases with commented (inactive) data blocks in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). ^b Data insufficient to estimate log K at temperatures other than 298.15K.

^c The log K value of 7.6001 appears to be in error. The recalculated log K value at 25°C from the same source is –7.4484.

^d These values for syngenite are from the Pitzer database (DTN: SN0302T0510102.002 [DIRS 162572]).

6.3.3.1 Calcium Silicate Hydrate

The data blocks for this phase are inactive in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). The following discussion is provided for qualification, for possible future application of thermodynamic data for this species.

CSH gels are the principle bonding material in Portland cements. This mineral phase has been the subject of much investigation into its solubility product and other thermodynamic properties. Studies done in MacPhee et al. (1989 [DIRS 145004]), Bennett et al. (1992 [DIRS 116990]), Berner (1987 [DIRS 116991], 1990 [DIRS 100707]), Atkins et al. (1992 [DIRS 100700], 1993 [DIRS 131758]), Greenberg and Chang (1965 [DIRS 144989]), Glasser et al. (1987) [DIRS 118111]), Fujii and Kondo (1983 [DIRS 144876]), Gartner and Jennings (1987) [DIRS 144879]), and Reardon (1990 [DIRS 100821]) all suggest the difficulty in determining thermodynamic properties for CSH. The general consensus is that CSH dissolves incongruently and behaves as a solid solution. The solubility of CSH is thought to be a function of the calcium to silica ratio ranging between approximately 0.85 < Ca/Si (mole ratio) < 1.70. This range could lead to the inclusion in the database of several CSH phases each with its own specific set of thermodynamic data. This is a reasonable approach, but it leads to difficulty in modeling the different phases. Each phase has to be suppressed or not allowed to form, to test the sensitivity to the solid solution. This approach can be evaluated in a different manner where one might model a specific CSH phase and then modify the log K as an input parameter. Both approaches work equally well in determining the effects of the possible solid solution behavior. But because Portland cement generally hydrates to give a CSH with a Ca/Si ratio close to 1.70 (Glasser et al. 1987 [DIRS 118111]), this specific ratio should be the most likely to form. Therefore, only selecting the values that are associated with a Ca/Si ratio of 1.70 will simplify data selection, and this is the basis for the CSH:1.7 species.

Based on this criterion, the data selection is simplified. Data for ΔH°_f, ΔG°_f, and S° from Fujii and Kondo (1983 [DIRS 144876]) for CSH at a Ca/Si ratio = 1.7 exist (Table 6-26), and the method for their derivation is technically reasonable. The source data used for the basis of these data (Fujii and Kondo 1983 [DIRS 144876]) along with data from Greenberg and Chang (1965 [DIRS 144989]) are also used in Glasser et al. (1987 [DIRS 118111]) as a basis for a solid solution solubility model for CSH. These same source data (Greenberg and Chang 1965 [DIRS 144989]) were also used in Berner (1987 [DIRS 116991]) for his solid solution solubility model. The source data are accepted by others in the scientific community, and a review of Fujii and Kondo (1981 [DIRS 158026]) indicates that the method for the derivation of the data in Table 6-26 is reasonable. Calculation of the log K grid was done in the Excel Spreadsheet *Minerals_j_DJ_CSH.xls* in DTN: MO0302SPATHDYN.001 ([DIRS 161886]). The estimation of heat capacity values for the temperature extrapolation using the data and method of Helgeson et al. 1978 [DIRS 101596]) are documented in the Spreadsheet *DJ Cp and Vm Calculations.xls* (DTN: MO0302SPATHDYN.001 [DIRS 161886]).

Table 6-26. Thermodynamic Data for CSH with Ca to Si Ratio of 1.7

		Heat Capacity Coefficients				
ΔH° _f (kJ/mol)	$\Delta G^{\circ}_{f}(kJ/mol)$	V°(cm³/mol)	S°(J/mol-K)	a (J/mol-K)	b × 10 ³ (J/mol-K ²)	c × 10 ^{−5} (J-K/mol)
-2890	-2630	86.22	200	194.72	38.80	-5.66

Sources: Fujii and Kondo 1983 [DIRS 144876].

DTN: MO0302SPATHDYN.001 ([DIRS 161886], Spreadsheets *Minerals_j_DJ_CSH.xls* and *DJ*

Cp and Vm Calculations.xls).

6.3.3.2 Ettringite

Two data sources exist for ettringite (Table 6-27). The log K value (57.0804) at 25°C from Perkins and Palmer (1999 [DIRS 152703]) and the log K value (56.8823) calculated in Spreadsheet *Minerals_cal_DJ_Cement.xls* in DTN: MO0302SPATHDYN.001 [DIRS 161886] with data from Babushkin et al. (1985 [DIRS 116981]) are both within 2σ variance of the Ion Activity Product for ettringite reported in Perkins and Palmer (1999 [DIRS 152703]) (± 0.81 log units). Since the data are within the experimental error, either the Perkins and Palmer or Babushkin data set could be used with confidence. To maintain consistency with previously selected data for other cement phases, the values from Babushkin et al. (1985 [DIRS 116981]) were included in the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) and the Perkins and Palmer (1999 [DIRS 152703]) data are used in this report for corroboration. Calculation of the log K grid was originally done in the Excel Spreadsheet *Minerals_cal_DJ_Cement.xls* (DTN: MO0302SPATHDYN.001 [DIRS 161886]).

Cr-ettringite data are obtained from the solubility study of Perkins and Palmer (2000 [DIRS 153349]). The study is a detailed investigation of the dissolution and precipitation of this phase at various solution compositions of combined with the accurate characterization of run products. The authors generated solubility data for ettringite, which is closely related to Cr-ettringite, in a previous study (Perkins and Palmer 1999 [DIRS 152703]), in which the thermodynamic parameters reported for ettringite were in good agreement with an established fact source (Babushkin et al. 1985 [DIRS 116981]). Accordingly, confidence in the log K value for Cr-ettringite in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) is justified given the expertise of the authors and the similarity of the thermodynamic parameters for ettringite and Cr-ettringite as shown in Table 4-11. This study also generates a log K value at 25°C (log K = -2.77) for the reaction CaCrO₄(aq) = Ca⁺⁺ + CrO₄⁻⁻ consistent with the solubility data for Cr-ettringite.

Table 6-27. Values of Gibbs Free Energy, Enthalpy, Entropy, and Heat Capacity for Ettringite $(3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O)$

Source	ΔG° _f (cal/mol)	ΔH° _f (cal/mol)	S° (cal/mol)	C _p ° a (cal/mol-K)	b × 10³ (cal/ mol-K²)	c × 10 ⁻⁵ (cal-K/mol)
Babushkin et al.	-3634260	-4201320	417.6	208	740.93	-
Perkins and Palmer	-3635516	-4194550	444.93	141	-	-

Sources: Babushkin et al. 1985 [DIRS 116981], Appendix 1; Perkins and Palmer 1999 [DIRS 152703].

6.3.3.3 Gismondine

Ca-gismondine The Na and species are active data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). The following discussion is provided for qualification of the log K values, and results in a conclusion that the data are questionable. Atkins et al. (1993 [DIRS 131758], Section 5.2.6) reported ΔG°_f values for Na- and Ca-gismondine (shown in Table 4-14). For development of the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), these values were entered into a spreadsheet (Cement_phases_Gismon_fixed_CFJC.xls; DTN: MO0302SPATHDYN.001 [DIRS 161886]) to determine the log K values at 25°C based on the following reactions:

$$Na_2Al_2Si_2O_8 \cdot 4H_2O + 8H^+ = 2Na^+ + 2Al^{+++} + 2SiO_2(aq) + 8H_2O$$
 (Eq. 6-24)

$$CaAl_2Si_2O_8 \cdot 4H_2O + 8H + = Ca^{++} + 2Al^{+++} + 2SiO_2(aq) + 8H_2O$$
 (Eq. 6-25)

Calculation of the log K grid was done in the Excel Spreadsheet *Cement_phases_Gismon_fixed_CFJC.xls* (output DTN: SN0410T0510404.001) and the results are shown in Table 6-28.

Thermodynamic data for Ca-gismondine are reported by Ogorodova et al. (2003) So far, these are the only thermodynamic data available to conduct a [DIRS 172005]). corroborative comparison with the values reported by Atkins et al. (1993 [DIRS 131758]. Unlike the work of Atkins et al. (1993 [DIRS 131758], the recent study by Ogorodova et al. (2003 [DIRS 172005]) reports a detailed calorimetric study on natural samples and also retrieves thermodynamic data for an ideal end-member composition of Ca-gismondine close to the one The only difference is that the Ca-Gismondine composition adopted in this report. (CaAl₂Si₂O₈·4.5H₂O) reported by Ogorodova et al. (2003 [DIRS 172005]) has 4.5 instead of 4 moles of H₂O relative to that reported by Atkins et al. (1993 [DIRS 131758]). To correct for this difference, it was assumed that H₂O is loosely bound to the zeolite structure (not treated as zeolitic H₂O) SO this difference is substracted (see Spreadsheet Cement_phases_Gismon_fixed_CFJC.xls; output DTN: SN0410T0510404.001) from the ΔG°_f value listed by Ogorodova et al. (2003 [DIRS 172005]). The resulting value given in Table 6-28 is -1236.32 kcal/mol. This value is about 49 kcal/mol different from the one reported by Atkins et al. (1993 [DIRS 131758]). This difference in ΔG°_{f} is substantial and generates a log K value (see Table 6-28) that is also very different from that computed using Atkins et al. (1993) [DIRS 131758]) data, therefore rendering the latter data questionable. One of the coauthors (Irina Kiseleva) of the work by Ogorodova et al. (2003 [DIRS 172005]) has published several articles on zeolite thermochemistry in peer-reviewed journals along with leading investigators in the field, thus establishing confidence in their calorimetric results and data analysis. A study by Vieillard (1995 [DIRS 172320]) on the estimation of enthalpies of formation at 25°C for various zeolite phases reports ΔH°_f data for Ca-gismondine (CaAl₂Si₂O₈·4.5H₂O) having the same compositions as that reported by Ogorodova et al. (2003 [DIRS 172005]). The ΔH°_{f} value reported by Vieillard (1995 [DIRS 172320], Table 4, p. 210) is -5613.35 kJ/mol. The value reported by Ogorodova et al. (2003 [DIRS 172005]) is -5631 kJ/mol and differs by approximately 18 kJ/mol relative to that reported by Vieillard (1995 [DIRS 172320]). This difference is within the overall uncertainty bounds given by both authors for their reported ΔH°_{f} values. This data corroboration between model and experimental measurements confirms that

the value given by Atkins et al. (1993 [DIRS 131758] is incorrect. Moreover, given the relatively close values for ΔG°_f obtained from Atkins et al. (1993 [DIRS 131758]) data between Na-gismondine and Ca-gismondine, their data for Na-gismondine are also questionable.

Table 6-28. Gibbs Free Energy of Formation and Log K Values for the Dissociation Reaction Represented by Eqs. 6-24 and 6-25 for Na- and Ca-Gismondine Minerals

Mineral	Formula	ΔG°_{f} (kcal/mol)	Log K (25°C)	Source
Gismondine-Na	Na ₂ Al ₂ Si ₂ O ₈ •4H ₂ O	-1179.16	21.8596	Atkins et al. 1993 [DIRS 131758]
Gismondine-Ca	CaAl ₂ Si ₂ O ₈ •4H ₂ O	-1187.45	20.8686	Atkins et al. 1993 [DIRS 131758]
Gismondine-Ca	CaAl ₂ Si ₂ O ₈ •4.5H ₂ O	-1234.70	-	Ogorodova et al. 2003 [DIRS 172005], Table 3, p.1545
Gismondine-Ca*	CaAl ₂ Si ₂ O ₈ •4H ₂ O	-1236.32	-14.9557	Ogorodova et al. 2003 [DIRS 172005], Table 3, p.1545

^{*} ΔG°_{f} estimated by substracting half of the ΔG°_{f} associated with one H₂O, assuming it is loosely bound to the zeolite structure (see Spreadsheet *Cement_phases_Gismon_fixed_CFJC.xls*, output DTN: SN0410T0510404.001).

6.3.3.4 Friedl Salt

The data block for this phase is inactive in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). The following discussion is relevant to possible future application of thermodynamic data for these species.

The composition given for this phase in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) is not that of Friedel's salt (as known in the cement literature; see Taylor 1990 [DIRS 120495]) but that of the cement phase calcium oxychloride hydrate. In the following discussion, the terms Friedl salt and Ca-oxychloride hydrate are used interchangeably.

The estimation of log K values for this phase extrapolated to temperatures other than 25°C was assessed for development of data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), using an approximation based on the non-oxide component CaCl₂. The needed heat capacity values were taken from Chase (1998 [DIRS 157874]) and calculated in the Spreadsheet Heat Capacity Regression for CaCl2 solid.xls (DTN: MO0302SPATHDYN.001 [DIRS 161886]). These values were added to the remaining oxides to determine elemental heat capacity. The Spreadsheet DJ calculations were conducted in Cp and Vmcalculations.xls (DTN: MO0302SPATHDYN.001 [DIRS 161886]). Calculation of the log K grid was done in Spreadsheet *Minerals_cal_DJ_Cement.xls* (DTN: MO0302SPATHDYN.001 [DIRS 161886]). The resulting log K values for the reaction in Eq. 6-26, shown as inactive data in the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), are relevant to cement calculations only and the low solubilities cause extreme precipitation if activated and not suppressed in an EQ3/6 run.

$$CaCl_2(CaO)_3:16H_2O + 6H^+ = 4Ca^{++} + 2Cl^- + 19H_2O$$
 (Eq. 6-26)

Subsequent revisiting of thermodynamic data for this Ca-oxychloride hydrate cement phase indicate that the Gibbs free energy of formation and standard entropy values given in the

Spreadsheet Minerals_cal_DJ_Cement.xls (DTN: MO0302SPATHDYN.001 [DIRS 161886]) could not be found in the source Babushkin et al. (1985 [DIRS 116981], Appendix I). Only enthalpy of formation data are given by this source. A literature search on this phase revealed another source of data for a similar composition given by Harvie et al. (1984 [DIRS 118163]) and adopted by Reardon (1990 [DIRS 100821]) in his model of cement-water interactions. The phase is designated "calcium oxychloride A" (CaCl₂(CaO)₃·13H₂O) and the only difference from the Ca-oxychloride hydrate phase discussed here are the three waters. Harvie et al. (1984 [DIRS 118163]) conducted a comprehensive review of salt solubility data of the system Ca(OH)₂-CaCl₂-H₂O and advanced a predictive model using the Pitzer approach. They obtained values for standard chemical potentials that can be converted to Gibbs free energies of formation Spreadsheet *Minerals_cal_DJ_Cement_CFJC_fix.xls*; DTN: SN0410T0510404.001). Assuming $\Delta H^{\circ}_{r} = 0$ for a reaction that adds three extra waters to the phase described by Harvie et al. (1984 [DIRS 118163]) or that water is loosely bound to the mineral structure, the recalculated Gibbs free energy of formation is -1745.14 kcal/mol. The difference in Gibbs free energy of formation between the input values and newly estimated values is significant (Table 6-29). Consequently, the estimated log K values for the dissociation reaction are also very different (Table 6-29). For this reason, the datablock for "Friedl Salt" in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) was commented out (i.e., inactivated) and is not considered for qualification in this report.

The analysis by Harvie et al. (1984 [DIRS 118163]) is considered comprehensive and the agreement between their model and solubility data is good (see Harvie et al. 1984 [DIRS 118163], Figure 11a, p. 738). The authors of this work have published numerous peer-reviewed studies in the evaluation of thermodynamic data for saline systems and proposed a robust thermodynamic model to explain the chemical equilibria between concentrated electrolytes and synthetic/natural phases. Thus, all these factors establish confidence in their retrieval of the standard chemical potential data for this phase. Moreover the model of Reardon (1990 [DIRS 100821] for evaluating cement-water interactions using the Pitzer approach adopts the standard chemical potential value given by Harvie et al. (1984 [DIRS 118163]).

6.3.3.5 Gehlenite Hydrate (Ca₂Al₂SiO₇•8H₂O)

Bennett et al. (1992 [DIRS 116990]) reported an average log K value of 49.16 for gehlenite hydrate (Ca₂Al₂SiO₇·8H₂O) based on the following reaction:

$$Ca_2Al_2SiO_7\cdot 8H_2O + 10H^+ = 2Ca^{++} + 2Al^{+++} + H_4SiO_4 + 11H_2O$$
 (Eq. 6-27)

Table 6-29.	Gibbs Free Energy of Formation and Log K Values for the Dissociation Reaction
	Represented by Eq. 6-26 for "Friedl Salt" in Data0.ymp.R2 Database ^a

Mineral	Formula	ΔG° _f (kcal/mol)	Log K ^b	Source
Ca-oxychloride Hydrate (R2) ^a	CaCl ₂ •3CaO•16H ₂ O	-1887	-160.3061	Spreadsheet Minerals_cal_DJ_Cement_CFJC_fix.xls (output DTN: SN0410T0510404.001)
Ca-oxychloride Hydrate (New) ^a	CaCl ₂ •3CaO•16H ₂ O	-1745.14	-56.3238	Harvie et al. 1984 [DIRS 118163]

Sources: Spreadsheet Minerals cal DJ Cement CFJC fix.xls (output DTN: SN0410T0510404.001). Babushkin et al. (1985 [DIRS 116981], Appendix I, p. 403) only reports ΔK°_f of this phase. Harvie et al. 1984 [DIRS 118163], Table 4, p.728.

Bennett et al. (1992 [DIRS 116990]) corroborated their data point using a ΔG_f° data point of -5710.281 kJ/mol at 25°C as reported in Atkins et al. (1992 [DIRS 100700], p. 73). For the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), using this value Solids j DJ Cement.xls Spreadsheet (DTN: MO0302SPATHDYN.001 [DIRS 161886]) and calculating log K gave a result of 49.22 based on the following reaction:

$$Ca_2Al_2SiO_7\cdot 8H_2O + 10H^+ = 2Ca^{++} + 2Al^{+++} + SiO_2(aq) + 13H_2O$$
 (Eq. 6-28)

This value (49.22) also compares well with the values reported in Bennett et al. (1992 [DIRS 116990]) and used data0.ymp.R2 (DTN: MO0302SPATHDYN.000 is in [DIRS 161756]).

An alternate way of corroborating these data is to take the Gibbs free energy of formation values for anhydrous gehlenite (Ca₂Al₂SiO₇) given by Babushkin et al. (1985 [DIRS 116981], Appendix I, p. 403) and Robie and Hemingway (1995 [DIRS 153683], p. 314) and approximate that of the hydrated phase by adding the equivalent Gibbs free energy of formation of eight moles of H₂O to the value for the anhydrous phase. This of course represents an approximation and implicitly assumes that H₂O is weakly attached to the mineral structure (i.e., no "structural" The resulting values are given in Table 6-30. Vieillard and Rassineux (1992) H₂O). [DIRS 120508], Table 2, p. 130) also provide a Gibbs free energy of formation value for this phase which is larger than all others reported by the above-mentioned sources.

Notice that the difference between the values obtained from various sources and that given by Atkins et al. (1992 [DIRS 100700], p. 73) is approximately within the range of 7 and 37 kJ/mol. These differences are relatively minor considering the overall uncertainty in thermochemical determinations, use of data from different sources, and the assumptions considered in this comparison. Accordingly, the comparison between the adopted value of Atkins et al. (1992) [DIRS 100700]) and handbook data ("established fact") sources provide justification for use in modeling cement-water interactions.

^a Phase incorrectly named "Friedl Salt" in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). The composition of this phase as given in the database file is for calcium oxychloride hydrate.

b See Spreadsheet *Minerals_cal_DJ_Cement_CFJC_fix.xls* (output DTN: SN0410T0510404.001) for details of the

log K calculations.

Mineral	Formula	ΔG°_{f} (kJ/mol)	Source
Gehlenite Hydrate	Ca ₂ Al ₂ SiO ₇ ·8H ₂ O ^a	-5703.22	Babushkin et al. 1985 [DIRS 116981]
Gehlenite Hydrate	Ca ₂ Al ₂ SiO ₇ ·8H ₂ O	-5673.5	Vieillard and Rassineux 1992 [DIRS 120508]
Gehlenite Hydrate	Ca ₂ Al ₂ SiO ₇ ·8H ₂ O ^a	-5682.95	Robie and Hemingway 1995 [DIRS 153683]
Gehlenite Hydrate	Ca ₂ Al ₂ SiO ₇ ·8H ₂ O ^b	-5710.28 ^b	Atkins et al. 1992 [DIRS 100700]

Table 6-30. Comparison of Gibbs Free Energy of Formation for Hydrated Gehlenite

Sources: Robie and Hemingway 1995 [DIRS 153683], p. 314.

Babushkin et al. 1985 [DIRS 116981], Appendix I, p. 403.

Atkins et al. 1992 [DIRS 100700], p. 73.

Vieillard and Rassineux 1992 [DIRS 120508], Table 2, p. 130.

6.3.3.6 Hydrotalcite (4MgO·Al₂O₃·10H₂O)

Bennett et al. (1992 [DIRS 116990]) report an average log K value for hydrotalcite of 73.78 based on the following reaction:

$$4MgO \cdot Al_2O_3 \cdot 10H_2O + 14H^+ = 4Mg^{++} + 2Al^{+++} + 17H_2O$$
 (Eq. 6-29)

The log K value for the above reaction was obtained from various solubility runs assuming congruent dissolution of the hydrotalcite phase. The distinct composition of this phase differs from hydrotalcites reported elsewhere. For this reason, obtaining corroborative thermodynamic data with the exact same composition is not possible at this point. Nevertheless, the solubility experiments of Bennett et al. (1992 [DIRS 116990]) were done on different runs and the solubility product obtained from solution composition yielded K (or K_{sp} as identified in the source) values of 73.68 and 73.87. An average value of 73.78 was then selected for data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). The authors have published numerous articles (Glasser et al. 1987 [DIRS 118111]; Atkins et al. 1991 [DIRS 116979]; Atkins et al. 1992 [DIRS 100700]; Atkins et al. 1993 [DIRS 131758]; Damidot et al. 1994 [DIRS 144866]) on the thermodynamic properties of several cement phases and this establishes confidence in the results obtained in this study. Moreover, similar K_{sp} values were obtained from duplicate runs in their study strengthening the confidence in the experimental results.

6.3.3.7 Monocarboaluminate (3CaO·Al₂O₃·CaCO₃·10H₂O)

Damidot et al. (1994 [DIRS 144866], Appendix 1) report a log K value of 69.99 for monocarboaluminate that was derived from solubility data using PHRQPITZ (a Pitzer equation version of PHREEQC). This log K was then recalculated for the following reaction:

$$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCO}_3 \cdot 10\text{H}_2\text{O} + 13\text{H}^+ = 4\text{Ca}^{++} + 2\text{Al}^{+++} + \text{HCO}_3^- + 16\text{H}_2\text{O}$$
 (Eq. 6-30)

^a Estimated from the anhydrous gehlenite phase. See text and Spreadsheet Solids_j_DJ_Cement CFJC fix.xls (output DTN: SN0410T0510404.001).

b Value adopted in this study.

The recalculated log K value (see *final carboaluminate solubility_TJW_mod.xls* in DTN: MO0302SPATHDYN.001 [DIRS 161886]) based on the solubility data using the Davies equation (Stumm and Morgan 1981 [DIRS 100829], Table 3.3) and approximating ionic strength using Eq. 2.69 in Garrels and Christ (1990 [DIRS 144877]) agrees within approximately two orders of magnitude with the value from Damidot et al. (1994 [DIRS 144866]). This value was then corrected for a basis species switch from CO₃⁻⁻ to HCO₃⁻ to give the value of 77.3538 before being entered into its data block in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]).

No alternate solubility data for this phase has been found for corroborative purposes. However, Vieillard and Rassineux (1992 [DIRS 120508], Table 2, p. 130) report an estimated value of Ca-carboaluminate phase stoichiometry ΔG°_{f} 25°C for the with the $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCO}_3 \cdot 12\text{H}_2\text{O}$. This value of ΔG°_f is -7598.1 kJ/mol. This stoichiometry has two additional waters relative to that of Damidot et al. (1994 [DIRS 144866]) given in Eq. 6-30. Assuming an enthalpy of reaction equal to zero (i.e., $\Delta H^{\circ}_{r} = 0$) and substracting the ΔG°_{f} for two moles of H₂O (i.e., -474.363 kJ/mol) from the ΔG°_{f} given by Vieillard and Rassineux (1992) [DIRS 120508]) yields a value of -7123.737 kJ/mol. The ΔG°_{f} value for the monocarboaluminate phase of Damidot et al. (1994 [DIRS 144866]) obtained from the recalculated log K of reaction (77.3538) of Eq. 6-30 and ΔG°_{f} data for the aqueous species and H₂O data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]) is -7118.885 kJ/mol. The difference between the two values is approximately 4.85 kJ/mol, which is well within the uncertainty of the experiments of Damidot et al. (1994 [DIRS 144866]) and the thermodynamic estimations of Vieillard and Rassineux (1992 [DIRS 120508]). Even though the experimental solubility data is unique, the results of the above data corroboration with all the considered assumptions qualifies the data for use in YMP. Also, the numerous contributions made by the authors in the field of experimental cement solubility further establish confidence in the data. As with other cement phases, these data are subject to large uncertainties due to limitations in the attainment of equilibrium and plausible co-existence with other cement phases (not present in the equilibrium reaction above) during the experiments.

6.3.3.8 Hemicarboaluminate (3CaO•Al₂O₃•0.5CaCO₃•0.5Ca(OH)₂•10.5H₂O)

Damidot et al. (1994 [DIRS 144866], Appendix 1) report a log K value of 85.738 for hemicarboaluminate that was derived from solubility data using PHRQPITZ. This log K is then corrected for the following reaction:

$$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 0.5\text{CaCO}_3 \cdot 0.5\text{Ca(OH)}_2 \cdot 10.5\text{H}_2\text{O} + 13.5\text{H}^+ = 4\text{Ca}^{++} + 2\text{Al}^{+++} + 0.5\text{HCO}_3^- + 17.5\text{H}_2\text{O}$$
 (Eq. 6-31)

The recalculated K value (see final carboaluminate log solubility.xls DTN: MO0302SPATHDYN.001 [DIRS 161886]) based on the solubility data using the Davies equation (Stumm and Morgan 1981 [DIRS 100829], Table 3.3) and approximating ionic strength using equation 2.69 in Garrels and Christ (1990 [DIRS 144877]) agrees within approximately two orders of magnitude with the value from Damidot et al. (1994 [DIRS 144866]). This value was then corrected for a basis species switch from CO₃⁻⁻ to HCO₃⁻ to give the value of 88.3235 before being entered into its data block in data0.vmp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]).

No alternate solubility data for this phase has been found for corroborative purposes. However, Vieillard and Rassineux (1992 [DIRS 120508], Table 2, p. 130) report an estimate if ΔG°_{f} for Ca-carboaluminate phase with the stoichiometry $3\text{CaO} \cdot \text{Al}_{2}\text{O}_{3} \cdot \text{CaCO}_{3} \cdot 12\text{H}_{2}\text{O}$ with a value of ΔG°_{f} is -7598.1 kJ/mol. Assuming an enthalpy of reaction equal to zero (i.e., $\Delta H^{\circ}_{r} = 0$), the ΔG°_{f} of the hemicarboaluminate phase can be approximated by the following reaction:

$$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 0.5\text{CaCO}_3 \cdot 0.5\text{Ca}(\text{OH})_2 \cdot 10.5\text{H}_2\text{O} = 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCO}_3 \cdot 12\text{H}_2\text{O} + 0.5\text{ Ca}(\text{OH})_2 - 0.5\text{ CaCO}_3 - 1.5\text{H}_2\text{O}$$
 (Eq. 6-32)

Using the ΔG°_f data reported by Vieillard and Rassineux (1992 [DIRS 120508], Table 2, p. 130) for 3CaO•Al₂O₃•CaCO₃•12H₂O (-7598.1 kJ/mol), Ca(OH)₂ (-898.49 kJ/mol), and CaCO₃ (-237.181kJ/mol) plus that of H₂O kJ/mol) from (-1128.76)data0.vmp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]), the resulting ΔG°_{f} at 25°C of the hemicarboaluminate phase obtained using the relation given by Eq. 6-32 yields a value of -7127.193 kJ/mol. The values for the phases CaCO₃ (calcite) and Ca(OH)₂ (portlandite) are almost identical to those in data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]). The ΔG°_{f} obtained from the data by Damidot et al. (1994 [DIRS 144866]) using the recalculated log K value (88.3235) given above and ΔG°_f data for the aqueous species and H₂O from data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]) is -7152.82 kJ/mol. The difference between the two estimated ΔG°_{f} values is approximately 26 kJ/mol, which is within the uncertainty of the experiments of Damidot et al. (1994 [DIRS 144866]) and the thermodynamic estimations of Vieillard and Rassineux (1992 [DIRS 120508]) plus all the assumptions considered in this analysis. Even though the solubility data of Damidot et al. (1994 [DIRS 144866]) is unique, the results obtained using the above relation and data corroboration qualifies the data for use in YMP. Also, the numerous contributions made by the authors in the field of experimental cement solubility further establish confidence in the data. As with other cement phases, these data are subject to large uncertainties due to limitations in the attainment of equilibrium and plausible co-existence with other cement phases (not present in the equilibrium reaction above) during the experiments.

6.3.3.9 Syngenite $(K_2Ca(SO_4)_2 \cdot H_2O)$

A log K value of -7.6 for the dissolution of syngenite for the following reaction in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) was obtained from Harvie et al. (1984 [DIRS 118163]).

$$K_2Ca(SO4)_2 \cdot H_2O = Ca^{++} + 2K^{+} + 2SO_4^{--} + H_2O$$
 (Eq. 6-33)

However, the log K value given above cannot be duplicated using the available data given in Harvie et al. (1984 [DIRS 118163]) and no documentation on how it was estimated is available. The recalculated value using the data of Harvie et al. (1984 [DIRS 118163]) yields a log K at 25°C -7.45; different from the one present in data0.vmp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) (see Table 6-25). It was decided to update this value with a more recent set of data up to elevated temperatures given by Greenberg and Moller (1989 [DIRS 152684]) from the qualified Pitzer thermodynamic database data0.ypf (DTN: SN0302T0510102.002 [DIRS 162572]). The updated value of -7.4484 will replace the

current one in the updated output database data0.ymp.R4 (output DTN: SN0410T0510404.002). The difference in log K at 25°C between both values is relatively small (approximately 0.15 log units), therefore the resulting impact of this difference is expected to be minimal considering that syngenite is a fairly soluble phase.

6.3.3.10 Uncertainty in Data for Cement Mineral Phases

The uncertainty evaluations in this section are not intended to be an exhaustive representation of all data reported. However, the data presented below represent the types of errors reported in the literature. Various reasons exist for the variation in data. They include charge imbalance in reported compositions of aqueous solutions, incongruency of dissolution, lack of complete data sets, minimal data points, and temperature dependency of dissolution to name a few. The following sections discuss two of the major sources of uncertainty inherent in geochemical modeling (experimental or analytical uncertainty and differences in results reported by different investigators).

6.3.3.10.1 Uncertainty in CSH Values

For uncertainty evaluations based on the solid solution behavior or incongruent dissolution of CSH, the information in Glasser et al. (1987 [DIRS 118111], Table I) can be used. The range in log K data reported in Glasser et al. (1987 [DIRS 118111], Table I) for the Fujii and Kondo (1981 [DIRS 158026]) data is from –16.09 to –26.17, (10.08 log units) and for the Greenberg and Chang (1965 [DIRS 144989]) data, from –15.01 to –24.34 (9.33 log units) across Ca/Si ratios of 0.76 to 1.83.

For uncertainty based on experimental and literature error, an evaluation was done using Table I in Glasser et al. (1987 [DIRS 118111]). The log K data in Glasser et al. (1987 [DIRS 118111]) was converted to log units. For the data with the Ca/Si ratio of 1.2 (labeled "Suzuki et al. [27]" in that table), the uncertainty in log K varies from -18.82 to -21.42 or about 2.61 log units. This would represent an approximate experimental error (95 percent confidence interval) in log K of \pm 1.31 log units. The differences in log K from alternative literature sources from Table I in Glasser et al. (1987 [DIRS 118111]) for all the data at or near a Ca/Si ratio of 1.2 (three separate data sets with Ca/Si ratios ranging from 1.17 to 1.25) gives the same range in variability in log K as for the single data set of Ca/Si ratio of 1.2.

6.3.3.10.2 Uncertainty in Ettringite Values

Perkins and Palmer (1999 [DIRS 152703], Table 1) provide an excellent compilation of literature sources for log K data at 25°C as well as the ranges in experimental error reported in several of the sources. The tabulated literature sources identify a 10-unit range in reported values for the log K for ettringite. The maximum experimental error reported by the sources is much smaller. For studies with charge balance errors <10%, the uncertainty is about \pm 0.6 log units (one standard deviation). Using two standard deviations or \pm 1.2 log units would represent an approximate 95 percent confidence interval.

6.3.3.10.3 Uncertainty in Hydrogarnet Values

Neall (1994 [DIRS 100807], Table C-3) evaluated both experimental and literature uncertainty for hydrogarnet log K values from six different studies. The minimum and maximum values reported in the literature are -86.6 and -89.8, respectively. These values give an uncertainty range of 3.2 log units.

The experimental or analytical error (2σ) on the mean of the six unbalanced log K values reported in Table C-2 of Neall (1994 [DIRS 100807]) is \pm 1.85 log units.

6.3.4 Evaluation and Qualification of Thermodynamic Data for Other Solids

As described in Section 4.1.7, the uranyl phases to be evaluated in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) are soddyite, uranophane, Na-weeksite, and Na-boltwoodite. The log K values given by the sources (some adjusted for changes in the mineral formulae) were used to calculate the $\Delta G^{\circ}_{\rm f}$ (standard Gibbs free energy of reaction), which was then used to calculate the $\Delta G^{\circ}_{\rm f}$ (standard Gibbs free energy of formation). The $\Delta G^{\circ}_{\rm f}$ was then used to calculate the temperature dependent log K values used in the database (calculations in Spreadsheet *Usilicates_yc_tls_ch.xls*; DTN: MO0302SPATHDYN.001 [DIRS 161886]). Extrapolation of ΔG^{0} and thus log K values to temperatures other than 25°C was done using the heat capacity estimation method used by Helgeson et al. (1978 [DIRS 101596]) and Section 6.1.4.1.

6.3.4.1 Soddyite $((UO_2)_2SiO_4\cdot 2H_2O)$

There have been several soddyite solubility studies. The Gibbs free energy of formation of soddyite was reported for a study by Nguyen et al. (1992 [DIRS 100809]) in which synthesized soddyite was used to measure solubilities at 30°C. Since equilibrium was approached from undersaturation, the value reported in Nguyen et al. (1992 [DIRS 100809]) for soddyite should be considered as its lower solubility limit (Murphy and Pabalan 1995 [DIRS 144449]) (Table 6-31).

	T		I
Source	Data Extracted	Value	Use
Nguyen et al. 1992 [DIRS 100809]	log K (25°C)	5.74 ± 0.21	Corroborative data
Moll et al. 1996 [DIRS 106349]	log K (N ₂ atmosphere experiments at 25°C)	6.03 ± 0.45	Inclusion in data0.ymp.R2 (DTN: MO0302SPATHDYN. 000 [DIRS 161756])
Moll et al. 1996 [DIRS 106349]*	$\DeltaG^_{\mathit{f}}$	-3654.41 kJ/mol	Inclusion in data0.ymp.R2 (DTN: MO0302SPATHDYN. 000 [DIRS 161756])
Chen et al. 1999 [DIRS 123270], Table 9, p. 658	ΔG°_{f} (predicted)	-3653.0 kJ/mol	Corroborative data
Chen et al. 1999 [DIRS 123270], Table 5, p. 657	ΔG°_f (measured)	-3652.8 kJ/mol	Corroborative data

Table 6-31. Sources of Soddyite Thermodynamic Data

Table 6-31. Sources of Soddyite Thermodynamic Data (Continued)

Finch 1997 [DIRS 106347], Table II, p. 1187; Nguyen et al. 1992 [DIRS 100809]	$\DeltaG^{\circ}{}_{\mathit{f}}$	-3658.0 kJ/mol	Corroborative data
McKenzie et al. 2001 [DIRS 172346], Table 1, p. 303	$\DeltaG^{\circ}{}_{f}$	–3671 kJ/mol	Corroborative data

^{*} As calculated in Spreadsheet *Usilicates_yc_tls_ch.xls* (DTN: MO0302SPATHDYN.001 [DIRS 161886]), with unit conversion from cal/mol.

Casas et al. (1994 [DIRS 100714]) reported their experimental study on the kinetics and thermodynamics of several uranium minerals. The solids used in their experiments are naturally occurring minerals, and chemical purity was not assured because of the existence of microscopic inclusions. The authors believe that soddyite formed as a secondary mineral during the process of uranophane dissolution and that soddyite was the U solubility-controlling phase. A solubility product constant for soddyite was given based on this experiment. However, this result is considered to be unreliable for several reasons as pointed out in Murphy and Pabalan (1995 [DIRS 144449]). The main reason is that the mineral of interest, soddyite, was a secondary phase of uranophane dissolution. Thus, this experiment was not a solubility experiment for soddyite per se, but rather, the solubility of soddyite was estimated from an experiment controlled by uranophane dissolution.

Moll et al. (1996 [DIRS 106349]) reported results from experiments at 25°C using synthesized soddyite. The pH in these experiments ranged from 3 to 9. Equilibrium was approached from undersaturation. The experiments were conducted in both ambient laboratory air conditions and under controlled N_2 atmosphere. The derived log K values at infinite dilution are 6.15 ± 0.53 and 6.03 ± 0.45 , respectively. Those results are relatively close to the value (5.74 ± 0.21) reported in Nguyen et al. (1992 [DIRS 100809]). The value obtained from N₂ atmosphere experiments was selected for data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), as it seems the N₂ atmosphere experiments might be better controlled (as shown in Figure 2 of Moll et al. 1996 [DIRS 106349]: the results in the N₂ atmosphere have far less irregularities than those obtained in air). The two values agree within the uncertainty range, and thus the difference between them is insignificant. To further establish confidence in this value, comparison of Gibbs free energy estimates from the empirical method used by Chen et al. (1999 [DIRS 123270], Tables 2, 5, and 9, pp. 654, 657, and 658, respectively) were compared to that extracted in this report. The value extracted using the log K (6.03 ± 0.45) given above is -873425.6 cal/mol or -3654.41 kJ/mol. The predicted value tabulated by Chen et al. (1999 [DIRS 123270], Table 9, p. 658) is -3653.0 kJ/mol. The "measured" value tabulated by Chen et al. (1999) [DIRS 123270], Table 5, p. 657) is -3652.8 kJ/mol. These values given by Chen et al. (1999) [DIRS 123270]) are in strong agreement with that estimated using the log K value of Moll et al. (1996 [DIRS 106349]). This value is also in good agreement with that reported by Finch (1997) [DIRS 106347]) and Nguyen et al. (1992 [DIRS 100809]) of -3658.0 kJ/mol. Furthermore, an intermediate value (within a range of proposed ΔG°_{f} values) of -3671 kJ/mol was estimated by the thermodynamic analysis for uranyl silicates. For these reasons, the Moll et al. (1996 [DIRS 106349]) data (Table 6-31) selected for use in this section are qualified for inclusion in the database by technical assessment and corroborative data.

There is a consistent discrepancy between data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) and the source Spreadsheet Minerals cal YC Usilicates.xls (DTN: MO0302SPATHDYN.001 [DIRS 161886]) for extrapolation of all log K values for soddyite to temperatures other than 25°C. The heat capacity coefficient data are estimated using the method of Helgeson et al. (1978 [DIRS 101596]) described in Section 6.1.4.1. These heat capacity data along with S° values are computed in Spreadsheet Usilicates vc tls ch.xls (DTN: MO0302SPATHDYN.001 [DIRS 161886]). This latter spreadsheet feeds data to Spreadsheet Minerals cal YC Usilicates.xls to calculate the extrapolated log K values. A transcription error in the S° value for soddyite was identified in Spreadsheet Minerals cal YC Usilicates.xls by comparison to the other source Spreadsheet Usilicates_vc_tls_ch.xls. Once the correct S° given by this spreadsheet is used, the log K values computed in the spreadsheet match those in data0.ymp.R2. Therefore the values in R2 are correct and are consistent with the heat capacity and standard entropy values given in Spreadsheet *Usilicates_yc_tls_ch.xls*.

6.3.4.2 Uranophane $(Ca(UO_2)_2(SiO_3OH)_2 \cdot 5H_2O)$

Table 6-32 lists the source of the uranophane thermodynamic data used for data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), and also other solubility studies, the results of which will be used as corroborative data.

Source	Data Extracted	Value	Use
Pérez et al. 2000 [DIRS 157910], p. 606	Log K (25°C)	11.7 ± 0.6	Inclusion in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756])
Pérez et al. 2000 [DIRS 157910], p. 606	$\DeltaG^{\circ}{}_{f}$	–6195.6 kJ/mol*	Inclusion in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756])
Chen et al. 1999 [DIRS 123270], Table 5, p. 657	ΔG°_{f} (measured)	-6192.3 kJ/mol	Corroborative data
Chen et al. 1999 [DIRS 123270], Table 5, p. 657	ΔG°_{f} (predicted)	-6189.2 kJ/mol	Corroborative data
Finch 1997 [DIRS 106347], Table II, p. 1187; Nguyen et al. 1992 [DIRS 100809]	$\DeltaG^_f$	–6210.6 kJ/mol	Corroborative data
McKenzie et al. 2001 [DIRS 172346], Table 1, p. 303	ΔG°_f	-6213 kJ/mol	Corroborative data

Table 6-32. Sources of Uranophane Thermodynamic Data

There have been several solubility studies conducted for uranophane. The Gibbs free energy of formation of uranophane has been reported in Nguyen et al. (1992 [DIRS 100809]) in which synthesized uranophane was used to conduct a solubility study at 30°C. A log K of 9.42 (± 0.48) was derived from experimental measurements. Since equilibrium was approached from undersaturation, the data reported in Nguyen et al. (1992 [DIRS 100809]) for uranophane should be considered as the lower solubility limit (Murphy and Pabalan 1995 [DIRS 144449]).

^{*} Value shown is calculated using input from Perez et al. (2000 [DIRS 157910]), in Spreadsheet *Usilicates_yc_tls_ch.xls* (DTN: MO0302SPATHDYN.000 [DIRS 161886]), with unit conversion from cal/mol.

Moreover, it was suspected that a secondary silica phase (e.g., amorphous silica) precipitated during the experiments (Murphy and Pabalan 1995 [DIRS 144449]).

Casas et al. (1994 [DIRS 100714]) reported their experimental study on the kinetics and thermodynamics of several uranium minerals, including uranophane. The solids used in their experiments are naturally occurring minerals, and chemical purity was not assured because of the existence of microscopic inclusions. Moreover, soddyite precipitation was observed in their uranophane solubility experiments. These observations can exert limitations in the use of their data to extract thermodynamic parameters for the single phase of interest.

Pérez et al. (2000 [DIRS 157910]) published their experimental study on uranophane dissolution thermodynamics and kinetics in bicarbonate solution in the respected peer-reviewed journal Geochimica et Cosmochimica Acta, though the results had been reported previously in a technical report (Casas et al. 1997 [DIRS 102432]). The starting material for this study at 25°C Their average measured log K value at infinite dilution is synthesized uranophane. is 11.7 (± 0.6). Pérez et al. (2000 [DIRS 157910]) also compared the Gibbs free energies of formation (ΔG°_{f}) calculated from their estimated solubility constant (log K = 11.7) obtaining a value of -6192.3 kJ/mol). The recalculated value for Gibbs free energy based on input from Perez et al. (2000 [DIRS 157910]), and thermodynamic data from data0.ymp.R2, (DTN: MO0302SPATHDYN.000 is -6195.6 kJ/mol [DIRS 161886], Spreadsheet Usilicates_vc_tls_ch.xls). These values are in very good agreement with that "predicted" by Chen et al. (1999 [DIRS 123270], Table 9, p. 658) of -6189.2 kJ/mol and the "measured" value of -6192.3 kJ/mol in the same source (Chen et al. 1999 [DIRS 123270], Table 5, p. 657). The Gibbs free energy of formation value obtained from Pérez et al. (2000 [DIRS 157910]) in this study is also in overall agreement with that of Nguyen et al. (1992 [DIRS 100809]) (and reported later by Finch (1997 [DIRS 106347]) of -6210.6 kJ/mol even with some of the limitations in the thermodynamic estimations using Nguyen et al. (1992 [DIRS 100809]) data. thermodynamic evaluation of McKenzie et al. (2001 [DIRS 172346]) recommended a ΔG°_f value of -6213 kJ/mol, which is also in overall agreement with that adopted in this study. Based on all these data comparisons, the Perez et al. (2000 [DIRS 157910]) data selected for use in this section are qualified for inclusion in the database by data corroboration.

There is a consistent discrepancy between data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) and source Spreadsheet *Minerals_cal_YC_Usilicates.xls* the (DTN: MO0302SPATHDYN.001 [DIRS 161886]) for extrapolation of all log K values for uranophane to temperatures other than 25°C. The heat capacity coefficient data are estimated using the method of Helgeson et al. (1978 [DIRS 101596]) described in Section 6.1.4.1. These heat capacity coefficient data along with So values are computed in the Spreadsheet Usilicates_yc_tls_ch.xls (MO0302SPATHDYN.001 [DIRS 161886]). This latter spreadsheet feeds data to Spreadsheet Minerals_cal_YC_Usilicates.xls to calculate the extrapolated log K values. A transcription error for the S° value for uranophane was identified in Spreadsheet Minerals_cal_YC_Usilicates.xls by comparison to the other source Usilicates ye tls ch.xls. When the correct S° value given by this spreadsheet is used, the log K values computed in the spreadsheet match those in data0.ymp.R2. Therefore the values in R2 are correct and are consistent with the heat capacity and standard entropy values given in Spreadsheet *Usilicates* yc tls ch.xls.

6.3.4.3 Sodium Weeksite $(Na_2(UO_2)_2(Si_5O_{13})\cdot 3H_2O)$

The reported log K at 30°C by Nguyen et al. (1992 [DIRS 100809]) is 1.50±0.08 for a formula of $Na_2(UO_2)_2(Si_2O_5)_3 \cdot 4H_2O$. Chen et al. (1999 [DIRS 106346]) suggest that a different formula (Na₂(UO₂)₂(Si₅O₁₃) ·3H₂O) be used for sodium weeksite (see Appendix 1 in Chen et al. (1999 [DIRS 106346], p. 66). With this formula, the log K value was rederived from the original experimental data reported in Nguyen et al. (1992 [DIRS 100809]), as 3.97 (at 30°C) (see Spreadsheet *Minerals_cal_YC_Usilicates.xls*; DTN: MO0302SPATHDYN.001 [DIRS 161886]). The extracted Gibbs free energy of formation at 25°C from this log K value given in this spreadsheet is -1912843.6 cal/mol or -8003.34 kJ/mol. The latter value is in strong agreement with that predicted by Chen et al. (1999 [DIRS 123270], Table 5, p. 657) of -8001.8 kJ/mol. The relatively small difference in the Gibbs free energies of formation between these two, which is much smaller than the Gibbs free energy of formation of one mole of H₂O, justifies the use of the stoichiometry proposed by Chen et al. (1999 [DIRS 123270]). Therefore, the log K value is used in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). The data selected for use in this section are qualified for inclusion in the database by data corroboration.

There is discrepancy between data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) Spreadsheet Minerals cal YC Usilicates.xls and the source (DTN: MO0302SPATHDYN.001 [DIRS 161886]) for log K values for Na-weeksite. transcription error in the S° value, similar to that identified for soddyite and uranophane, was identified for this phase as well. However, after correcting this value the discrepancy in the calculated log K values still remains. The maximum difference between the corrected values and those in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) is insignificant (approximately 0.003 log K units) and within the uncertainty in the log K at 25°C given by the source (± 0.08). Hence the values used in data0.ymp.R2 for Na-weeksite are qualified although the cause of the discrepancy cannot be determined (it may be related to extrapolation of log K from 30°C to 25°C).

6.3.4.4 Sodium Boltwoodite (Na(UO₂)(SiO₃)(OH)·1.5H₂O)

The reported log K value for this phase at 30°C by Nguyen et al. (1992 [DIRS 100809]) is $\geq 5.82 \pm 0.16$ for a formula of Na(H₃O)(UO₂)(SiO₄)·H₂O. Since soddyite was observed in this solubility experiment, the log K value should be considered to be a minimum value. In a recent comprehensive study of boltwoodite, Burns (1998 [DIRS 127210]) recommended that a different formula (Na(UO₂)(SiO₃)(OH)·1.5H₂O) be adopted. With this formula, the log K value was rederived from the original experimental data reported in Nguyen et al. (1992 [DIRS 100809]), extrapolated to infinite dilution, as ≥ 5.97 at 25°C (no significant change in log K because of the (DTN: MO0302SPATHDYN.001 different formula) [DIRS 161886], Spreadsheet: Minerals cal YC Usilicates.xls, Worksheet: Na-boltwoodite 30Cto25C). extracted Gibbs free energy of formation based on this log K value is -2845.42 kJ/mol (at 25°C). The predicted value for Gibbs free energy of formation given by the empirical thermodynamic estimation of Chen et al. (1999 [DIRS 123270], Table 5, p. 657) is -2838.9 kJ/mol which is in strong agreement with that extracted from Nguyen et al. (1992 [DIRS 100809]) data and the analysis explained above. Moreover, McKenzie et al. (2001 [DIRS 172346]) recommended a value of -2839 kJ/mol based on their analysis of thermodynamic properties of uranyl silicates. The "measured" value of -2844.8 kJ/mol given by Chen et al. (1999 [DIRS 123270], Table 5, p. 657) (see also Appendix 1 in Chen et al. (1999 [DIRS 106346], p. 66)) is even closer to that determined from Nguyen et al. (1992 [DIRS 100809]) data. Therefore, this log K value is recommended for inclusion in the database. The data selected for use in this section are qualified for inclusion in the database by data corroboration.

There is discrepancy between data0.ymp.R2 (DTN: MO0302SPATHDYN.000 source Spreadsheet Minerals cal YC Usilicates.xls [DIRS 161756]) and the (DTN: MO0302SPATHDYN.001 [DIRS 161886]) for log K values for Na-boltwoodite. A transcription error in the S° value, similar to that identified for soddyite and uranophane, was identified for this phase as well. However, after correcting this value the discrepancy in the calculated log K values still remains. The maximum difference between the corrected values and those in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) is insignificant (approximately 0.007 log K units) and within the uncertainty in the log K at 25°C given by the source (±0.16). Hence the values used in data0.ymp.R2 for Na-boltwoodite are qualified although the cause of the discrepancy cannot be determined (it may be related to extrapolation of log K from 30°C to 25°C).

6.3.4.5 Qualified Equilibrium Constant Grids for Other Solid Phases from Compilations and Handbooks

Large data sets were obtained from well known compilations that include the OECD/NEA Database (Lemire 2001 [DIRS 159027]) and the compilations in Binnewies and Milke (1999 [DIRS 158955]) and Barin and Platzki (1995 [DIRS 157865]). Binnewies and Milke (1999 [DIRS 158955]) is a recent comprehensive compilation of thermodynamic data that draws on six references, four of which are relevant to this effort. The six references draw on a large set of published and unpublished thermodynamic data, although those references are not listed in Binnewies and Milke (1999 [DIRS 158955]). Barin and Platzki (1995 [DIRS 157865]) is also a comprehensive compilation of thermodynamic data that includes extensive lists of references. The OECD/NEA has recently published the results of an extensive peer review of thermodynamic data for neptunium and plutonium (Lemire 2001 [DIRS 159027]). This panel gathered a wide range of peer review publications, government publications, and previous compilations of data. Using corroborating data, peer review, and technical assessment, details of which are documented in the published book, the panel of internationally recognized scientists reached consensus on the best available thermodynamic data for neptunium and plutonium. These handbooks were chosen because they are recent, comprehensive, unique, and generally accepted within the scientific community. Their data sources were reviewed and assessed (to varying degrees) with regard to data quality prior to publication. The data selected for inclusion in the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) were derived from these sources using the methods discussed in Section 6.1. Results are shown in Table 6-33.

In the current qualification stage of this database, transcription errors in the heat capacity coefficients were found for Np and Pu solids as obtained from Lemire (2001 [DIRS 159027]). Also, other transcription errors related to the "c" heat capacity coefficient for several solids species from Binnewies and Milke (1999 [DIRS 158955]) were found in the calculation spreadsheets. For all these solids, the problem stems from the incorrect scaling of heat capacity

coefficients when implemented in the spreadsheets used in the development of the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]). Np and Pu heat capacity coefficients were extracted from Tables 3.3 and 4.3 of Lemire (2001 [DIRS 159027]) to correspond with the parameters a, b, and c of the Maier-Kelly equation (Eq. 4-1). The problems with this approach are: 1) a difference by a factor of 1000 on the "b" parameter, 2) the "c" parameter was ignored in many cases, and 3) in a few cases the adopted coefficients were inappropriately applied as Maier-Kelly parameters. For the last case, the heat capacity equation used by Lemire (2001 [DIRS 159027]) contains the same terms as the Maier-Kelley equation but also has additional terms that are entirely different. Taking into account that if the only fitting terms used by Lemire (2001 [DIRS 159027]) match those of the Maier-Kelly equation (assuming the other terms are zero), then these are readily transferable to Eq. 4-1. Conversely, if more terms are used by Lemire (2001 [DIRS 159027]) that do not correspond to the Maier-Kelly equation, then a complete refitting of the data must be done since there is a break in correspondence between the usage of the two formulations.

In this case of inappropriate implementation of Maier-Kelley parameters (Item 3 above), only one Np and several Pu species were affected: $NpC_{0.91}(cr)$, $Pu_2C_3(cr)$, $PuC_{0.84}(cr)$, PuOI(cr), PuOF(cr), and $PuO_2(cr)$. The effect of this error on these species is not quantitatively evaluated in this report, and the corrected log K values listed in Table 6-34 are based on the assumption of a negligible effect on the computed heat capacity as a function of temperature. Accordingly, a reevaluation of these log K values using the proper heat capacity function is recommended if log K values for temperatures other than 25°C are to be used.

For all these reasons, the log K values extrapolated to temperatures other than 25°C are incorrect. In many cases, except for two exceptions, the maximum deviations in the log K values are relatively small, generally less than 0.2 log K at 300°C. There are two cases (NpF₆ and PuF₆) in which the difference can be as large as 1 log K unit. These deviations increase with increasing temperature. Table 6-34 shows the affected Np and Pu solid phases with the corrected log K values. Table 6-35 shows the difference in log K as a function of temperature. Notice that in general, the maximum differences do not exceed a $\Delta \log K$ of approximately 0.3 in the worst The located in the source case. corrected values can Spreadsheets Minerals_j_PVB_Pu_CFJC_fix.xls and *Minerals_j_PVB_Np_CFJC_fix.xls* (output DTN: SN0410T0510404.001) and have been incorporated in data0.vmp.R4 (output DTN: SN0410T0510404.002).

Log K values for other solid species computed using thermodynamic data from Barin and Platzki (1995 [DIRS 157865]) and Binnewies and Milke (1999 [DIRS 158955]) are listed in Table 6-33. In revising the heat capacity coefficient data in Table 4-14, an error was identified corresponding to the correct scaling of the "c" coefficient for the solid species shown in Table 6-36. The scaling difference between source and adopted values in this work is by a factor of 10. The corrected log K values upon correction of this heat capacity term in the source spreadsheets are given in Table 6-37. The ΔLog K (difference between incorrect and corrected values) values are given in Table 6-38. Notice in this table that the maximum difference is on the order of 0.1 to 0.6 log K units at 300°C which is considered insignificant given the inherent uncertainties in the source data.

The combined use of different sets of thermodynamic could generate discrepancy between the retrieved thermodynamic parameters generated to this study (e.g., ΔG_f° and log K). In this report, two types of thermodynamic data (ΔG_f° and ΔH_f° ; S° and Cp°) from two different sources (Barin and Platzki 1995 [DIRS 157865], and Binnewies and Milke 1999 [DIRS 158955], respectively) were combined in the source spreadsheets. To anyone knowledgeable in the manipulation of thermodynamic parameters such mixing of data could translate into some level of inconsistency that could affect the resulting log K value adopted in this report. That is, the retrieved log K value as obtained using reference-state thermodynamic data from two different sources can have some level of discrepancy due to differences in the standard-state thermodynamic data adopted by each source. In the case of the affected solid species given in Table 6-39, the ΔG_f° values were obtained from Barin and Platzki (1995 [DIRS 157865]) and the heat capacity data (Cp°) used to extrapolate the apparent Gibbs free energy of formation to temperatures other than 25°C were obtained from Binnewies and Milke (1999 [DIRS 158955]). This combination of data can be justified if the source thermodynamic data used to derived values of ΔG_f° (i.e., ΔH_f° and S°) are identical or at least very close within the uncertainty reported in each source. Table 6-39 show a comparison of ΔH_f° and S° values given by Barin and Platzki (1995 [DIRS 157865]) and Binnewies and Milke (1999 [DIRS 158955]) for the affected solid species, respectively. As can be seen in Table 6-39, in general the maximum difference in ΔH₅° is approximately 41 kJ/mol (the case for Ferrite-Ca). The majority of the differences in ΔH_f° values between the two sources range from less than 5 kJ/mol to approximately 15 kJ/mol. For the most part, even when these differences can have non-negligible effects on the estimated log K of reaction, the average percentage difference evaluated for the whole ΔH_f° data set in Table 6-39 does not exceed approximately 0.5%. Of course, in some cases, the difference can be larger but this needs to be evaluated separately for specific cases.

The difference in S° values between the two sources does not exceed 7 kJ/mol in most cases. These differences are deemed small given the observed range of values observed for this thermodynamic parameter. If all the differences in the data were evaluated as a whole, the average difference would be on the order of 0.2 J/mol-K or approximately 1.2%. In general, given the observed bulk differences, it is not expected that the combined use of these data should generate large inconsistencies that could significantly affect the extrapolation of log K values at various temperatures. However, in cases where substantial inconsistencies exist and/or data is deemed suspect, further evaluation of the thermodynamic parameter is required.

Table 6-33. Log K EQ3/6 Grids for Solid Phases

Data0.ymp.R2 Species Name ^a	Reaction	log K 0.01°C	log K 25°C	log K 60°C	log K 100°C	log K 150°C	log K 200°C	log K 250°C	log K 300°C
(NH ₄) ₄ NpO ₂ (CO ₃) ₃	$(NH_4)_4NpO_2(CO_3)_3 = NpO_2^{++} + H^+ + 4NH_3(aq) + 3HCO_3^-$	-	-32.7086	-	-	-	-	-	-
Portlandite	$Ca(OH)_2 + 2H^+ = Ca^{++} + 2H_2O$	24.6086	22.5444	20.1812	18.0331	15.9215	14.2416	12.8472	11.6332
Ferrite-Dicalcium	$Ca_2Fe_2O_5 + 10H^+ = 2Ca^{++} + 2Fe^{+++} + 5H_2O$	64.4019	56.8114	48.0430	40.0003	31.9910	25.4933	19.9542	14.9759
Ca ₃ Al ₂ O ₆	$Ca_3Al_2O_6 + 12H^+ = 3Ca^{++} + 2Al^{+++} + 6H_2O$	124.6741	111.6139	96.5236	82.6676	68.8804	57.7558	48.3914	40.1572
CaAl ₂ O ₄	$CaAl_2O_4 + 8H^+ = Ca^{++} + 2Al^{+++} + 4H_2O$	52.2849	45.5699	37.7772	30.5932	23.3999	17.5331	12.5163	8.0178
Pseudowollastonite	$CaSiO_3 + 2H^+ = Ca^{++} + SiO_2(aq) + H_2O$	15.4002	14.0344	12.3769	10.8345	9.3058	8.0809	7.0433	6.0865
Titanite	CaSiTiO ₅ + 2H ⁺ + H ₂ O = Ti(OH) ₄ + Ca ⁺⁺ + SiO ₂ (aq)	2.8906	1.9918	0.7864	-0.3694	-1.5167	-2.4339	-3.2249	-4.0075
Perovskite	$CaTiO_3 + 2H^+ + H_2O = Ti(OH)_4 + Ca^{++}$	12.8665	11.0419	8.8548	6.8252	4.8119	3.1997	1.8439	0.6201
Co(OH) ₂	$Co(OH)_2 + 2H^+ = Co^{++} + 2H_2O$	14.5818	13.0671	11.3386	9.7790	8.2566	7.0476	6.0355	5.1363
Spinel-Co	$Co_3O_4 + 8H^+ = Co^{++} + 2Co^{+++} + 4H_2O$	-8.7738	-10.4344	-12.3917	-14.2060	-16.0687	-17.6943	-19.2575	-20.8940
CoCl ₂	$CoCl_2(s) = Co^{++} + 2Cl^{-}$	9.4850	8.2904	6.7186	5.0820	3.2084	1.4315	-0.3634	-2.3549
CoF ₃ ^b	$CoF_3 = Co^{+++} + 3F^-$	0.5298	-1.3201	-3.7465	-6.2538	-9.1083	-11.8169	-14.5685	-17.6326
Sphaerocobaltite	$CoCO_3(s) + H^+ = Co^{++} + HCO_3^-$	1.3201	0.7971	0.1047	-0.6184	-1.4547	-2.2664	-3.1146	-4.0936
CoCr ₂ O ₄	$CoCr_2O_4 + 8H^+ = Co^{++} + 2Cr^{+++} + 4H_2O$	19.2781	15.0442	10.1278	5.6052	1.0693	-2.6715	-5.9511	-9.0071
CoF ₂	$CoF_2 = Co^{++} + 2F^{-}$	-0.6816	-1.5187	-2.6692	-3.9012	-5.3543	-6.7866	-8.3009	-10.0662
CoFe ₂ O ₄	$CoFe_2O_4 + 8H^+ = Co^{++} + 2Fe^{+++} + 4H_2O$	13.4374	10.0104	6.0324	2.3757	-1.2984	-4.3496	-7.0622	-9.6472
CoO	$CoO + 2H^{+} = Co^{++} + H_2O$	15.2509	13.5557	11.6049	9.8261	8.0691	6.6585	5.4696	4.4118
CoTiO ₃	$CoTiO_3 + 2H^+ + H_2O = Co^{++} + Ti(OH)_4(aq)$	18.2260	17.0136	15.5294	14.1469	12.7758	11.6719	10.7238	9.8303
CoWO ₄	$CoWO_4 = Co^{++} + WO_4^{}$	-11.9847	-11.7760	-11.7291	-11.8788	-12.2822	-12.8981	-13.7588	-14.9905

Table 6-33. Log K EQ3/6 Grids for Solid Phases (Continued)

Data0.ymp.R2 Species Name ^a	Reaction	log K 0.01°C	log K 25°C	log K 60°C	log K 100°C	log K 150°C	log K 200°C	log K 250°C	log K 300°C
Eskolaite	$Cr_2O_3 + 2H_2O + 1.5O_2(g) = 2CrO_4^{} + 4H^+$	-11.5436	-12.2116	-13.4372	-15.0171	-17.1381	-19.4062	-21.9006	-24.8658
CrCl₃	$CrCl3(s) = Cr^{+++} + 3Cl^{-}$	22.9486	19.9413	16.1747	12.4178	8.3039	4.5844	1.0134	-2.7177
CrF ₃	$CrF_3(s) = Cr^{+++} + 3F^{-}$	-7.8776	-9.0957	-10.7894	-12.6210	-14.8039	-16.9783	-19.2950	-21.9974
Crl ₃	$Crl_3 = Cr^{+++} + 3l^-$	30.7636	27.4198	23.2699	19.1619	14.7015	10.7132	6.9359	3.0557
CrO ₃	$CrO_3 + H_2O = CrO_4^{} + 2H^+$	-3.2049	-3.2201	-3.4762	-3.9529	-4.7213	-5.6408	-6.7279	-8.0893
Cs ₂ NaPuCl ₆	$Cs_2NaPuCl_6 = Pu^{+++} + Na^+ + 2Cs^+ + 6Cl^-$	12.6910	11.9903	10.7216	9.1448	7.0406	4.7083	1.9462	-1.6789
Cs ₂ NpBr ₆	$Cs_2NpBr_6 = Np^{++++} + 2Cs^+ + 6Br^-$	-	13.8968	-	-	-	-	-	-
Cs ₂ NpCl ₆	$Cs_2NpCl_6 = Np^{++++} + 2Cs^+ + 6Cl^-$	-	5.2219	-	_	-	-	-	-
Cs ₂ PuBr ₆	$Cs_2PuBr_6 = Pu^{++++} + 2Cs^{+} + 6Br^{-}$	-	8.9929	-	_	-	-	-	-
Cs ₂ PuCl ₆	$Cs_2PuCl_6 = Pu^{++++} + 2Cs^{+} + 6Cl^{-}$	-	1.8950	-	-	-	-	-	-
Cs ₃ PuCl ₆	$Cs_3PuCl_6 = Pu^{+++} + 3Cs^{+} + 6Cl^{-}$	76.2003	70.6870	63.7161	56.7397	49.1001	42.2114	35.6138	28.7057
CsPu ₂ Cl ₇	$CsPu_2Cl_7 = 2Pu^{+++} + Cs^+ + 7Cl^-$	31.8161	28.1392	23.2011	17.9835	11.9216	6.0813	0.0880	-6.6516
Ferrite-Cu	$CuFe_2O_4 + 8H^+ = Cu^{++} + 2Fe^{+++} + 4H_2O$	13.0021	9.5266	5.4967	1.7969	-1.9118	-4.9806	-7.6956	-10.2679
Iron	$Fe + 2H^{+} + 0.5O_{2}(g) = Fe^{++} + H_{2}O$	63.6422	57.5836	50.6277	44.2848	38.0433	33.1025	29.0637	25.6580
Fe(OH) ₂	$Fe(OH)_2(s) + 2H^+ = Fe^{++} + 2H_2O$	15.3413	13.8214	12.0765	10.4910	8.9312	7.6838	6.6348	5.7012
Fe(OH)₃	$Fe(OH)_3(s) + 3H^+ = Fe^{+++} + 3H_2O$	6.9977	5.6581	4.1257	2.7413	1.3775	0.2679	-0.7022	-1.6141
Fe ₂ (SO ₄) ₃	$Fe_2(SO_4)_3(s) = Fe^{+++} + 3SO_4^{}$	4.5147	0.8936	-3.9957	-9.1664	-15.1498	-20.8688	-26.6630	-33.0596
hercynite	$FeAl_2O_4 + 8H^+ = Fe^{++} + 2Al^{+++} + 4H_2O$	27.2135	22.4207	16.8317	11.6611	6.4509	2.1479	-1.6071	-5.0680
lawrencite	FeCl ₂ = Fe ⁺⁺ + 2Cl ⁻	10.3376	9.0646	7.4040	5.6877	3.7361	1.8968	0.0484	-1.9931
molysite	FeCl ₃ (s) = Fe ⁺⁺⁺ + 3Cl ⁻	15.8514	13.5217	10.5451	7.5206	4.1357	0.9961	-2.1068	-5.4602
chromite	$FeCr_2O_4 + 8H^+ = Fe^{++} + 2Cr^{+++} + 4H_2O$	21.4464	16.9730	11.7841	7.0157	2.2433	-1.6773	-5.0937	-8.2518
FeF ₂	$FeF_2(s) = Fe^{++} + 2F^{-}$	-0.5959	-1.4320	-2.5782	-3.8024	-5.2429	-6.6604	-8.1584	-9.9065
FeF ₃	$FeF_3(s) = Fe^{+++} + 3F^{-}$	-19.1368	-19.2386	-19.6397	-20.2803	-21.2782	-22.5050	-24.0432	-26.0946
Goethite	$FeOOH(s) + 3H^{+} = Fe^{+++} + 2H_{2}O$	1.5251	0.5347	-0.6066	-1.6494	-2.7014	-3.5942	-4.4184	-5.2402
Ferrite-Ca	$CaFe_2O_4 + 8H^+ = 2Fe^{+++} + Ca^{++} + 4H_2O$	25.8281	21.5945	16.7003	12.2140	7.7348	4.0632	0.8671	-2.0967
Ferrite-Ni	$NiFe_2O_4 + 8H^+ = 2Fe^{+++} + Ni^{++} + 4H_2O$	13.1975	9.7959	5.8444	2.2106	-1.4416	-4.4763	-7.1766	-9.7520

Table 6-33. Log K EQ3/6 Grids for Solid Phases (Continued)

Data0.ymp.R2 Species Name ^a	Reaction	log K 0.01°C	log K 25°C	log K 60°C	log K 100°C	log K 150°C	log K 200°C	log K 250°C	log K 300°C
FeSO ₄	$FeSO_4(s) = Fe^{++} + SO_4^{}$	3.0095	1.9396	0.4732	-1.0933	-2.9213	-4.6831	-6.4843	-8.4996
Ilmenite	$FeTiO_3 + 2H^+ + H_2O = Ti(OH)_4 + Fe^{++}$	4.7306	3.3187	1.6078	0.0209	-1.5482	-2.8051	-3.8743	-4.8659
K ₄ NpO ₂ (CO ₃) ₃	$K_4NpO_2(CO_3)_3 + 3H^+ = NpO_2^{++} + 4K^+ + 3HCO_3^-$	-	4.5920	-	-	-	-	-	-
MgBr ₂	$MgBr_2 = Mg^{++} + 2Br^-$	30.5643	27.6871	24.1881	20.8077	17.2423	14.1551	11.3222	8.4951
Chloromagnesite	$MgCl_2 = Mg^{++} + 2Cl^-$	24.2691	21.8099	18.7942	15.8518	12.7075	9.9394	7.3482	4.7003
MgSO ₄	$MgSO_4 = Mg^{++} + SO_4^{}$	6.2374	4.8818	3.0998	1.2626	-0.8107	-2.7478	-4.6772	-6.7870
Bixbyite	$Mn_2O_3 + 6H^+ = 2Mn^{+++} + 3H_2O$	2.5123	0.0527	-2.8289	-5.5008	-8.2129	-10.4932	-12.5452	-14.5141
Tephroite	$Mn_2SiO_4 + 4H^{+} = 2Mn^{++} + SiO_2(aq) + 2H_2O$	26.8129	24.2091	21.1411	18.3322	15.5705	13.3635	11.4914	9.7712
Scacchite	$MnCl_2 = Mn^{++} + 2Cl^-$	10.3334	9.2222	7.7576	6.2301	4.4744	2.7984	1.0891	-0.8326
MnSO ₄	$MnSO_4 = Mn^{++} + SO_4^{}$	4.0667	3.1105	1.7833	0.3516	-1.3374	-2.9856	-4.6947	-6.6381
MoO ₂ Cl ₂	$MoO_2Cl_2 + 2H_2O = MoO_4^{} + 2Cl^- + 4H^+$	1.0071	0.5936	-0.2793	-1.4889	-3.2010	-5.1125	-7.2954	-9.9885
Na ₂ CO ₃	$Na_2CO_3 + H^+ = 2Na^+ + HCO_3^-$	11.6083	10.9840	10.2407	9.5499	8.8427	8.2248	7.6155	6.9083
Na ₂ CrO ₄	$Na_2CrO_4 = 2Na^+ + CrO_4^{}$	3.8172	3.5616	3.0862	2.4882	1.6936	0.8277	-0.1710	-1.4480
Na ₃ NpF ₈	$Na_3NpF_8 + 2H_2O = NpO_2^+ + 3Na^+ + 4H^+ + 8F^-$	-7.2108	-8.4426	-10.5799	-13.2060	-16.6535	-20.3726	-24.6157	-29.9430
Na ₃ NpO ₂ (CO ₃) ₂	$Na_3NpO_2(CO_3)_2 + 2H^+ = NpO_2^+ + 3Na^+ + 2HCO_3^-$	-	5.9485	-	-	-	-	-	-
Nahcolite	NaHCO ₃ = Na ⁺ + HCO ₃ ⁻	-1.0584	-0.7061	-0.3492	-0.0651	0.1539	0.2439	0.1989	-0.0343
NaNpO ₂ CO ₃	$NaNpO_2CO_3 + H^+ = NpO_2^+ + Na^+ + HCO_3^-$	-	-1.3265	-	-	-	-	-	-
NaNpO ₂ CO ₃ ·3.5H ₂ O	$NaNpO_2CO_3 \cdot 3.5H_2O + H^+ = NpO_2^+ + Na^+ + HCO_3^- + 3.5H_2O$	-	-0.8000	-	-	-	-	-	-
Heazlewoodite	$Ni_3S_2 + 4H^+ + 0.5O_2(g) = 3Ni^{++} + 2HS^- + H_2O$	28.6004	24.4693	19.5027	14.7638	9.8201	5.5688	1.6743	-2.2027
NiCl ₂	$NiCl_2(s) = Ni^{++} + 2Cl^-$	9.8343	8.5926	6.9613	5.2662	3.3313	1.5025	-0.3371	-2.3675
NiCO ₃	$NiCO_3 + H^+ = Ni^{++} + HCO_3^-$	3.3189	2.5700	1.6085	0.6310	-0.4648	-1.4889	-2.5152	-3.6457
NiCr ₂ O ₄	$NiCr_2O_4 + 8H^+ = Ni^{++} + 2Cr^{+++} + 4H_2O$	28.7772	23.6681	17.7383	12.2829	6.8212	2.3437	-1.5369	-5.0928

Table 6-33. Log K EQ3/6 Grids for Solid Phases (Continued)

Data0.ymp.R2 Species Name ^a	Reaction	log K 0.01°C	log K 25°C	log K 60°C	log K 100°C	log K 150°C	log K 200°C	log K 250°C	log K 300°C
NiF ₂	$NiF_2(s) = Ni^{++} + 2F^-$	0.7826	-0.2087	-1.5390	-2.9364	-4.5527	-6.1140	-7.7328	-9.5842
Trevorite	$NiFe_2O_4 + 8H^+ = Ni^{++} + 2Fe^{+++} + 4H_2O$	13.1975	9.7959	5.8444	2.2106	-1.4395	-4.4690	-7.1591	-9.7170
NiSO ₄	NiSO ₄ = Ni ⁺⁺ + SO ₄	6.7405	5.3469	3.4997	1.5773	-0.6099	-2.6624	-4.7049	-6.9235
NiTiO ₃	$NiTiO_3 + 2H^+ + H_2O = Ti(OH)_4 + Ni^{++}$	3.5707	2.2603	0.6583	-0.8359	-2.3208	-3.5179	-4.5440	-5.5036
NiWO ₄	$NiWO_4 = Ni^{++} + WO_4^{}$	-11.3005	-11.1792	-11.2395	-11.4931	-12.0046	-12.7110	-13.6490	-14.9474
Np	$Np + 3H^{+} + 0.75O_{2}(g) = Np^{+++} + 1.5H_{2}O$	167.5198	152.1799	134.5685	118.5020	102.6895	90.1833	79.9918	71.4644
Np ₂ C ₃	$Np_2C_3 + 3H^+ + 4.5O_2(g) = 2Np^{+++} + 3HCO_3^-$	-	454.4742	-	-	-	-	-	-
Np ₂ O ₅	$Np_2O_5 + 2H^+ = 2NpO_2^+ + H_2O$	4.9273	3.7031	2.1851	0.7083	-0.8437	-2.1654	-3.3362	-4.4215
NpBr ₃	$NpBr_3 = Np^{+++} + 3Br^{-}$	23.3944	20.9379	17.8033	14.6332	11.1113	7.8740	4.7046	1.3143
NpBr ₄	$NpBr_4 = Np^{++++} + 4Br^{-}$	34.0066	29.8101	24.6456	19.5826	14.1296	9.2708	4.6508	-0.1567
NpC _{0.91} ^c	$NpC_{0.91} + 2.09H^{+} + 1.66O_{2}(g) = Np^{+++} + 0.91HCO_{3}^{-} + 0.59H_{2}O$	214.6543	194.6217	171.5153	150.3170	129.3115	112.5628	98.7826	87.0847
NpCl ₃	$NpCl_3 = Np^{+++} + 3Cl^-$	15.4616	13.4766	10.8967	8.2378	5.2187	2.3732	-0.4864	-3.6310
NpCl ₄	NpCl ₄ = Np ⁺⁺⁺⁺ + 4Cl ⁻	24.9789	21.2634	16.6639	12.1176	7.1657	2.6901	-1.6343	-6.2149
NpF ₃	$NpF_3 = Np^{+++} + 3F^-$	-17.9938	-17.9369	-18.1661	-18.6598	-19.5272	-20.6659	-22.1483	-24.1670
NpF ₄	$NpF_4 = Np^{++++} + 4 F^-$	-28.6696	-28.9106	-29.5061	-30.3649	-31.6518	-33.2169	-35.1861	-37.8324
NpF ₅	$NpF_5 + 2H_2O = NpO_2^+ + 5F^- + 4H^+$	3.4168	1.3534	-1.5326	-4.6702	-8.3916	-12.0297	-15.7970	-20.0725
NpF ₆	$NpF_6 + 2H_2O = NpO_2^{++} + 4H^+ + 6F^-$	34.9278	29.8193	23.4792	17.2248	10.4509	4.3751	-1.4543	-7.6196
NpI ₃	$NpI_3 = Np^{+++} + 3I^-$	30.2029	27.3544	23.7833	20.2153	16.2960	12.7396	9.3101	5.7084
NpN	$NpN + 3H^{+} = Np^{+++} + NH_{3}(aq)$	52.2385	47.2199	41.4250	36.1113	30.8387	26.6081	23.0814	20.0350
NpO ₂	$NpO_2 + 4H^+ = Np^{++++} + 2H_2O$	-8.8615	-9.7398	-10.7021	-11.5341	-12.3305	-12.9874	-13.6028	-14.2445
NpO ₂ (hyd, aged)	$NpO_2 + 4H^+ = Np^{++++} + 2H_2O$	-	1.5445	-	-	-	-	-	-
NpO ₂ (NO ₃) ₂ ·6H ₂ O	$NpO_2(NO_3)_2 \cdot 6H_2O = NpO_2^{++} + 2NO_3^{-} + 6H_2O$	-	2.2370	-	-	-	-	-	-
NpO ₂ CO ₃	$NpO_2CO_3 + H^+ = NpO_2^{++} + HCO_3^-$	-	242.0251	-	-	-	-	-	-
NpO ₂ OH(am)	$NpO_2OH + H^+ = NpO_2^+ + H_2O$	-	4.7072	-	-	-	-	-	-
NpO ₂ OH(am, aged)	$NpO_2OH + H^+ = NpO_2 + + H_2O$	-	5.3074	-	-	-	-	-	-

Table 6-33. Log K EQ3/6 Grids for Solid Phases (Continued)

Data0.ymp.R2 Species Name ^a	Reaction	log K 0.01°C	log K 25°C	log K 60°C	log K 100°C	log K 150°C	log K 200°C	log K 250°C	log K 300°C
NpO₃·H₂O	$NpO_3 \cdot H_2O + 2H^+ = NpO_2^{++} + 2H_2O$	-	5.4844	-	-	-	-	-	-
NpOBr ₂	$NpOBr_2 + 2H^+ = Np^{++++} + 2 Br^- + H_2O$	7.3740	5.2794	2.7147	0.2116	-2.4896	-4.9259	-7.2945	-9.8236
NpOCl ₂	$NpOCl_2 + 2H^+ = Np^{++++} + 2CI^- + H_2O$	7.6908	5.4117	2.6464	-0.0340	-2.9065	-5.4782	-7.9587	-10.5850
Pu	$Pu + O_2(g) + 4H^+ = Pu^{++++} + 2H_2O$	184.6832	166.8458	146.4193	127.8270	109.5673	95.1509	83.4149	73.5976
Pu(HPO ₄) ₂ (am,hyd)	$Pu(HPO_4)_2 = Pu^{++++} + 2HPO_4^{}$	-	-32.8499	-	-	-	-	-	-
Pu(OH) ₃	$Pu(OH)_3 + 3H^+ = Pu^{+++} + 3H_2O$	-	15.8218	-	-	-	-	-	-
Pu ₂ C ₃ ^c	$Pu_2C_3 + 3H^+ + 4.5O_2(g) = 2Pu^{+++} + 3HCO_3^-$	533.5333	483.9154	426.6236	373.9963	321.7747	280.0729	245.7040	216.4445
Pu ₂ O ₃	$Pu_2O_3 + 6H^+ = 3H_2O + 2Pu^{+++}$	56.7969	50.6550	43.5378	36.9885	30.4486	25.1389	20.6280	16.6232
Pu ₃ C ₂	$Pu_3C_2 + 7H^+ + 4.25O_2(g) = 3Pu^{+++} + 2HCO_3^- + 2.5H_2O$	652.3279	592.2086	522.9563	459.5238	396.7967	346.9117	306.0016	271.4409
PuAs	$PuAs + 2O_2(g) + 2H^+ = Pu^{+++} + H_2AsO_4^-$	-	191.0895	-	-	-	-	-	-
PuBi	PuBi + $6H^{+}$ +1.5 O ₂ (g) = Pu^{+++} + Bi^{+++} + $3H_{2}O$	-	188.3637	-	-	-	-	-	-
PuBi ₂	PuBi ₂ + 8H ⁺ + 3O ₂ (g) = PuO ₂ ⁺⁺ + 2Bi ⁺⁺⁺ + 4H ₂ O	-	244.4113	-	-	-	-	-	-
PuBr ₃	PuBr ₃ = Pu ⁺⁺⁺ + 3Br ⁻	24.2043	21.6939	18.5470	15.4240	12.0179	8.9338	5.9388	2.7339
PuC _{0.84} ^c	$PuC_{0.84} + 1.59O_2(g) + 2.16H^+ = 0.84HCO_3^- + 0.66H_2O + Pu^{+++}$	227.5352	206.5054	182.2538	160.0100	137.9775	120.4229	105.9970	93.7775
PuCl ₃	PuCl ₃ = Pu ⁺⁺⁺ + 3Cl ⁻	16.2123	14.1989	11.5854	8.8960	5.8478	2.9809	0.1054	-3.0511
PuCl ₃ ·6H ₂ O	$PuCl_3 \cdot 6H_2O = Pu^{+++} + 3Cl^- + 6H_2O$	-	5.3599	-	-	-	-	-	-
PuCl ₄	PuCl ₄ = Pu ⁺⁺⁺⁺ + 4Cl ⁻	-	21.6853	-	-	-	-	-	-
PuF ₃	$PuF_3 = Pu^{+++} + 3F^-$	-16.2624	-16.3164	-16.6721	-17.2795	-18.2556	-19.4767	-21.0227	-23.0916
PuF ₆	$PuF_6 + 2H_20 = 6F^- + PuO_2^{++} + 4H^+$	49.7872	43.5597	35.9292	28.4915	20.5480	13.5459	6.9645	0.1760
Pul ₃	Pul ₃ = Pu ⁺⁺⁺ + 3I ⁻	30.1003	27.2872	23.7566	20.2269	16.3475	12.8253	9.4258	5.8508
PuN	$PuN + 3H^{+} = NH_{3}(aq) + Pu^{+++}$	-	58.1593	-	-	-	-	_	-
PuO _{1.61}	$PuO_{1.61} + 0.195O_2(g) + 4H^+ = Pu^{++++} + 2H_2O$	24.3995	20.5992	16.2792	12.3796	8.5623	5.5209	2.9735	0.7320

Table 6-33. Log K EQ3/6 Grids for Solid Phases (Continued)

Data0.ymp.R2		log K							
Species Name ^a	Reaction	0.01°C	25°C	60°C	100°C	150°C	200°C	250°C	300°C
PuO ₂ ^c	$PuO_2 + 4H^+ = Pu^{++++} + 2H_2O$	-7.1094	-8.0173	-9.0228	-9.9038	-10.7586	-11.4701	-12.1362	-12.8255
PuO ₂ (hyd, aged)	PuO ₂ (hyd, aged) + 4H ⁺ = Pu ⁺⁺⁺⁺ + 2H ₂ O	-	-1.9803	-	-	-	-	-	-
PuO ₂ (NO ₃) ₂ ·6H ₂ O	$PuO_2(NO_3)_2 \cdot 6H_2O = PuO_2^{++} + 6H_2O + 2NO_3^{-}$	-	2.4443	-	-	-	-	-	-
$PuO_2(OH)_2 \cdot H_2O^d$	$PuO_2(OH)_2 \cdot H_2O + 2H^+ = PuO_2^{++} + 3H_2O$	-	5.5000-	-	-	-	-	-	-
PuO ₂ CO ₃	$PuO_2CO_3 + H^+ = PuO_2^{++} + HCO_3^-$	-	-3.8567	-	-	-	-	-	-
PuO₂OH(am)	$PuO_2OH(am) + H^+ = PuO_2^+ + H_2O$	-	5.0073	-	-	-	-	-	-
PuOBr	$PuOBr + 2H^{+} = Pu^{+++} + Br^{-} + H_{2}O$	16.3616	14.3427	11.9072	9.5748	7.1268	5.0040	3.0407	1.0763
PuOCI	$PuOCI + 2H^{+} = Pu^{+++} + CI^{-} + H_{2}O$	13.1692	11.3957	9.2448	7.1717	4.9765	3.0494	1.2404	-0.6016
PuOF ^c	$PuOF + 2H^{+} = Pu^{+++} + F^{-} + H_{2}O$	2.2336	1.1116	-0.2857	-1.6605	-3.1569	-4.5256	-5.8808	-7.3490
PuOI ^c	$PuOI + 2H^{+} = Pu^{+++} + I^{-} + H_{2}O$	18.1012	16.0237	13.5298	11.1490	8.6571	6.5028	4.5174	2.5390
PuP	$PuP + H^{+} + 2O_{2}(g) = Pu^{+++} + HPO_{4}^{}$	-	237.2760	-	-	-	-	-	-
PuPO ₄ (s, hyd)	$PuPO_4(s, hyd) + H^+ = Pu^{+++} + HPO_4^{}$	-	-13.4500	-	-	-	-	-	-
PuSb	PuSb + $2H^+$ +1.5 $O_2(g) = Pu^{+++} + SbO_2^-$ + H_2O	-	176.7466	-	-	-	-	-	-
Ti ₂ O ₃	$Ti_2O_3(s) + 4H_2O + 0.5O_2 = 2Ti(OH)_4(aq)$	51.9834	46.0376	39.0528	32.6332	26.3242	21.3632	17.3404	13.9500
Ti ₃ O ₅	$Ti_3O_5(s) + 6H_2O + 0.5O_2 = 3Ti(OH)_4(aq)$	45.9328	39.8764	32.6557	25.9696	19.3745	14.1780	9.9526	6.3600
TiB ₂	$TiB_2 + 5H_2O + 2.5O_2(g) = Ti(OH)_4(aq) + 2B(OH)_3$	338.0284	307.4013	272.0411	239.6090	207.5561	182.1678	161.5438	144.4436
TiBr₃	$TiBr_3 + 3.5H_2O + 0.25O_2(g) = Ti(OH)_4(aq) + 3Br^- + 3H^+$	54.0865	48.8970	42.5601	36.4515	30.0678	24.6382	19.7839	15.0958
TiBr₄	$TiBr_4 + 4H_2O = Ti(OH)_4(aq) + 4Br^- + 4H^+$	38.6712	34.9543	30.2039	25.4361	20.2355	15.5928	11.2104	6.6851
TiCl ₂	$TiCl_2(s) + 3H_2O + 0.5O_2 = Ti(OH)_4(aq) + 2Cl^- + 2H^+$	79.0523	71.4576	62.4643	54.0315	45.4854	38.4830	32.5072	27.1059
TiCl ₃	$TiCl_3(s) + 3.5H_2O + 0.25O_2 = Ti(OH)_4(aq) + 3Cl^- + 3H^+$	45.2725	40.6359	34.9411	29.4180	23.6060	18.6214	14.1207	9.7170

Table 6-33. Log K EQ3/6 Grids for Solid Phases (Continued)

Data0.ymp.R2 Species Name ^a	Reaction	log K 0.01°C	log K 25°C	log K 60°C	log K 100°C	log K 150°C	log K 200°C	log K 250°C	log K 300°C
TiF ₃	$TiF_3(s) + 3.5H_2O + 0.25O_2 =$ $Ti(OH)_4(aq) + 3F^- + 3H^+$	-25.4440	-24.9948	-24.8495	-25.0287	-25.5696	-26.3961	-27.5442	-29.1977
TiF ₄ (am)	$TiF_4(s) + 4H_2O = Ti(OH)_4(aq) + 4F^- + 4H^+$	-9.2957	-10.2028	-11.6980	-13.4568	-15.6579	-17.9151	-20.3679	-23.3138
Til ₄	$Til_4 + 4H_2O = Ti(OH)_4(aq) + 4l^- + 4H^+$	40.4343	36.9635	32.5191	28.0374	23.1169	18.6929	14.4885	10.1176
TiO	$TiO(s) + 2H_2O + 0.5O_2 = Ti(OH)_4(aq)$	65.1565	58.6942	51.1924	44.3201	37.5613	32.2405	27.9350	24.3501
Uranium	$U + 2H^{+} + 1.5O_{2}(g) = UO_{2}^{++} + H_{2}O$	229.3696	208.4445	184.4377	162.5347	140.9842	123.9704	110.1644	98.6912
U(SO ₄) ₂	$U(SO_4)_2 = U^{++++} + 2SO_4^{}$	-10.6470	-11.9785	-13.8994	-16.0361	-18.6520	-21.3227	-24.2285	-27.6849
U_2S_3	$U_2S_3 + 3H^+ = 2U^{+++} + 3HS^-$	13.0324	10.4341	7.0450	3.5631	-0.3624	-4.0266	-7.6673	-11.6110
UBr ₃	$UBr_3 = U^{+++} + 3Br^-$	22.2645	19.9367	16.9090	13.7994	10.3020	7.0598	3.8722	0.4518
UBr₄	$UBr_4 = U^{++++} + 4Br^-$	35.4871	31.2328	25.9892	20.8389	15.2802	10.3192	5.5990	0.6917
UCI ₃	UCI ₃ = U ⁺⁺⁺ + 3CI ⁻	14.9578	13.0401	10.4960	7.8326	4.7734	1.8720	-1.0474	-4.2567
UCI ₄	UCI ₄ = U ⁺⁺⁺⁺ + 4CI ⁻	25.6364	21.9229	17.3180	12.7569	7.7768	3.2649	-1.1027	-5.7335
UCl₅	$UCI_5 + 2H_2O = UO_2^+ + 5CI^- + 4H^+$	37.2989	33.8207	29.2712	24.5499	19.1927	14.2091	9.3248	4.1144
UCI ₆	$UCI_6 + 2H_2O = UO_2^{++} + 6CI^- + 4H^+$	58.6497	53.1432	46.2494	39.3547	31.7911	24.9671	18.4514	11.6658
UF ₃	UF ₃ = U ⁺⁺⁺ + 3F ⁻	-21.2939	-20.9385	-20.8561	-21.0915	-21.7266	-22.6949	-24.0446	-25.9613
UF ₄	UF ₄ = U ⁺⁺⁺⁺ + 4F ⁻	-30.3023	-30.3553	-30.7379	-31.4059	-32.5086	-33.9313	-35.7859	-38.3366
UF ₅ (beta)	$UF_5(beta) + 2H_2O = UO_2^+ + 5F^- + 4H^+$	-12.6329	-13.1683	-14.3055	-15.8537	-18.0219	-20.4464	-23.2437	-26.7308
UF ₆	$UF_6 + 2H_2O = UO_2^{++} + 6F^- + 4H^+$	21.5553	17.5678	12.4557	7.2463	1.3981	-4.0509	-9.4686	-15.3832
UI ₃	UI ₃ = U ⁺⁺⁺ + 3I ⁻	32.9911	29.9408	26.0968	22.2421	18.0049	14.1734	10.5065	6.6935
UI ₄	$UI_4 = U^{++++} + 4I^-$	45.2686	40.4934	34.6660	28.9791	22.8794	17.4804	12.3999	7.1975
UO ₂ Br ₂	$UO_2Br_2 = UO_2^{++} + 2Br^-$	18.4072	16.4880	14.0969	11.7192	9.1185	6.7682	4.5068	2.1241
UO ₂ CI ₂	$UO_2CI_2 = UO_2^{++} + 2CI^-$	13.7845	12.1037	9.9923	7.8698	5.5163	3.3543	1.2376	-1.0345
UO ₂ F ₂	$UO_2F_2 = UO_2^{++} + 2F^-$	-5.6669	-6.2647	-7.1248	-8.0882	-9.2818	-10.5178	-11.8836	-13.5398
UO ₂ SO ₄	$UO_2SO_4 = UO_2^{++} + SO_4^{}$	3.6829	2.4282	0.7802	-0.9327	-2.8940	-4.7579	-6.6467	-8.7462
UO₃(gamma)	$UO_3(gamma) + 2H^+ = UO_2^{++} + H_2O$	9.1979	7.8659	6.3470	4.9650	3.5935	2.4792	1.5215	0.6449
UOBr ₂	$UOBr_2 + 2H^+ = U^{++++} + 2Br^- + H_2O$	10.2611	7.9817	5.2022	2.4995	-0.4037	-3.0057	-5.5155	-8.1697
UOBr ₃	$UOBr_3 + H_2O = UO_2^+ + 3Br^- + 2H^+$	25.8237	23.5777	20.6216	17.5499	14.0696	10.8442	7.7008	4.3767

Table 6-33. Log K EQ3/6 Grids for Solid Phases (Continued)

Data0.ymp.R2		log K	log K	log K	log K				
Species Name ^a	Reaction	0.01°C	25°C	60°C	100°C	150°C	200°C	250°C	300°C
UOCI	$UOCI + 2H^{+} = U^{+++} + CI^{-} + H_{2}O$	-9.8816	-9.7309	-9.7123	-9.8415	-10.1594	-10.6310	-11.2776	-12.1751
UOCI ₂	$UOCl_2 + 2H^+ = U^{++++} + 2Cl^- + H_2O$	8.1372	5.8869	3.1513	0.4936	-2.3634	-4.9300	-7.4145	-10.0529
UOCl ₃	$UOCl_3 + H_2O = UO_2^+ + 3Cl^- + 2H^+$	9.6633	8.5736	6.9562	5.1092	2.8309	0.5461	-1.8456	-4.5610
WCl ₂ (s)	$WCl_2(s) + 2H_2O + O_2(g) = WO_4^{} + 2Cl^-$ +4H ⁺	93.6338	84.5211	73.6761	63.3790	52.7437	43.8115	35.9624	28.6009
WCl ₄ (s)	$WCl_4(s) + 3H_2O + 0.5O_2 = WO_4^{} + 4Cl^- + 6H^+$	71.3689	64.5388	56.1177	47.8276	38.9055	31.0428	23.7400	16.3841
WCI ₅ (s)	$WCl_5(s) + 3.5H_2O + 0.25O_2 = WO_4^{} + 5Cl^- + 7H^+$	65.4016	59.3442	51.7106	44.0347	35.5828	27.9461	20.6622	13.0949
WCl ₆ (s)	$WCI_6(s) + 4H_2O = WO_4^{} + 6CI^- + 8H^+$	57.2682	52.1561	45.5135	38.6433	30.8566	23.6054	16.4742	8.8097
WO ₂ Cl ₂ (s)	$WO_2Cl_2(s) + 2H_2O = WO_4^{} + 2Cl^- + 4H^+$	0.6693	-0.0612	-1.2805	-2.7892	-4.7792	-6.8982	-9.2424	-12.0657
WOCl ₄ (s)	$WOCl_4(s) + 3H_2O = WO_4^{} + 4Cl^- + 6H^+$	34.4557	31.2806	27.0555	22.5950	17.4379	12.5397	7.6296	2.2438
WOF ₄ (s)	$WOF_4(s) + 3H_2O = WO_4^{} + 4F^- + 6H^+$	10.1133	7.7357	4.4528	0.8968	-3.3209	-7.4485	-11.7279	-16.5992

DTN: MO0302SPATHDYN.000 [DIRS 161756].

^a See data file data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) for spreadsheets used to calculate log K grids.
^b The equation for CoF₃ is corrected from the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), which gives an equation for CoCl₃.

^c For the species NpC_{0.91}(cr), Pu₂C₃(cr), PuC_{0.84}(cr), PuOI(cr), PuOF(cr), and PuO₂(cr), the heat capacity coefficients given by Lemire (2001 [DIRS 159027]) were inappropriately applied as Maier-Kelly parameters (see Section 6.3.4.5).

^d The formula for PuO₂(OH)₂·H₂O is corrected from the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), which gives PuO₂(OH)₂·2H₂O. The corrected form is consistent with Lemire (2001 [DIRS 159027], Section 17.2.2.1).

Table 6-34. Corrected Log K EQ3/6 Grids for Np and Pu Solid Phases

Data0.ymp.R2 Species Name	Reaction	log K 0.01°C	log K 25°C	log K 60°C	log K 100°C	log K 150°C	log K 200°C	log K 250°C	log K 300°C
Na ₃ NpF ₈	$Na_3NpF_8 + 2H_2O = NpO_2^+ + 3Na^+ + 4H^+ + 8F^-$	-7.2110	-8.4426	-10.5811	-13.2128	-16.6747	-20.4159	-24.6880	-30.0499
Np	$Np + 3H^{+} + 0.75O_{2}(g) = Np^{+++} + 1.5H_{2}O$	167.5129	152.1799	134.5579	118.4599	102.5893	90.0115	79.7396	71.1257
Np ₂ O ₅	$Np_2O_5 + 2H^+ = 2NpO_2^+ + H_2O$	4.9214	3.7031	2.1757	0.6695	-0.9387	-2.3319	-3.5852	-4.7609
NpBr ₃	$NpBr_3 = Np^{+++} + 3Br^{-}$	23.3940	20.9379	17.8023	14.6289	11.0996	7.8519	4.6698	1.2647
NpBr ₄	$NpBr_4 = Np^{++++} + 4Br^{-}$	34.0049	29.8101	24.6427	19.5708	14.1006	9.2201	4.5750	-0.2600
NpC _{0.91} *	$NpC_{0.91} + 2.09H^{+} + 1.66O_{2}(g) = Np^{+++} + 0.91HCO_{3}^{-} + 0.59H_{2}O$	214.6573	194.6217	171.5199	150.3350	129.3544	112.6364	98.8906	87.2297
NpCl ₃	$NpCl_3 = Np^{+++} + 3Cl^-$	15.4590	13.4766	10.8928	8.2227	5.1830	2.3122	-0.5754	-3.7500
NpCl ₄	$NpCl_4 = Np^{++++} + 4Cl^-$	24.9771	21.2634	16.6608	12.1047	7.1338	2.6337	-1.7192	-6.3314
NpF ₃	NpF ₃ = Np ⁺⁺⁺ + 3F ⁻	-17.9914	-17.9369	-18.1629	-18.6483	-19.5023	-20.6271	-22.0960	-24.1022
NpF ₄	NpF ₄ = Np ⁺⁺⁺⁺ + 4 F ⁻	-28.6681	-28.9106	-29.5043	-30.3588	-31.6397	-33.1997	-35.1650	-37.8092
NpF ₅	$NpF_5 + 2H_2O = NpO2^+ + 5F^- + 4H^+$	3.4150	1.3534	-1.5354	-4.6820	-8.4205	-12.0804	-15.8728	-20.1758
NpF ₆	$NpF_6 + 2H_2O = NpO_2^{++} + 4H^+ + 6F^-$	34.9067	29.8193	23.4454	17.0862	10.1113	3.7797	-2.3444	-8.8333
NpI ₃	NpI ₃ + Np ⁺⁺⁺ + 3I ⁻	30.2017	27.3544	23.7814	20.2075	16.2767	12.7058	9.2596	5.6395
NpN	$NpN + 3H^{+} = Np^{+++} + NH_{3}(aq)$	52.2383	47.2199	41.4246	36.1091	30.8326	26.5962	23.0622	20.0070

Table 6-34. Corrected Log K EQ3/6 Grids for Np and Pu Solid Phases (Continued)

Data0.ymp.R2		log K							
Species Name	Reaction	0.01°C	25°C	60°C	100°C	150°C	200°C	250°C	300°C
NpOBr ₂	$NpOBr_2 + 2H^+ = Np^{++++} + 2 Br^- + H_2O$	7.3768	5.2794	2.7183	0.2240	-2.4643	-4.8887	-7.2475	-9.7693
NpOCl ₂	$NpOCl_2 + 2H^+ = Np^{++++} + 2Cl^- + H_2O$	7.6917	5.4117	2.6473	-0.0317	-2.9041	-5.4784	-7.9642	-10.5985
Cs ₃ PuCl ₆	$Cs_3PuCl_6 = Pu^{+++} + 3Cs^{+} + 6Cl^{-}$	76.2000	70.6870	63.7152	56.7349	49.0858	42.1827	35.5667	28.6366
CsPu ₂ Cl ₇	$CsPu_2Cl_7 = 2Pu^{+++} + Cs^+ + 7Cl^-$	31.8127	28.1392	23.1957	17.9614	11.8680	5.9881	-0.0505	-6.8394
Pu	$Pu + O_2(g) + 4H^+ = Pu^{++++} + 2H_2O$	184.6805	166.8458	146.4150	127.8093	109.5241	95.0752	83.3017	73.4433
Pu ₂ C ₃ *	$Pu_2C_3 + 3H^+ + 4.5O_2(g) = 2Pu^{+++} + 3HCO_3^-$	533.5625	483.9329	426.6540	374.0675	321.9198	280.3062	246.0339	216.8757
Pu ₂ O ₃	$Pu_2O_3 + 6H^+ = 3H_2O + 2Pu^{+++}$	56.8079	50.6550	43.5537	37.0502	30.5909	25.3763	20.9682	17.0707
Pu ₃ C ₂	$Pu_3C_2 + 7H^+ + 4.25O_2(g) = 3Pu^{+++} + 2HCO_3^- + 2.5H_2O$	652.3246	592.2086	522.9512	459.5030	396.7466	346.8247	305.8727	271.2665
PuBr ₃	$PuBr_3 = Pu^{+++} + 3Br^{-}$	24.1856	21.6939	18.5185	15.3107	11.7509	8.4824	5.2862	1.8718
PuC _{0.84} *	$PuC_{0.84} + 1.59O_2(g) + 2.16H_+ = 0.84HCO_3^- + 0.66H_2O + Pu^{+++}$	227.5412	206.5054	182.2628	160.0451	138.0603	120.5633	106.2012	94.0495
PuCl ₃	PuCl ₃ = Pu ⁺⁺⁺ + 3Cl ⁻	16.2103	14.1989	11.5823	8.8837	5.8185	2.9307	0.0318	-3.1500
PuF ₃	PuF ₃ = Pu ⁺⁺⁺ + 3F ⁻	-16.2599	-16.3164	-16.6688	-17.2675	-18.2297	-19.4362	-20.9682	-23.0240
PuF ₆	$PuF_6 + 2H_20 = 6F^- + PuO_2^{++} + 4H^+$	49.7680	43.5597	35.8984	28.3650	20.2382	13.0028	6.1526	-0.9311
Pul ₃	Pul ₃ = Pu ⁺⁺⁺ + 3I ⁻	30.0992	27.2872	23.7547	20.2190	16.3282	12.7915	9.3753	5.7819
PuO _{1.61}	$PuO_{1.61} + 0.195O_2(g) + 4H^+ = Pu^{++++} + 2H_2O$	24.4008	20.5992	16.2807	12.3845	8.5714	5.5327	2.9861	0.7435
PuO ₂ *	$PuO_2 + 4H^+ = Pu^{++++} + 2H_2O$	-7.1053	-8.0173	-9.0177	-9.8854	-10.7201	-11.4116	-12.0598	-12.7335
PuOBr	$PuOBr + 2H^{+} = Pu^{+++} + Br^{-} + H_{2}O$	16.3619	14.3427	11.9073	9.5742	7.1237	4.9960	3.0258	1.0526
PuOCI	$PuOCI + 2H^{+} = Pu^{+++} + CI^{-} + H_{2}O$	13.1696	11.3957	9.2450	7.1719	4.9750	3.0439	1.2289	-0.6210
PuOF*	$PuOF + 2H^{+} = Pu^{+++} + F^{-} + H_{2}O$	2.2342	1.1116	-0.2852	-1.6594	-3.1564	-4.5278	-5.8875	-7.3622
PuOI*	$PuOI + 2H^{+} = Pu^{+++} + I^{-} + H_{2}O$	18.0993	16.0237	13.5267	11.1361	8.6251	6.4461	4.4321	2.4222

Output DTN: SN0410T0510404.001 (Spreadsheets *Minerals_j_PVB_Pu_CFJC_fix.xls* and *Minerals_j_PVB_Np_CFJC_fix.xls*).

^{*} For the species $NpC_{0.91}(cr)$, $Pu_2C_3(cr)$, $PuC_{0.84}(cr)$, PuOI(cr), PuOF(cr), and $PuO_2(cr)$, the heat capacity coefficients given by Lemire (2001 [DIRS 159027]) were inappropriately applied as Maier-Kelly parameters (see Section 6.3.4.5).

Table 6-35. △ Log K (Difference Between Incorrect and Corrected Values) for Np and Pu Solid Phases

Data0.ymp.R2 Species Name	Reaction	log K 0.01°C	log K 25°C	log K 60°C	log K 100°C	log K 150°C	log K 200°C	log K 250°C	log K 300°C
Na ₃ NpF ₈	$Na_3NpF_8 + 2H_2O = NpO_2^+ + 3Na^+ + 4$ $H^+ + 8F^-$	-0.0002	0.0000	-0.0012	-0.0068	-0.0212	-0.0433	-0.0723	-0.1069
Np	$Np + 3H^{+} + 0.75O_{2}(g) = Np^{+++} + 1.5H_{2}O$	-0.0069	0.0000	-0.0105	-0.0420	-0.1002	-0.1718	-0.2522	-0.3387
Np ₂ O ₅	$Np_2O_5 + 2H^{\dagger} = 2NpO_2^{\dagger} + H_2O$	-0.0059	0.0000	-0.0095	-0.0388	-0.0950	-0.1665	-0.2489	-0.3394
NpBr ₃	$NpBr_3 = Np^{+++} + 3Br^{-}$	-0.0004	0.0000	-0.0009	-0.0043	-0.0117	-0.0221	-0.0348	-0.0495
NpBr ₄	$NpBr_4 = Np^{++++} + 4Br^-$	-0.0018	0.0000	-0.0029	-0.0118	-0.0289	-0.0507	-0.0757	-0.1033
NpC _{0.91}	$NpC_{0.91} + 2.09H^{+} + 1.66O_{2}(g) = Np^{+++} + 0.91HCO_{3}^{-} + 0.59H_{2}O$	0.0030	0.0000	0.0045	0.0180	0.0429	0.0736	0.1080	0.1450
NpCl ₃	$NpCl_3 = Np^{+++} + 3Cl^-$	-0.0025	0.0000	-0.0038	-0.0151	-0.0357	-0.0609	-0.0890	-0.1190
NpCl ₄	$NpCl_4 = Np^{++++} + 4Cl^-$	-0.0019	0.0000	-0.0031	-0.0129	-0.0319	-0.0564	-0.0849	-0.1165
NpF ₃	$NpF_3 = Np^{+++} + 3F^-$	0.0024	0.0000	0.0032	0.0115	0.0249	0.0388	0.0523	0.0648
NpF ₄	$NpF_4 = Np^{++++} + 4 F^-$	0.0015	0.0000	0.0018	0.0061	0.0121	0.0173	0.0210	0.0232
NpF ₅	$NpF_5 + 2H_2O = NpO_2^+ + 5F^- + 4H^+$	-0.0018	0.0000	-0.0029	-0.0118	-0.0289	-0.0507	-0.0757	-0.1033
NpF ₆	$NpF_6 + 2H_2O = NpO_2^{++} + 4H^+ + 6 F^-$	-0.0210	0.0000	-0.0338	-0.1387	-0.3396	-0.5954	-0.8901	-1.2137
Npl ₃	$NpI_3 + Np^{+++} + 3I^-$	-0.0012	0.0000	-0.0019	-0.0079	-0.0193	-0.0338	-0.0505	-0.0689
NpN	$NpN + 3H^{+} = Np^{+++} + NH_{3}(aq)$	-0.0002	0.0000	-0.0004	-0.0021	-0.0061	-0.0119	-0.0193	-0.0279
NpO ₂	$NpO_2 + 4H^+ = Np^{++++} + 2H_2O$	0.0004	0.0000	0.0001	-0.0007	-0.0046	-0.0120	-0.0226	-0.0362
NpOBr ₂	$NpOBr_2 + 2H^+ = Np^{++++} + 2 Br^- + H_2O$	0.0029	0.0000	0.0035	0.0124	0.0253	0.0372	0.0469	0.0543
NpOCl ₂	$NpOCl_2 + 2H^+ = Np^{++++} + 2CI^- + H_2O$	0.0009	0.0000	0.0009	0.0023	0.0024	-0.0002	-0.0055	-0.0135
Cs ₃ PuCl ₆	$Cs_3PuCl_6 = Pu^{+++} + 3Cs^+ + 6Cl^-$	-0.0002	0.0000	-0.0009	-0.0048	-0.0144	-0.0287	-0.0471	-0.0691
CsPu ₂ Cl ₇	$CsPu_2Cl_7 = 2Pu^{+++} + Cs^+ + 7Cl +^-$	-0.0035	0.0000	-0.0054	-0.0221	-0.0536	-0.0932	-0.1385	-0.1878
Pu	$Pu + O_2(g) + 4H^{+} = Pu^{++++} + 2H_2O$	-0.0027	0.0000	-0.0043	-0.0176	-0.0432	-0.0757	-0.1132	-0.1543
Pu ₂ C ₃	$Pu_2C_3 +3H^+ +4.5O_2(g) = 2Pu^{+++} +3HCO_3^-$	0.0292	0.0175	0.0304	0.0712	0.1451	0.2334	0.3299	0.4312
Pu ₂ O ₃	$Pu_2O_3 + 6H^+ = 3H_2O + 2Pu^{+++}$	0.0110	0.0000	0.0159	0.0617	0.1423	0.2374	0.3403	0.4475
Pu ₃ C ₂	$Pu_3C_2 + 7H^{+} + 4.25O_2(g) = 3Pu^{+++} + 2HCO_3^{-} + 2.5H_2O$	-0.0033	0.0000	-0.0051	-0.0207	-0.0501	-0.0870	-0.1289	-0.1745
PuBr ₃	$PuBr_3 = Pu^{+++} + 3Br^{-}$	-0.0187	0.0000	-0.0285	-0.1132	-0.2669	-0.4514	-0.6526	-0.8620
PuC _{0.84}	$PuC_{0.84} + 1.59O_2(g) + 2.16H^+ = 0.84HCO_3^- + 0.66H_2O + Pu^{+++}$	0.0060	0.0000	0.0089	0.0352	0.0828	0.1404	0.2042	0.2720

Table 6-35. △ Log K (Difference Between Incorrect and Corrected Values) for Np and Pu Solid Phases (Continued)

Data0.ymp.R2 Species Name	Reaction	log K 0.01°C	log K 25°C	log K 60°C	log K 100°C	log K 150°C	log K 200°C	log K 250°C	log K 300°C
PuCl ₃	PuCl ₃ = Pu ⁺⁺⁺ + 3Cl ⁻	-0.0020	0.0000	-0.0031	-0.0123	-0.0293	-0.0502	-0.0736	-0.0989
PuF ₃	PuF ₃ = Pu ⁺⁺⁺ + 3F ⁻	0.0025	0.0000	0.0033	0.0120	0.0259	0.0404	0.0545	0.0676
PuF ₆	$PuF_6 + 2H_20 = 6F^- + PuO_2^{++} + 4H^+$	-0.0192	0.0000	-0.0309	-0.1265	-0.3098	-0.5431	-0.8119	-1.1071
Pul ₃	$Pul_3 = Pu^{+++} + 3l^-$	-0.0012	0.0000	-0.0019	-0.0079	-0.0193	-0.0338	-0.0505	-0.0689
PuO _{1.61}	$PuO_{1.61} + 0.195O_2(g) + 4H^+ = Pu^{++++} + 2H_2O$	0.0013	0.0000	0.0015	0.0049	0.0091	0.0118	0.0126	0.0115
PuO ₂	$PuO_2 + 4H^+ = Pu^{++++} + 2H_2O$	0.0040	0.0000	0.0051	0.0184	0.0385	0.0584	0.0764	0.0919
PuOBr	$PuOBr + 2H^{+} = Pu^{+++} + Br^{-} + H_{2}O$	0.0003	0.0000	0.0000	-0.0006	-0.0032	-0.0080	-0.0149	-0.0237
PuOCI	$PuOCI + 2H^{+} = Pu^{+++} + CI^{-} + H_{2}O$	0.0004	0.0000	0.0002	0.0002	-0.0015	-0.0054	-0.0115	-0.0194
PuOF	$PuOF + 2H^{+} = Pu^{+++} + F^{-} + H_{2}O$	0.0006	0.0000	0.0005	0.0011	0.0005	-0.0021	-0.0067	-0.0131
PuOI	$PuOI + 2H^{+} = Pu^{+++} + I^{-} + H_{2}O$	-0.0019	0.0000	-0.0031	-0.0130	-0.0321	-0.0567	-0.0852	-0.1168

Output DTN: SN0410T0510404.001 (Spreadsheets *Minerals_j_PVB_Pu_CFJC_fix.xls* and *Minerals_j_PVB_Np_CFJC_fix.xls*).

Table 6-36. Thermodynamic Data Input for Gas Phases with the Correct Scaling of the "c" Heat Capacity Coefficient

				Heat Ca	icients ^a		
	ΔG° _f	ΔH° _f	S°	a	b x 10 ³	c x 10 ⁻⁶	
Name	(J/mol)	(J/mol)	(J/mol-K)	(J/mol-K)	(J/mol-K ²)	(J-K/mol) ^b	Source
Portlandite Ca(OH) ₂	-898,470	-986,100	83.40	101.790	18.0000	-1.740	1, 2
Ferrite- Dicalcium (Ca ₂ Fe ₂ O ₅) ^c	-2,001,686	-2,133,700	188.70	248.610	0.0000 (original value was –4.8900)	-4.8900 (original value was 0.0000)	1, 2
Ferrite-Mg	-1,317,429	-1,440,100	123.8	167.19	14.23	-2.99	1, 2
Ca ₃ Al ₂ O ₆	-3,411,786	-3,587,800	205.90	260.580	19.1600	-5.030	1, 2
CaAl ₂ O ₄	-2,208,820	-2,326,300	114.20	150.620	24.9400	-3.330	1, 2
Pseudo wollastonite CaSiO ₃	-1,544,739	-1,628,400	87.40	108.160	16.4800	-2.360	1, 2
Titanite CaSiTiO ₅	-2,461,780	-2,603,300	129.20	177.360	23.1800	-4.030	1, 2
Perovskite CaTiO ₃	-1,575,247	-1,659,000	93.70	127.490	5.6900	-2.800	1, 2
Co(OH) ₂	-454,168	-541,300	93.30	82.840	47.7000	0.000	1, 2
Spinel-Co Co ₃ O ₄	-794,901	-918,700	109.30	131.650	66.0200	-2.480	1, 2
CoCl ₂	-269,650	-312,500	109.30	81.580	7.4100	-0.470	1, 2
CoF ₃	-718,899	-790,400	94.60	100.280	4.8800	-0.880	1, 2
Sphaerocobaltite CoCO ₃	-636,782	-713,000	87.90	88.280	38.9100	-1.800	1, 2
CoCr ₂ O ₄	-1,329,788	-1,438,300	126.80	167.650	17.7400	-1.400	1, 2
CoF ₂	-626,562	-672,400	82.00	80.910	6.1500	-1.240	1, 2
CoFe ₂ O ₄	-980,455	-1,088,700	142.70	173.220	54.3900	-3.280	1, 2
CoO	-214,198	-237,700	53.00	45.260	10.6900	0.600	1, 2
CoTiO ₃	-1,129,498	-1,207,400	96.90	123.470	9.7100	-1.650	1, 2
CoWO ₄	-1,035,813	-1,142,700	126.40	115.480	48.4900	0.000	1, 2
Eskolaite Cr ₂ O ₃	-1,058,067	-1,140,600	81.20	109.650	15.4600	0.000	1, 2
CrCl ₃	-486,316	-556,500	123.00	98.830	13.9800	-1.000	1, 2
CrF ₃	-1,103,441	-1,173,200	93.90	93.970	10.2500	-1.620	1, 2
Crl ₃	-205,530	-205,000	199.60	105.440	20.9200	0.000	1, 2
CrO₃	-512,562	-587,000		71.760	87.8700	-1.670	1, 2
Ferrite-Cu (CuFe₂O₄) ^c	-863,240	–966,500 (original value was –1,025,100)	148.6 (original value was 177.70)	138.74 (original value was 200.080)	119.0000 (original value was 20.2500)	–2.260 (original value was –3.360)	1, 2
Iron Fe	0	0	27.30	14.950	28.0800	0.160	1, 2
Fe(OH) ₂	-486,975	-574,000	87.90	116.060	8.6500	-2.870	1, 2
Fe(OH) ₃	-696,486	-832,600	104.60	127.610	41.6400	-4.220	1, 2
Fe ₂ (SO ₄) ₃	-2,262,753	-2,583,000	307.50	361.300	54.7600	-10.640	1, 2
Hercynite FeAl ₂ O ₄	-1,879,669	-1,969,500	106.30	155.310	26.1500	-3.520	1, 2
Lawrencite FeCl ₂	-302,343	-341,600	117.90	78.260	9.9500	-0.420	1, 2
Molysite FeCl ₃	-333,926	-399,200	147.80	74.590	78.2700	-0.090	1, 2
Chromite FeCr ₂ O ₄	-1,355,891	-1,458,600	146.90	163.010	22.3400	-3.190	1, 2

Table 6-36. Thermodynamic Data Input for Gas Phases with the Correct Scaling of the "c" Heat Capacity Coefficient (Continued)

				Heat Ca	icients ^a		
	ΔG° _f	ΔH° _f	S°	а	b x 10 ³	c x 10 ⁻⁶	
Name	(J/mol)	(J/mol)	(J/mol-K)	(J/mol-K)	(J/mol-K ²)	(J-K/mol) ^b	Source
FeF ₂	-663,179	-705,800	87.00	73.080	9.6100	-0.700	1, 2
FeF ₃	-972,303	-1,039,300		90.750	11.3100	-0.220	1, 2
Ferrite-Ca	-1,412,731	-1,479,400		164.930	19.9200	-1.530	1, 2
Ferrite-Ni	-972,893	-1,084,500		152.670	77.8200	-1.490	1, 2
FeSO ₄	-824,892	-928,900		122.000	37.8200	-2.930	1, 2
Ilmenite FeTiO ₃	-1,158,045	-1,239,200		116.610	18.2400	-2.000	1, 2
MgBr ₂	-504,060	-524,300	117.20	70.510	18.0700	-0.110	1, 2
Chloro magnesite MgCl ₂	-592,074	-644,200		76.400	9.2500	-0.700	1, 2
MgSO ₄	-1,170,579	-1,261,800	91.40	106.440	46.2800	-2.190	1, 2
Bixbyite Mn ₂ O ₃	-881,114	-959,000	110.50	102.800	35.6700	-1.280	1, 2
Tephroite Mn ₂ SiO ₄	-1,632,130	-1,725,300	142.20	159.080	19.5000	-3.110	1, 2
Scacchite MnCl ₂	-440,478	-481,300	118.20	73.800	15.2300	-0.470	1, 2
MnSO ₄	-957,243	-1,065,300	112.10	122.420	37.3200	-2.950	1, 2
MoO ₂ Cl ₂	-623,302	-725,800	120.50	127.400	7.0300	-1.940	1, 2
Na ₂ CO ₃	-1,048,005	-1,130,800	138.80	11.000	244.0500	2.450	1, 2
Na ₂ CrO ₄	-1,234,795	-1,334,300	176.60	101.040	140.0000	0.000	1, 2
Nahcolite NaHCO ₃	-852,851	-936,300	101.20	45.310	143.1000	0.000	1, 2
Heazlewoodite Ni ₃ S ₂	-210,396	-216,300	133.90	110.790	51.6700	-0.750	1, 2
NiCl ₂	-259,139	-305,300	98.00	73.190	13.1200	-0.480	1, 2
NiCO ₃	-617,876	-696,300	86.20	88.700	38.9100	-1.230	1, 2
NiCr ₂ O ₄	-1,271,777	-1,392,400	129.70	167.150	17.8700	-2.110	1, 2
NiF ₂	-610,298	-657,700	73.60	66.600	13.9400	-0.590	1, 2
Trevorite NiFe ₂ O ₄	-972,893	-1,084,500	125.90	152.670	77.8200	-1.490	1, 2
NiSO ₄	-759,545	-873,200	101.30	125.940	27.8200	-3.260	1, 2
NiTiO ₃	-1,118,188	-1,201,400	82.60	115.100	15.9800	-1.830	1, 2
NiWO ₄	-1,023,620	-1,127,800	118.00	110.630	53.3900	-0.440	1, 2
Ti ₂ O ₃	-1,433,824	-1,520,900	77.30	53.070	163.4400		1, 2
Ti ₃ O ₅	-2,317,294	-2,459,100	129.40	231.040	-24.7700	-6.130	1, 2
TiB ₂	-319,648	-315,900	28.50	56.380	25.8600	-1.750	1, 2
TiBr ₃	-525,596	-551,900	176.60	73.070	87.2500	0.080	1, 2
TiBr ₄	-590,646	-619,700	243.50	80.930	169.6200		1, 2
TiCl ₂ ^c	-465,823	–515,000 (original value was	87.30	68.370	18.0300	-0.350	1, 2
TiCL	GEA 454	–5,155)		05.040	44.0000	0.400	4.0
TiCl ₃	-654,451	-721,700 1 425 500		95.810	11.0600	-0.180	1, 2
TiF ₃	-1,361,861	-1,435,500		79.080	29.2900	0.340	1, 2
TiF₄(am)	-1,559,179	-1,649,300		123.310	36.2400	-1.770	1, 2
Til ₄	-370,647	-375,700		71.420	181.8700	- 200	1, 2
TiO	-513,278	-542,700	34.80	44.220	15.0600	-0.780	1, 2
Uranium U	0	0	50.30	27.590	-4.0400	-0.110	1, 2

Table 6-36. Thermodynamic Data Input for Gas Phases with the Correct Scaling of the "c" Heat Capacitiy Coefficient (Continued)

				Heat Ca	pacity Coeff	icients ^a	
	ΔG° _f	ΔH^{o}_{f}	S°	а	b x 10 ³	c x 10 ⁻⁶	
Name	(J/mol)	(J/mol)	(J/mol-K)	(J/mol-K)	(J/mol-K ²)	(J-K/mol) ^b	Source
$U(SO_4)_2$	-2,087,195	-2,318,000	164.00	104.600	230.9600	-	1, 2
U ₂ S ₃	-854,730	-854,000	199.20	140.830	16.1100	-0.380	1, 2
UBr ₃	-673,463	-699,100	192.50	100.000	29.2900	-	1, 2
UBr ₄	-767,852	-802,500	238.50	134.730	20.5000	-1.130	1, 2
UCl₃	-794,530	-861,900	159.00	87.780	31.1300	0.490	1, 2
UCI ₄	-929,927	-1,018,800	197.20	113.810	35.8600	-0.330	1, 2
UCl₅	-950,061	-1,041,500	246.90	140.040	35.4400	-0.540	1, 2
UCI ₆	-962,649	-1,068,200	285.80	173.400	35.0600	-0.740	1, 2
UF ₃	-1,439,861	-1,502,100	123.40	85.980	30.5400	-	1, 2
UF₄	-1,830,173	-1,914,200	151.70	123.560	9.6200	-0.930	1, 2
UF₅(beta)	-1,970,577	-2,083,200	179.50	125.520	30.2100	-0.200	1, 2
UF ₆	-2,068,477	-2,197,000	227.60	52.720	384.9300	-	1, 2
UI ₃	-459,962	-460,700	222.00	102.970	30.5400	-	1, 2
UI ₄	-506,462	-512,100	263.60	149.370	9.9600	-1.590	1, 2
UO ₂ Br ₂	-1,066,612	-1,137,600	169.50	117.950	17.5300	-1.070	1, 2
UO ₂ Cl ₂	-1,146,105	-1,243,500	150.60	115.230	18.2000	-1.140	1, 2
UO ₂ F ₂	-1,551,873	-1,651,400	135.60	122.880	8.6200	-1.990	1, 2
UO ₂ SO ₄	-1,683,212	-1,845,100	154.80	112.470	108.7800	-	1, 2
UO₃(gamma)	-1,144,896	-1,226,500	98.80	90.370	11.0500	-1.110	1, 2
UOBr ₂	-929,638	-973,600	157.60	110.580	13.6800	-1.490	1, 2
UOBr₃	-901,429	-954,000	205.00	130.540	20.5000	-1.380	1, 2
UOCI	-899,108	-833,900	102.50	75.810	14.3500	-0.830	1, 2
UOCl ₂	-996,062	-1,067,500	138.30	98.950	14.6400	-0.740	1, 2
UOCI ₃	-1,068,773	-1,151,600	170.70	122.590	20.9200	-1.190	1, 2
WCl ₂ (s)	-219,977	-260,300	130.50	71.280	21.9000	-	1, 2
WCl ₄ (s)	-359,433	-443,100	198.30	113.450	54.6000	-	1, 2
WCI ₅ (s)	-401,783	-513,000	217.60	124.450	109.9200	-0.140	1, 2
WCl ₆ (s)	-455,511	-593,700	238.50	125.560	167.2300	-	1, 2
WO ₂ Cl ₂ (s)	-702,770	-780,300	200.80	79.510	94.1100	-0.290	1, 2
WOCl ₄ (s)	-549,270	-671,100	172.80	115.000	104.6900	-	1, 2
WOF ₄ (s)	-1,285,507	-1,406,900	175.70	83.650	167.4200	-	1, 2

All values of ΔG°_{f} are from Barin and Platzki (1995 [DIRS 157865]). Sources: 1

Ferrite-Dicalcium: Spreadsheet Minerals_j_psd_8_DS_fix.xls, Worksheet Ferrite-Dicalcium (fix). Ferrite-Cu (CuFe₂O₄): Spreadsheet *Minerals_i_psd_9_DS_fix.xls*, Worksheet *Ferrite-Cu (fix)*.

TiCl₂: Spreadsheet *Minerals_i_psd_1_DS_fix.xls*, Worksheet *TiCl2(s) (fix)*.

All values of ΔH°_f, S°, and heat capacity coefficients are from Binnewies and Milke (1999 [DIRS 158955]).

 $^{^{\}rm a}$ Heat capacity coefficients a, b, and c defined in Eq. 4-1. $^{\rm b}$ Scaling corrected from 10⁻⁵ to 10⁻⁶ in the formula used to calculate apparent Gibbs energies within the respective species spreadsheet.

c Values in boldface are corrected in output DTN: SN0410T0510404.001, from errors identified in the original source spreadsheets (DTN: MO0302SPATHDYN.001 [DIRS 161886]). The corrected values in the output DTN are developed in the following spreadsheets:

Table 6-37. Corrected Log K EQ3/6 Grids for Affected Solid Phases

Data0.ymp.R2		log K							
Species Name	Reaction	0.01°C	25°C	60°C	100°C	150°C	200°C	250°C	300°C
Witherite (BaCO ₃)	BaCO ₃ + H ⁺ = Ba ⁺⁺ + HCO ₃ ⁻	1.9041	1.7639	1.5062	1.1717	0.7100	0.1917	-0.4144	-1.1855
Portlandite (Ca(OH) ₂)	$Ca(OH)_2 + 2H^+ = Ca^{++} + 2H_2O$	24.6125	22.5444	20.1862	18.0517	15.9616	14.3045	12.9323	11.7391
Ferrite Dicalcium (Ca ₂ Fe ₂ O ₅)	$Ca_2Fe_2O_5 + 10H^+ = 2Ca^{++} + 2Fe^{+++} + 5H_2O$	64.4136	56.8114	48.0584	40.0564	32.1116	25.6815	20.2076	15.2897
Ferrite-Mg (MgFe ₂ O ₄)	Ferrite-Mg + 8H ⁺ = 2Fe ⁺⁺⁺ + Mg ⁺⁺ + 4H ₂ O	25.4526	20.9808	15.8346	11.1482	6.5052	2.7292	-0.5359	-3.5453
Ca ₃ Al ₂ O ₆	$Ca_3Al_2O_6 + 12H^+ = 3Ca^{++} + 2Al^{+++} + 6H_2O$	124.6852	111.6139	96.5383	82.7213	68.9964	57.9377	48.6374	40.4634
CaAl ₂ O ₄	$CaAl_2O_4 + 8H^+ = Ca^{++} + 2AI^{+++} + 4H_2O$	52.2923	45.5699	37.7870	30.6288	23.4767	17.6536	12.6792	8.2205
Pseudo-wollastonite (CaSiO ₃)	$CaSiO_3 + 2H^+ = Ca^{++} + SiO_2(aq) + H_2O$	15.4054	14.0344	12.3838	10.8597	9.3603	8.1663	7.1587	6.2301
Titanite (CaSiTiO ₅)	CaSiTiO ₅ + 2H ⁺ + H ₂ O = Ti(OH) ₄ + Ca_2^+ + SiO ₂ (aq)	2.8995	1.9918	0.7981	-0.3263	-1.4237	-2.2881	-3.0278	-3.7622
Perovskite (CaTiO ₃)	$CaTiO_3 + 2H^+ + H_2O = Ti(OH)_4 + Ca^{++}$	12.8727	11.0419	8.8630	6.8551	4.8765	3.3010	1.9809	0.7905
Co(OH) ₂	$Co(OH)_2 + 2H^+ = Co^{++} + 2H_2O$	14.5818	13.0671	11.3386	9.7790	8.2566	7.0476	6.0355	5.1363
Spinel-Co (Co ₃ O ₄)	$Co_3O_4 + 8H^+ = Co^{++} + 2Co^{+++} + 4H_2O$	-8.7683	-10.4344	-12.3845	-14.1795	-16.0115	-17.6046	-19.1362	-20.7431
CoCl ₂	$CoCl_2(s) = Co^{++} + 2Cl^{-}$	9.4861	8.2904	6.7200	5.0870	3.2193	1.4485	-0.3404	-2.3262
CoF ₃ *	$CoF_3 = Co^{+++} + 3F^{-+}$	0.5317	-1.3201	-3.7439	-6.2444	-9.0880	-11.7850	-14.5255	-17.5790
Sphaerocobaltite (CoCO ₃)	$CoCO_3(s) + H^+ = Co^{++} + HCO_3^-$	1.3240	0.7971	0.1099	-0.5992	-1.4131	-2.2012	-3.0266	-3.9840
CoCr ₂ O ₄	$CoCr_2O_4 + 8H^+ = Co^{++} + 2Cr^{+++} + 4H_2O$	19.2812	15.0442	10.1319	5.6202	1.1016	-2.6209	-5.8826	-8.9219
CoF ₂	$CoF_2 = Co^{++} + 2F^-$	-0.6789	-1.5187	-2.6656	-3.8880	-5.3257	-6.7418	-8.2402	-9.9907
CoFe ₂ O ₄	$CoFe_2O_4 + 8H^+ = Co^{++} + 2Fe^{+++} + 4H_2O$	13.4446	10.0104	6.0420	2.4107	-1.2228	-4.2310	-6.9018	-9.4475
CoO	$CoO + 2H^{+} = Co^{++} + H_2O$	15.2495	13.5557	11.6031	9.8196	8.0552	6.6368	5.4402	4.3753
CoTiO ₃	$CoTiO_3 + 2H^+ + H_2O = Co^{++} + Ti(OH)_4(aq)$	18.2297	17.0136	15.5343	14.1645	12.8139	11.7316	10.8045	9.9308
CoWO ₄	$CoWO_4 = Co^{++} + WO_4^{}$	-11.9847	-11.7760	-11.7291	-11.8788	-12.2822	-12.8981	-13.7588	-14.9905

Table 6-37. Corrected Log K EQ3/6 Grids for Affected Solid Phases (Continued)

Data0.ymp.R2 Species Name	Reaction	log K 0.01°C	log K 25°C	log K 60°C	log K 100°C	log K 150°C	log K 200°C	log K 250°C	log K 300°C
Eskolaite (Cr ₂ O ₃)	$Cr_2O_3 + 2H_2O + 1.5O_2(g) = 2CrO_4^{} + 4H^+$	-11.5436	-12.2116	-13.4372	-15.0171	-17.1381	-19.4062	-21.9006	-24.8658
CrCl ₃	$CrCl_3(s) = Cr^{+++} + 3Cl^{-}$	22.9508	19.9413	16.1776	12.4285	8.3270	4.6206	1.0623	-2.6568
CrF ₃	$CrF_3(s) = Cr^{+++} + 3F^-$	-7.8740	-9.0957	-10.7847	-12.6037	-14.7665	-16.9197	-19.2158	-21.8988
Crl ₃	$Crl_3 = Cr^{+++} + 3l^-$	30.7636	27.4198	23.2699	19.1619	14.7015	10.7132	6.9359	3.0557
CrO ₃	$CrO_3 + H_2O = CrO_4^{} + 2H^+$	-3.2012	-3.2201	-3.4714	-3.9351	-4.6827	-5.5804	-6.6462	-7.9877
Ferrite-Cu (CuFe ₂ O ₄)	$CuFe_2O_4 + 8H^+ = Cu^{++} + 2Fe^{+++} + 4H_2O$	12.8745	9.5266	5.6722	2.1613	-1.3333	-4.2134	-6.7633	-9.1921
Iron (Fe)	$Fe + 2H^+ + 0.5O_2(g) = Fe^{++} + H_2O$	63.6419	57.5836	50.6273	44.2830	38.0396	33.0967	29.0558	25.6483
Fe(OH) ₂	$Fe(OH)_2(s) + 2H^+ = Fe^{++} + 2H_2O$	15.3477	13.8214	12.0849	10.5217	8.9974	7.7876	6.7751	5.8759
Fe(OH) ₃	$Fe(OH)_3(s) + 3H^+ = Fe^{+++} + 3H_2O$	7.0070	5.6581	4.1380	2.7863	1.4749	0.4205	-0.4958	-1.3572
Fe ₂ (SO ₄) ₃	$Fe_3(SO_4)_3(s) = Fe^{+++} + 3SO_4^{}$	4.5382	0.8936	-3.9646	-9.0528	-14.9043	-20.4839	-26.1426	-32.4119
Hercynite (FeAl ₂ O ₄)	$FeAl_2O_4 + 8H^+ = Fe^{++} + 2Al^{+++} + 4H_2O$	27.2213	22.4207	16.8420	11.6987	6.5321	2.2752	-1.4349	-4.8537
Lawrencite (FeCl ₂)	$FeCl_2(g) = Fe^{++} + 2Cl^-$	10.3385	9.0646	7.4052	5.6922	3.7458	1.9119	0.0690	-1.9676
Molysite (FeCl ₃)	$FeCl_3(s) = Fe^{+++} + 3Cl^-$	15.8516	13.5217	10.5454	7.5215	4.1378	0.9993	-2.1023	-5.4547
Chromite (FeCr ₂ O ₄)	$FeCr_2O_4 + 8H^+ = Fe^{++} + 2Cr^{+++} + 4H_2O$	21.4534	16.9730	11.7934	7.0498	2.3169	-1.5620	-4.9377	-8.0576
FeF ₂	$FeF_2(s) = Fe^{++} + 2F^{-}$	-0.5943	-1.4320	-2.5761	-3.7949	-5.2267	-6.6351	-8.1241	-9.8639
FeF ₃	$FeF_3(s) = Fe^{+++} + 3F^{-}$	-19.1363	-19.2386	-19.6390	-20.2780	-21.2731	-22.4970	-24.0325	-26.0812
Ferrite-Ca (CaFe ₂ O ₄)	Ferrite-Ca + $8H^{+}$ = $2Fe^{+++}$ + Ca^{++} + $4H_{2}O$	25.8315	21.5945	16.7047	12.2304	7.7701	4.1185	0.9419	-2.0036
Ferrite-Ni (NiFe ₂ O ₄)	Ferrite-Ni + $8H^+$ = $2Fe^{+++}$ + Ni^{++} + $4H_2O$	13.2008	9.7959	5.8487	2.2265	-1.4072	-4.4224	-7.1037	-9.6613
FeSO ₄	$FeSO_4(s) = Fe^{++} + SO_4^{}$	3.0160	1.9396	0.4818	-1.0620	-2.8537	-4.5771	-6.3409	-8.3212
Ilmenite (FeTiO ₃)	$FeTiO_3 + 2H^+ + H_2O = Ti(OH)_4 + Fe^{++}$	4.7351	3.3187	1.6136	0.0422	-1.5020	-2.7328	-3.7765	-4.7442
MgBr ₂	$MgBr_2 = Mg^{++} + 2Br^-$	30.5646	27.6871	24.1884	20.8089	17.2448	14.1591	11.3276	8.5018
Chloromagnesite (MgCl ₂)	MgCl ₂ = Mg ⁺⁺ + 2Cl ⁻	24.2706	21.8099	18.7962	15.8593	12.7237	9.9647	7.3824	4.7429
MgSO ₄	$MgSO_4 = Mg^{++} + SO_4^{}$	6.2422	4.8818	3.1062	1.2859	-0.7602	-2.6686	-4.5701	-6.6537
Bixbyite (Mn ₂ O ₃)	$Mn_2O_3 + 6H^+ = 2Mn^{+++} + 3H_2O$	2.5151	0.0527	-2.8252	-5.4871	-8.1834	-10.4469	-12.4826	-14.4362
Tephroite (Mn ₂ SiO ₄)	$Mn_2SiO_4 + 4H^+ = 2Mn^{++} + SiO_2(aq) + 2H_2O$	26.8198	24.2091	21.1502	18.3654	15.6422	13.4760	11.6435	9.9606
Scacchite (MnCl ₂)	$MnCl_2 = Mn^{++} + 2Cl^-$	10.3344	9.2222	7.7590	6.2351	4.4853	2.8154	1.1121	-0.8040
MnSO ₄	$MnSO_4 = Mn^{++} + SO_4^{}$	4.0732	3.1105	1.7919	0.3831	-1.2693	-2.8789	-4.5504	-6.4586

Table 6-37. Corrected Log K EQ3/6 Grids for Affected Solid Phases (Continued)

Data0.ymp.R2	Donation.	log K	log K	log K 60°C	log K	log K	log K	log K	log K 300°C
Species Name	Reaction	0.01°C 1.0114	25°C 0.5936		100°C -1.4682	150°C -3.1562	200°C -5.0424	250°C -7.2005	-9.8704
MoO ₂ Cl ₂	$MoO_2Cl_2 + 2H_2O = MoO_4^{} + 2Cl^- + 4H^+$	11.6028	10.9840			8.7862	8.1362	7.4957	6.7592
Na ₂ CO ₃	$Na_2CO_3 + H^+ = 2Na^+ + HCO_3^-$								
Na ₂ CrO ₄	$Na_2CrO_4 = 2Na^+ + CrO_4^{}$	3.8172	3.5616		2.4882	1.6936	0.8277	-0.1710	-1.4480
Nahcolite (NaHCO ₃)	NaHCO ₃ = Na ⁺ + HCO ₃ ⁻	-1.0584	-0.7061	-0.3492	-0.0651	0.1539	0.2439	0.1989	-0.0343
Heazlewoodite (Ni ₃ S ₂)	$Ni_3S_2 + 4H^+ + 0.5O_2(g) = 3Ni^{++} + 2HS^- + H_2O$	28.6021	24.4693	19.5049	14.7718	9.8374	5.5959	1.7110	-2.1571
NiCl ₂	$NiCl_2(s) = Ni^{++} + 2Cl^{-}$	9.8354	8.5926	6.9627	5.2714	3.3424	1.5199	-0.3136	-2.3383
NiCO ₃	NiCO ₃ + H ⁺ = Ni ⁺⁺ + HCO ₃ ⁻	3.3217	2.5700	1.6121	0.6441	-0.4364	-1.4444	-2.4551	-3.5709
NiCr ₂ O ₄	$NiCr_2O_4 + 8H^+ = Ni^{++} + 2Cr^{+++} + 4H_2O$	28.7818	23.6681	17.7445	12.3055	6.8699	2.4200	-1.4337	-4.9644
NiF ₂	$NiF_2(s) = Ni^{++} + 2F^-$	0.7839	-0.2087	-1.5373	-2.9301	-4.5391	-6.0927	-7.7040	-9.5483
Trevorite (NiFe ₂ O ₄)	$NiFe_2O_4 + 8H^+ = Ni^{++} + 2Fe^{+++} + 4H_2O$	13.2008	9.7959	5.8487	2.2265	-1.4051	-4.4151	-7.0862	-9.6263
NiSO ₄	NiSO ₄ = Ni ⁺⁺ + SO ₄	6.7477	5.3469	3.5093	1.6121	-0.5346	-2.5445	-4.5454	-6.7251
NiTiO ₃	$NiTiO_3 + 2H^+ + H_2O = Ti(OH)_4 + Ni^{++}$	3.5747	2.2603	0.6636	-0.8164	-2.2786	-3.4517	-4.4545	-5.3922
NiWO ₄	$NiWO_4 = Ni^{++} + WO_4^{}$	-11.2995	-11.1792	-11.2383	-11.4884	-11.9944	-12.6951	-13.6275	-14.9206
Ti ₂ O ₃	$Ti_2O_3(s) + 4H_2O + 0.5O_2 = 2Ti(OH)_4$ (aq)	51.9834	46.0376	39.0528	32.6332	26.3242	21.3632	17.3404	13.9500
Ti ₃ O ₅	$Ti_3O_5(s) + 6H_2O + 0.5O_2 = 3Ti(OH)_4$ (aq)	45.9463	39.8764	32.6736	26.0351	19.5159	14.3998	10.2524	6.7332
TiB ₂	$TiB_2 + 5H_2O + 2.5O_2(g) = Ti(OH)_4 + 2B(OH)_3$	338.0323	307.4013	272.0462	239.6276	207.5965	182.2311	161.6294	144.5501
TiBr ₃	$TiBr_3 + 3.5H_2O + 0.25O_2(g) = Ti(OH)_4 + 3Br^- + 3H^+$	54.0864	48.8970	42.5599	36.4506	30.0659	24.6353	19.7800	15.0909
TiBr ₄	$TiBr_4 + 4H_2O = Ti(OH)_4 + 4Br^- + 4H^+$	38.6712	34.9543	30.2039	25.4361	20.2355	15.5928	11.2104	6.6851
TiCl ₂	$TiCl_2(s) + 3H_2O + 0.5O_2 = Ti(OH)_4(aq) + 2Cl^- + 2H^+$	79.0531	71.4576	62.4653	54.0353	45.4934	38.4957	32.5244	27.1272
TiCl3	$TiCl_3(s) + 3.5H_2O + 0.25O_2 = $ $Ti(OH)_4(aq) + 3Cl^- + 3H^+$	45.2729	40.6359	34.9416	29.4199	23.6102	18.6279	14.1295	9.7279
TiF3	$TiF_3(s) + 3.5H_2O + 0.25O_2 = Ti(OH)_4(aq) + 3F^- + 3H^+$	-25.4447	-24.9948	-24.8505	-25.0324	-25.5775	-26.4084	-27.5609	-29.2184
TiF ₄ (am)	$TiF_4(s) + 4H_2O = Ti(OH)_4(aq) + 4F^- + 4H^+$	-9.2918	-10.2028	-11.6928	-13.4379	-15.6171	-17.8511	-20.2813	-23.2060

Table 6-37. Corrected Log K EQ3/6 Grids for Affected Solid Phases (Continued)

Data0.ymp.R2		log K							
Species Name	Reaction	0.01°C	25°C	60°C	100°C	150°C	200°C	250°C	300°C
Til ₄	$TiI_4 + 4H_2O = Ti(OH)_4 + 4I^- + 4H^+$	40.4343	36.9635	32.5191	28.0374	23.1169	18.6929	14.4885	10.1176
TiO	$TiO(s) + 2H_2O + 0.5O_2 = Ti(OH)_4$ (aq)	65.1583	58.6942	51.1947	44.3284	37.5793	32.2687	27.9731	24.3976
Uranium U	$U + 2H^+ + 1.5O_2(g) = UO_2^{++} + H_2O$	229.3698	208.4445	184.4380	162.5359	140.9867	123.9744	110.1697	98.6979
U(SO ₄) ₂	$U(SO_4)_2 = U^{++++} + 2SO_4^{}$	-10.6470	-11.9785	-13.8994	-16.0361	-18.6520	-21.3227	-24.2285	-27.6849
U_2S_3	$U_2S_3 + 3H^+ = 2U^{+++} + 3HS^-$	13.0332	10.4341	7.0461	3.5671	-0.3536	-4.0128	-7.6487	-11.5878
UBr ₃	UBr ₃ = U ⁺⁺⁺ + 3Br ⁻	22.2645	19.9367	16.9090	13.7994	10.3020	7.0598	3.8722	0.4518
UBr ₄	UBr ₄ = U ⁺⁺⁺⁺ + 4Br ⁻	35.4896	31.2328	25.9925	20.8510	15.3063	10.3601	5.6542	0.7605
UCI ₃	UCI ₃ = U ⁺⁺⁺ + 3CI ⁻	14.9568	13.0401	10.4946	7.8273	4.7621	1.8543	-1.0714	-4.2865
UCI ₄	UCI ₄ = U ⁺⁺⁺⁺ + 4CI ⁻	25.6371	21.9229	17.3189	12.7604	7.7844	3.2769	-1.0866	-5.7135
UCI ₅	$UCI_5 + 2H_2O = UO_2^+ + 5CI^- + 4H^+$	37.3001	33.8207	29.2728	24.5557	19.2052	14.2286	9.3512	4.1472
UCI ₆	$UCI_6 + 2H_2O = UO_2^{++} + 6CI^- + 4H^+$	58.6513	53.1432	46.2515	39.3626	31.8081	24.9939	18.4876	11.7108
UF ₃	UF ₃ = U ⁺⁺⁺ + 3F ⁻	-21.2939	-20.9385	-20.8561	-21.0915	-21.7266	-22.6949	-24.0446	-25.9613
UF ₄	UF ₄ = U ⁺⁺⁺⁺ + 4F ⁻	-30.3003	-30.3553	-30.7351	-31.3960	-32.4872	-33.8977	-35.7404	-38.2800
UF ₅ (beta)	$UF_5 + 2H_2O = UO_2^+ + 5F^- + 4H^+$	-12.6325	-13.1683	-14.3049	-15.8516	-18.0173	-20.4392	-23.2340	-26.7186
UF ₆	$UF_6 + 2H_2O = UO_2^{++} + 6F^- + 4H^+$	21.5553	17.5678	12.4557	7.2463	1.3981	-4.0509	-9.4686	-15.3832
UI ₃	UI ₃ = U ⁺⁺⁺ + 3I ⁻	32.9911	29.9408	26.0968	22.2421	18.0049	14.1734	10.5065	6.6935
UI ₄	UI ₄ = U ⁺⁺⁺⁺ + 4I ⁻	45.2721	40.4934	34.6706	28.9961	22.9161	17.5379	12.4777	7.2943
UO ₂ Br ₂	$UO_2Br_2 = UO_2^{++} + 2Br^-$	18.4096	16.4880	14.1001	11.7306	9.1432	6.8069	4.5591	2.1893
UO ₂ Cl ₂	$UO_2CI_2 = UO_2^{++} + 2CI^-$	13.7870	12.1037	9.9956	7.8820	5.5426	3.3955	1.2934	-0.9651
UO ₂ F ₂	$UO_2F_2 = UO_2^{++} + 2F^-$	-5.6625	-6.2647	-7.1190	-8.0669	-9.2359	-10.4458	-11.7863	-13.4186
UO ₂ SO ₄	$UO_2SO_4 = UO_2^{++} + SO_4^{}$	3.6829	2.4282	0.7802	-0.9327	-2.8940	-4.7579	-6.6467	-8.7462
UO ₃ (gamma)	$UO_3 + 2H^+ = UO_2^{++} + H_2O$	9.2004	7.8659	6.3502	4.9769	3.6191	2.5193	1.5758	0.7124
UOBr ₂	$UOBr_2 + 2H^+ = U^{++++} + 2Br^- + H_2O$	10.2644	7.9817	5.2065	2.5154	-0.3693	-2.9518	-5.4426	-8.0790
UOBr ₃	$UOBr_3 + H_2O = UO_2^+ + 3Br^- + 2H^+$	25.8267	23.5777	20.6256	17.5646	14.1014	10.8941	7.7683	4.4607
UOCI	UOCI + 2H ⁺ = U ⁺⁺⁺ +CI ⁻ + H ₂ O	-9.8798	-9.7309	-9.7099	-9.8326	-10.1403	-10.6010	-11.2370	-12.1246
UOCl ₂	$UOCl_2 + 2H^+ = U^{++++} + 2CI^- + H_2O$	8.1388	5.8869	3.1534	0.5015	-2.3463	-4.9033	-7.3783	-10.0079
UOCl ₃	$UOCl_3 + H_2O = UO_2^+ + 3Cl^- + 2H^+$	9.6660	8.5736	6.9597	5.1220	2.8583	0.5891	-1.7874	-4.4886
WCl ₂ (s)	$WCl_2(s) + 2H_2O + O_2(g) = WO_4^{} + 2Cl^- + 4H^+$	93.6338	84.5211	73.6761	63.3790	52.7437	43.8115	35.9624	28.6009

Table 6-37. Corrected Log K EQ3/6 Grids for Affected Solid Phases (Continued)

Data0.ymp.R2 Species Name	Reaction	log K 0.01°C	log K 25°C	log K 60°C	log K 100°C	log K 150°C	log K 200°C	log K 250°C	log K 300°C
WCl ₄ (s)	$WCl_4(s) + 3H_2O + 0.5O_2 = WO_4^{} + 4Cl^- + 6H^+$	71.3689	64.5388	56.1177	47.8276	38.9055	31.0428	23.7400	16.3841
WCl ₅ (s)	$WCI_5(s) + 3.5H_2O + 0.25O_2 = WO_4^{} + 5CI^- + 7H^+$	65.4019	59.3442	51.7110	44.0362	35.5861	27.9512	20.6691	13.1034
WCl ₆ (s)	$WCI_6(s) + 4H_2O = WO_4^{} + 6CI^- + 8H^+$	57.2682	52.1561	45.5135	38.6433	30.8566	23.6054	16.4742	8.8097
WO ₂ Cl ₂ (s)	$WO_2CI_2(s) + 2H_2O = WO_4^{} + 2CI^- + 4H^+$	0.6699	-0.0612	-1.2796	-2.7861	-4.7725	-6.8877	-9.2282	-12.0481
WOCl ₄ (s)	$WOCl_4(s) + 3H_2O = WO_4^{} + 4Cl^- + 6H^+$	34.4557	31.2806	27.0555	22.5950	17.4379	12.5397	7.6296	2.2438
WOF ₄ (s)	$WOF_4(s) + 3H_2O = WO_4^{} + 4F^- + 6H^+$	10.1133	7.7357	4.4528	0.8968	-3.3209	-7.4485	-11.7279	-16.5992

^{*} The equation for CoF₃ is corrected from the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), which gives an equation for CoCl₃. Note that the corrected values in this table are not implemented in the data0.ymp.R4 database (output DTN: SN0410T0510404.002).

Table 6-38. Δ Log K (Difference Between Incorrect and Corrected Values) for Solid Phases

Data0.ymp.R2		∆ log K	Δ log K	∆ log K	∆ log K	∆ log K	∆ log K	Δ log K	∆ log K
Species Name	Reaction	0.01°C	25°C	60°C	100°C	150°C	200°C	250°C	300°C
Witherite (BaCO ₃)	$BaCO_3 + H^+ = Ba^{++} + HCO_3^-$	0.0027	0.0000	0.0035	0.0128	0.0277	0.0434	0.0587	0.0730
Portlandite (Ca(OH) ₂)	$Ca(OH)_2 + 2H^+ = Ca^{++} + 2H_2O$	0.0039	0.0000	0.0051	0.0186	0.0401	0.0629	0.0851	0.1059
Ferrite Dicalcium (Ca ₂ Fe ₂ O ₅)	$Ca_2Fe_2O_5 + 10H^{\dagger} = 2Ca^{\dagger\dagger} + 2Fe^{\dagger\dagger\dagger} + 5H_2O$	0.0117	0.0000	0.0154	0.0561	0.1207	0.1883	0.2534	0.3139
Ferrite-Mg (MgFe ₂ O ₄)	Ferrite-Mg + $8H^{+}$ = $2Fe^{+++}$ + Mg^{++} + $4H_{2}O$	0.0066	0.0000	0.0087	0.0319	0.0690	0.1082	0.1462	0.1820
Ca ₃ Al ₂ O ₆	$Ca_3Al_2O_6 + 12H^+ = 3Ca^{++} + 2Al^{+++} + 6H_2O$	0.0111	0.0000	0.0147	0.0537	0.1161	0.1819	0.2460	0.3062
CaAl ₂ O ₄	$CaAl_2O_4 + 8H^+ = Ca^{++} + 2Al^{+++} + 4H_2O$	0.0074	0.0000	0.0097	0.0356	0.0768	0.1205	0.1629	0.2027
Pseudo-wollastonite (CaSiO ₃)	CaSiO ₃ + 2H ⁺ = Ca ⁺⁺ + SiO ₂ (aq) + H_2O	0.0052	0.0000	0.0069	0.0252	0.0545	0.0854	0.1154	0.1437
Titanite (CaSiTiO ₅)	CaSiTiO ₅ + 2H ⁺ + H ₂ O = Ti(OH) ₄ + Ca^{++} + SiO ₂ (aq)	0.0089	0.0000	0.0118	0.0430	0.0930	0.1458	0.1971	0.2453
Perovskite (CaTiO ₃)	$CaTiO_3 + 2H^+ + H_2O = Ti(OH)_4 + Ca^{++}$	0.0062	0.0000	0.0082	0.0299	0.0646	0.1013	0.1370	0.1704
Co(OH) ₂	$Co(OH)_2 + 2H^+ = Co^{++} + 2H_2O$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Spinel-Co (Co ₃ O ₄)	$Co_3O_4 + 8H^+ = Co^{++} + 2Co^{+++} + 4H_2O$	0.0055	0.0000	0.0072	0.0265	0.0572	0.0897	0.1213	0.1510
CoCl ₂	CoCl2(s) = Co++ + 2Cl-	0.0010	0.0000	0.0014	0.0050	0.0108	0.0170	0.0230	0.0286
CoF ₃ *	CoF ₃ = Co ⁺⁺⁺ + 3F ⁻ *	0.0019	0.0000	0.0026	0.0094	0.0203	0.0318	0.0430	0.0536
Sphaerocobaltite (CoCO ₃)	$CoCO_3(s) + H^+ = Co^{++} + HCO_3^-$	0.0040	0.0000	0.0053	0.0192	0.0415	0.0651	0.0880	0.1096
CoCr ₂ O ₄	$CoCr_2O_4 + 8H^+ = Co^{++} + 2Cr^{+++} + 4H_2O$	0.0031	0.0000	0.0041	0.0150	0.0323	0.0506	0.0685	0.0852
CoF ₂	$CoF_2 = Co^{++} + 2F^{-}$	0.0027	0.0000	0.0036	0.0132	0.0286	0.0449	0.0606	0.0755
CoFe ₂ O ₄	CoFe ₂ O ₄ + 8H ⁺ = Co ⁺⁺ + 2Fe ⁺⁺⁺ + 4H ₂ O	0.0073	0.0000	0.0096	0.0350	0.0757	0.1186	0.1604	0.1997
CoO	$CoO + 2H^{+} = Co^{++} + H_2O$	-0.0013	0.0000	-0.0018	-0.0064	-0.0138	-0.0217	-0.0293	-0.0365
CoTiO ₃	$CoTiO_3 + 2H^+ + H_2O = Co^{++} + Ti(OH)_4(aq)$	0.0037	0.0000	0.0048	0.0176	0.0381	0.0597	0.0807	0.1004

Table 6-38. △ Log K (Difference Between Incorrect and Corrected Values) for Solid Phases (Continued)

Data0.ymp.R2	Penetion	∆ log K 0.01°C	∆ log K 25°C	∆ log K 60°C	∆ log K 100°C	∆ log K	∆ log K	∆ log K 250°C	∆ log K 300°C
Species Name	Reaction	0.0000	0.0000		0.0000	150°C 0.0000	200°C 0.0000	0.0000	0.0000
CoWO ₄	$CoWO_4 = Co^{++} + WO_4^{}$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Eskolaite (Cr ₂ O ₃)	$Cr_2O_3 + 2H_2O + 1.5O_2(g) = 2CrO_4^{} + 4H^+$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CrCl ₃	$CrCl_3(s) = Cr^{+++} + 3Cl^-$	0.0022	0.0000	0.0029	0.0107	0.0231	0.0362	0.0489	0.0609
CrF ₃	$CrF_3(s) = Cr^{+++} + 3F^{-}$	0.0036	0.0000	0.0047	0.0173	0.0374	0.0586	0.0792	0.0986
Crl ₃	$Crl_3 = Cr^{+++} + 3l^-$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CrO ₃	$CrO_3 + H_2O = CrO_4^{} + 2H^+$	0.0037	0.0000	0.0049	0.0178	0.0385	0.0604	0.0817	0.1017
Ferrite-Cu (CuFe ₂ O ₄)	$CuFe_2O_4 + 8H^+ = Cu^{++} + 2Fe^{+++} + 4H_2O$	-0.1276	0.0000	0.1755	0.3644	0.5785	0.7672	0.9322	1.0758
Iron (Fe)	Fe + $2H^+$ + $0.5O_2(g)$ = Fe^{++} + H_2O	-0.0004	0.0000	-0.0005	-0.0017	-0.0037	-0.0058	-0.0078	-0.0097
Fe(OH) ₂	$Fe(OH)_2(s) + 2H^+ = Fe^{++} + 2H_2O$	0.0064	0.0000	0.0084	0.0307	0.0662	0.1038	0.1404	0.1747
Fe(OH) ₃	$Fe(OH)_3(s) + 3H^+ = Fe^{+++} + 3H_2O$	0.0093	0.0000	0.0123	0.0451	0.0974	0.1526	0.2064	0.2569
Fe ₂ (SO ₄) ₃	$Fe_3(SO_4)_3(s) = Fe^{+++} + 3SO_4^{}$	0.0235	0.0000	0.0311	0.1137	0.2455	0.3849	0.5204	0.6477
Hercynite (FeAl ₂ O ₄)	$FeAl_2O_4 + 8H^+ = Fe^{++} + 2AI^{+++} + 4H_2O$	0.0078	0.0000	0.0103	0.0376	0.0812	0.1273	0.1722	0.2143
Lawrencite (FeCl ₂)	$FeCl_2(g) = Fe^{++} + 2Cl^{-}$	0.0009	0.0000	0.0012	0.0045	0.0097	0.0152	0.0205	0.0256
Molysite (FeCl ₃)	$FeCl_3(s) = Fe^{+++} + 3Cl^-$	0.0002	0.0000	0.0003	0.0010	0.0021	0.0033	0.0044	0.0055
Chromite (FeCr ₂ O ₄)	$FeCr_2O_4 + 8H^+ = Fe^{++} + 2Cr^{} + 4H_2O$	0.0071	0.0000	0.0093	0.0341	0.0736	0.1154	0.1560	0.1942
FeF ₂	$FeF_2(s) = Fe^{++} + 2F^{-}$	0.0015	0.0000	0.0020	0.0075	0.0162	0.0253	0.0342	0.0426
FeF ₃	$FeF_3(s) = Fe^{+++} + 3F^{-}$	0.0005	0.0000	0.0006	0.0024	0.0051	0.0080	0.0108	0.0134
Ferrite-Ca (CaFe ₂ O ₄)	Ferrite-Ca + $8H^+$ = $2Fe^{+++}$ + Ca^{++} + $4H_2O$	0.0034	0.0000	0.0045	0.0163	0.0353	0.0553	0.0748	0.0931
Ferrite-Ni (NiFe ₂ O ₄)	Ferrite-Ni + $8H^{+}$ = $2Fe^{+++}$ + Ni^{++} + $4H_{2}O$	0.0033	0.0000	0.0043	0.0159	0.0344	0.0539	0.0729	0.0907
FeSO ₄	$FeSO_4(s) = Fe^{++} + SO_4^{}$	0.0065	0.0000	0.0086	0.0313	0.0676	0.1060	0.1433	0.1784
Ilmenite (FeTiO ₃)	$FeTiO_3 + 2H^{+} + H_2O = Ti(OH)_4 + Fe^{++}$	0.0044	0.0000	0.0058	0.0214	0.0461	0.0723	0.0978	0.1217
MgBr ₂	$MgBr_2 = Mg^{++} + 2Br^{-}$	0.0002	0.0000	0.0003	0.0012	0.0025	0.0040	0.0054	0.0067

Table 6-38. △ Log K (Difference Between Incorrect and Corrected Values) for Solid Phases (Continued)

Data0.ymp.R2 Species Name	Reaction	∆ log K 0.01°C	∆ log K 25°C	∆ log K 60°C	∆ log K 100°C	∆ log K 150°C	∆ log K 200°C	∆ log K 250°C	∆ log K 300°C
Chloromagnesite (MgCl ₂)	$MgCl_2 = Mg^{++} + 2Cl^{-}$	0.0015	0.0000	0.0020	0.0075	0.0162	0.0253	0.0342	0.0426
MgSO ₄	$MgSO_4 = Mg^{++} + SO_4^{}$	0.0048	0.0000	0.0064	0.0234	0.0505	0.0792	0.1071	0.1333
Bixbyite (Mn ₂ O ₃)	$Mn_2O_3 + 6H^+ = 2Mn^{+++} + 3H_2O$	0.0028	0.0000	0.0037	0.0137	0.0295	0.0463	0.0626	0.0779
Tephroite (Mn ₂ SiO ₄)	$Mn_2SiO_4 + 4H^+ = 2Mn^{++} + SiO_2(aq)$ +2H ₂ O	0.0069	0.0000	0.0091	0.0332	0.0718	0.1125	0.1521	0.1893
Scacchite (MnCl ₂)	$MnCl_2 = Mn^{++} + 2Cl^-$	0.0010	0.0000	0.0014	0.0050	0.0108	0.0170	0.0230	0.0286
MnSO ₄	$MnSO_4 = Mn^{++} + SO_4^{}$	0.0065	0.0000	0.0086	0.0315	0.0681	0.1067	0.1443	0.1796
MoO ₂ Cl ₂	$MoO_2Cl_2 + 2H_2O = MoO_4^{} + 2Cl^- + 4H^+$	0.0043	0.0000	0.0057	0.0207	0.0448	0.0702	0.0949	0.1181
Na ₂ CO ₃	$Na_2CO_3 + H^+ = 2Na^+ + HCO_3^-$	-0.0054	0.0000	-0.0072	-0.0262	-0.0565	-0.0886	-0.1198	-0.1491
Na ₂ CrO ₄	$Na_2CrO_4 = 2Na^+ + CrO_4^{}$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Nahcolite (NaHCO ₃)	NaHCO ₃ = Na ⁺ + HCO ₃ ⁻	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Heazlewoodite (Ni ₃ S ₂)	$Ni_3S_2 + 4H^+ + 0.5O_2(g) = 3Ni^{++} + 2HS^- + H_2O$	0.0017	0.0000	0.0022	0.0080	0.0173	0.0271	0.0367	0.0457
NiCl ₂	$NiCl_2(s) = Ni^{++} + 2Cl^{-}$	0.0011	0.0000	0.0014	0.0051	0.0111	0.0174	0.0235	0.0292
NiCO ₃	$NiCO_3 + H^+ = Ni^{++} + HCO_3^-$	0.0027	0.0000	0.0036	0.0131	0.0284	0.0445	0.0602	0.0749
NiCr ₂ O ₄	$NiCr_2O_4 + 8H^+ = Ni^{++} + 2Cr^{+++} + 4H_2O$	0.0047	0.0000	0.0062	0.0225	0.0487	0.0763	0.1032	0.1284
NiF ₂	$NiF_2(s) = Ni^{++} + 2F^-$	0.0013	0.0000	0.0017	0.0063	0.0136	0.0213	0.0289	0.0359
Trevorite (NiFe ₂ O ₄)	$NiFe_2O_4 + 8H^+ = Ni^{++} + 2Fe^{+++} + 4H_2O$	0.0033	0.0000	0.0043	0.0159	0.0344	0.0539	0.0729	0.0907
NiSO ₄	$NiSO_4 = Ni^{++} + SO_4^{}$	0.0072	0.0000	0.0095	0.0348	0.0752	0.1179	0.1595	0.1984
NiTiO ₃	$NiTiO_3 + 2H^+ + H_2O = Ti(OH)_4 + Ni^{++}$	0.0040	0.0000	0.0053	0.0195	0.0422	0.0662	0.0895	0.1114
NiWO ₄	$NiWO_4 = Ni^{++} + WO_4^{}$	0.0010	0.0000	0.0013	0.0047	0.0102	0.0159	0.0215	0.0268
Ti ₂ O ₃	$Ti_2O_3(s) + 4H_2O + 0.5O_2 = 2Ti(OH)_4$ (aq)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Ti ₃ O ₅	$Ti_3O_5(s) + 6H_2O + 0.5O_2 = 3Ti(OH)_4$ (aq)	0.0136	0.0000	0.0179	0.0655	0.1414	0.2217	0.2998	0.3732

Table 6-38. △ Log K (Difference Between Incorrect and Corrected Values) for Solid Phases (Continued)

Data0.ymp.R2 Species Name	Reaction	∆ log K 0.01°C	∆ log K 25°C	∆ log K 60°C	∆ log K 100°C	∆ log K 150°C	∆ log K 200°C	∆ log K 250°C	∆ log K 300°C
TiB ₂	$TiB_2 + 5H_2O + 2.5O_2(g) = Ti(OH)_4 + 2B(OH)_3$	0.0039	0.0000	0.0051	0.0187	0.0404	0.0633	0.0856	0.1065
TiBr ₃	TiBr ₃ + 3.5H ₂ O + 0.25O ₂ (g) = Ti(OH) ₄ + 3Br ⁻ + 3H ⁺	-0.0002	0.0000	-0.0002	-0.0009	-0.0018	-0.0029	-0.0039	-0.0049
TiBr ₄	$TiBr_4 + 4H_2O = Ti(OH)_4 + 4Br^- + 4H^+$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
TiCl ₂	$TiCl_2(s) + 3H_2O + 0.5O_2 =$ $Ti(OH)_4(aq) + 2Cl^- + 2H^+$	0.0008	0.0000	0.0010	0.0037	0.0081	0.0127	0.0171	0.0213
TiCl ₃	$TiCl_3(s) + 3.5H_2O + 0.25O_2 = Ti(OH)_4(aq) + 3Cl^- + 3H^+$	0.0004	0.0000	0.0005	0.0019	0.0042	0.0065	0.0088	0.0110
TiF ₃	$TiF_3(s) + 3.5H_2O + 0.25O_2 = Ti(OH)_4(aq) + 3F^- + 3H^+$	-0.0008	0.0000	-0.0010	-0.0036	-0.0078	-0.0123	-0.0166	-0.0207
TiF ₄ (am)	$TiF_4(s) + 4H_2O = Ti(OH)_4(aq) + 4F^- + 4H^+$	0.0039	0.0000	0.0052	0.0189	0.0408	0.0640	0.0866	0.1077
Til ₄	$TiI_4 + 4H_2O = Ti(OH)_4 + 4I^- + 4H^+$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
TiO	$TiO(s) + 2H_2O + 0.5O_2 = Ti(OH)_4$ (aq)	0.0017	0.0000	0.0023	0.0083	0.0180	0.0282	0.0382	0.0475
Uranium U	$U + 2H^{+} + 1.5O_{2}(g) = UO_{2}^{++} + H_{2}O$	0.0002	0.0000	0.0003	0.0012	0.0025	0.0040	0.0054	0.0067
U(SO ₄) ₂	$U(SO_4)_2 = U^{++++} + 2SO_4^{}$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
U_2S_3	$U_2S_3 + 3H^+ = 2U^{+++} + 3HS^-$	0.0008	0.0000	0.0011	0.0041	0.0088	0.0137	0.0186	0.0231
UBr₃	UBr ₃ = U ⁺⁺⁺ + 3Br ⁻	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
UBr ₄	UBr ₄ = U ⁺⁺⁺⁺ + 4Br ⁻	0.0025	0.0000	0.0033	0.0121	0.0261	0.0409	0.0553	0.0688
UCl₃	UCI ₃ = U ⁺⁺⁺ + 3CI ⁻	-0.0011	0.0000	-0.0014	-0.0052	-0.0113	-0.0177	-0.0240	-0.0298
UCI ₄	UCI ₄ = U ⁺⁺⁺⁺ + 4CI ⁻	0.0007	0.0000	0.0010	0.0035	0.0076	0.0119	0.0161	0.0201
UCI ₅	$UCI_5 + 2H_2O = UO_2^+ + 5CI^- + 4H^+$	0.0012	0.0000	0.0016	0.0058	0.0125	0.0195	0.0264	0.0329
UCI ₆	$UCI_6 + 2H_2O = UO_2^{++} + 6CI^- + 4H^+$	0.0016	0.0000	0.0022	0.0079	0.0171	0.0268	0.0362	0.0450
UF ₃	UF ₃ = U ⁺⁺⁺ + 3F ⁻	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
UF ₄	UF ₄ = U ⁺⁺⁺⁺ + 4F ⁻	0.0021	0.0000	0.0027	0.0099	0.0215	0.0336	0.0455	0.0566
UF ₅ (beta)	$UF_5 + 2H_2O = UO_2^+ + 5F^- + 4H^+$	0.0004	0.0000	0.0006	0.0021	0.0046	0.0072	0.0098	0.0122
UF ₆	$UF_6 + 2H_2O = UO_2^{++} + 6F^- + 4H^+$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 6-38. △ Log K (Difference Between Incorrect and Corrected Values) for Solid Phases (Continued)

Data0.ymp.R2		Δ log K							
Species Name	Reaction	0.01°C	25°C	60°C	100°C	150°C	200°C	250°C	300°C
UI ₃	UI ₃ = U ⁺⁺⁺ + 3I ⁻	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
UI ₄	$UI_4 = U^{++++} + 4I^-$	0.0035	0.0000	0.0046	0.0170	0.0367	0.0575	0.0778	0.0968
UO ₂ Br ₂	$UO_2Br_2 = UO_2^{++} + 2Br^{-}$	0.0024	0.0000	0.0031	0.0114	0.0247	0.0387	0.0523	0.0651
UO ₂ CI ₂	$UO_2CI_2 = UO_2^{++} + 2CI^-$	0.0025	0.0000	0.0033	0.0122	0.0263	0.0412	0.0558	0.0694
UO ₂ F ₂	$UO_2F_2 = UO_2^{++} + 2F^-$	0.0044	0.0000	0.0058	0.0213	0.0459	0.0720	0.0973	0.1211
UO ₂ SO ₄	$UO_2SO_4 = UO_2^{++} + SO_4^{}$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
UO ₃ (gamma)	$UO_3 + 2H^+ = UO_2^{++} + H_2O$	0.0025	0.0000	0.0032	0.0119	0.0256	0.0402	0.0543	0.0676
UOBr ₂	$UOBr_2 + 2H^+ = U^{++++} + 2Br^- + H_2O$	0.0033	0.0000	0.0043	0.0159	0.0344	0.0539	0.0729	0.0907
UOBr ₃	$UOBr_3 + H_2O = UO_2^+ + 3Br^- + 2H^+$	0.0031	0.0000	0.0040	0.0147	0.0318	0.0499	0.0675	0.0840
UOCI	UOCI + 2H ⁺ = U ⁺⁺⁺ +CI ⁻ + H ₂ O	0.0018	0.0000	0.0024	0.0089	0.0192	0.0300	0.0406	0.0505
UOCl ₂	$UOCl_2 + 2H^+ = U^{++++} + 2Cl^- + H_2O$	0.0016	0.0000	0.0022	0.0079	0.0171	0.0268	0.0362	0.0450
UOCI ₃	$UOCl_3 + H_2O = UO_2^+ + 3Cl^- + 2H^+$	0.0026	0.0000	0.0035	0.0127	0.0275	0.0430	0.0582	0.0724
WCl ₂ (s)	$WCl_2(s) + 2H_2O + O_2(g) = WO_4^{} + 2Cl^- + 4H^+$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
WCl ₄ (s)	$WCl_4(s) + 3H_2O + 0.5O_2 = WO_4^{} + 4Cl^- + 6H^+$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
WCI ₅ (s)	$WCl_5(s) + 3.5H_2O + 0.25O_2 = WO_4^{} + 5Cl^- + 7H^+$	0.0003	0.0000	0.0004	0.0015	0.0032	0.0051	0.0068	0.0085
WCl ₆ (s)	$WCl_6(s) + 4H_2O = WO_4^{} + 6Cl^- + 8H^+$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
WO ₂ Cl ₂ (s)	$WO_2Cl_2(s) + 2H_2O = WO_4^{} + 2Cl^- + 4H+$	0.0006	0.0000	0.0008	0.0031	0.0067	0.0105	0.0142	0.0177
WOCI ₄ (s)	$WOCl_4(s) + 3H_2O = WO_4^{} + 4Cl^- + 6H^+$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
WOF ₄ (s)	$WOF_4(s) + 3H_2O = WO_4^{} + 4F^- + 6H^+$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

^{*} The equation for CoF₃ is corrected from the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), which gives an equation for CoCl₃.

Table 6-39. Comparison of $\Delta H_{\rm f}^{\circ}$ and S° Values for Solid Species from Binnewies and Milke, and Barin and Platzki

Solid Species	ΔH _f ° (J/mol) 99Bin/Mil ¹	ΔH _f ° (J/mol) 95Bar/Pla²	Difference in ΔH _f ° (J/mol)	S° (J/mol-K) 99Bin/Mil ¹	S° (J/mol-K) 95Bar/Pla ²	Difference in S° (J/mol-K)	Page Numbers 99Bin/Mil ¹	Page Numbers 95Bar/Pla ²
Portlandite Ca(OH) ₂	-986,100	-986,085	-15.00	83.4	83.387	0.013	281	455
Ferrite- Dicalcium Ca ₂ Fe ₂ O ₅	-2,133,700	-2,139,279	5579.00	188.7	188.782	-0.082	289	453
Ferrite-Mg	-1,440,100	-1,428,857	-11243.00	123.8	123.800	0.000	544	706
Ca ₃ Al ₂ O ₆	-3,587,800	-3,587,801	1.00	205.9	205.899	0.001	46	445
CaAl ₂ O ₄	-2,326,300	-2,326,304	4.00	114.2	114.223	-0.023	45	442
Wollastonite	-1,634,900	-1634940	40.00	82*	81.919	0.081	285	461
Pseudo wollastonite CaSiO ₃	-1,628,400	-1,628,400	0.00	87.4	87.362	0.038	286	462
Titanite CaSiTiO₅	-2,603,300	-2,603,302	2.00	129.2	129.202	-0.002	287	473
Perovskite CaTiO ₃	-1,659,000	-1,660,596	1596.00	93.7	93.638	0.062	286	470
Co(OH) ₂	-541,300	-539,698	-1602.00	93.3	78.998	14.302	408	545
Spinel-Co Co ₃ O ₄	-918,700	-910,020	-8680.00	109.3	114.307	-5.007	414	544
CoCl ₂	-312,500	-312,545	45.00	109.3	109.286	0.014	333	536
CoF ₃	-790,400	-790,358	-42.00	94.6	94.558	0.042	407	541
Sphaerocobaltite CoCO ₃	-713,000	-713,000	0.00	87.9	87.864	0.036	227	535
CoCr ₂ O ₄	-1,438,300	-1,437,497	-803.00	126.8	126.357	0.443	406	544
CoF ₂	-672,400	-671,532	-868.00	81.9*	82.006	-0.106	406	540
CoFe ₂ O ₄	-1,088,700	-1,087,840	-860.00	142.7	134.725	7.975	408	545
CoO	-237,700	-237,944	244.00	53	52.969	0.031	408	543
CoTiO₃	-1,207,400	-1,210,431	3031.00	96.9	97.069	-0.169	409	547
CoWO ₄	-1,142,700	-1,136,918	-5782.00	126.4	133.888	-7.488	410	554
Eskolaite Cr ₂ O ₃	-1,140,600	-1,139,701	-899.00	81.2	81.199	0.001	422	573
CrCl₃	-556,500	-556,472	-28.00	123	123.010	-0.010	359	563
CrF ₃	-1,173,200	-1,173,194	-6.00	93.9	93.881	0.019	416	565
Crl ₃	-205,000	-205,016	16.00	199.6	199.577	0.023	416	566
CrO ₃	-587,000	-589,526	2526.00	73.2	73.220	-0.020	419	571
Ferrite-Cu CuFe₂O₄ (alpha)	-966,500	-967,968	1468.00	146.8	146.758	0.042	436	624
Iron Fe	0	0	0.00	27.3	27.280	0.020	534	675
Fe(OH) ₂	-574,000	-568,999	-5001.00	87.9	87.998	-0.098	535	705
Fe(OH) ₃	-832,600	-822,997	-9603.00	104.6	106.700	-2.100	536	705
Fe ₂ (SO ₄) ₃	-2,583,000	-2,582,992	-8.00	307.5	307.524	-0.024	546	721
Hercynite FeAl ₂ O ₄	-1,969,500	-1,995,299	25799.00	106.3	106.299	0.001	49	704
Lawrencite FeCl ₂	-341,600	-341,833	233.00	117.9	117.947	-0.047	336	686

Table 6-39. Comparison of ΔH_f° and S° Values for Solid Species from Binnewies and Milke, and Barin and Platzki (Continued)

0.11.10	ΔH _f ° (J/mol)	ΔH _f ° (J/mol)	Difference in ΔH _f °	S° (J/mol-K)	S° (J/mol-K)	Difference in S°	Page Numbers	Page Numbers
Solid Species		95Bar/Pla ²	(J/mol)	99Bin/Mil ¹	95Bar/Pla ²	(J/mol-K)	99Bin/Mil ¹	95Bar/Pla ²
Molysite FeCl ₃	-399,200	-399,405	205.00	147.8	142.336	5.464	362	687
Chromite FeCr ₂ O ₄	-1,458,600	-1,458,124	-476.00	146.9	141.963	4.937	421	575
FeF ₂	-705,800	-705,841	41.00	87	86.985	0.015	475	691
FeF ₃	-1,039,300	-1,041,816	2516.00	98.3	98.324	-0.024	493	692
Goethite FeOOH	-558,100	-	-	60.4	-	-	535	-
Ferrite-Ca (CaFe ₂ O ₄)	-1,479,400	-1,520,340	40940.00	145.2	145.352	-0.152	279	453
Ferrite-Ni (NiFe ₂ O ₄)	-1,084,500	-1,081,100	-3400.00	125.9	131.800	-5.900	545	709
FeSO ₄	-928,900	-928,848	-52.00	121	120.959	0.041	539	720
Ilmenite FeTiO ₃	-1,239,200	-1,235,535	-3665.00	105.9	105.855	0.045	538	714
MgBr ₂	-524,300	-524,255	-45.00	117.2	117.152	0.048	184	997
Chloro magnesite MgCl ₂	-644,200	-641,616	-2584.00	89.5	89.630	-0.130	340	1003
MgSO ₄	-1,261,800	-1,284,898	23098.00	91.4	91.600	-0.200	676	1028
Bixbyite Mn2O3	-959,000	-959,002	2.00	110.5	110.499	0.001	689	1047
Tephroite Mn ₂ SiO ₄	-1,725,300	-1,730,498	5198.00	142.2	163.201	-21.001	690	1051
Scacchite MnCl ₂	-481,300	-481,290	-10.00	118.2	118.240	-0.040	341	1040
MnSO ₄	-1,065,300	-1,065,251	-49.00	112.1	112.098	0.002	686	1056
MoO ₂ Cl ₂	-725,800	-717,100	-8700.00	120.5	142.256	-21.756	342	1074
Na ₂ CO ₃	-1,130,800	-1,130,768	-32.00	138.8	138.783	0.017	243	1117
Na ₂ CrO ₄	-1,334,300	-1,342,198	7898.00	176.6	176.611	-0.011	418	1121
Nahcolite NaHCO ₃	-936,300	-950,810	14510.00	101.2	101.701	-0.501	232	1125
Heazlewoodite Ni ₃ S ₂	-216,300	-216,313	13.00	133.9	133.888	0.012	740	1222
NiCl ₂	-305,300	-305,348	48.00	98	98.006	-0.006	344	1207
NiCO ₃	-696,300	-694,544	-1756.00	86.2	86.190	0.010	244	1205
NiCr ₂ O ₄	-1,392,400	-1,381,557	-10843.00	129.7	119.244	10.456	422	577
NiF ₂	-657,700	-657,725	25.00	73.6	73.597	0.003	483	1210
Trevorite NiFe ₂ O ₄	-1,084,500	-1,081,100	-3400.00	125.9	131.800	-5.900	545	709
NiSO ₄	-873,200	-872,908	-292.00	101.3	92.002	9.298	735	1223
NiTiO ₃	-1,201,400	-1,202,440	1040.00	82.6	85.772	-3.172	734	1217
NiWO ₄	-1,127,800	-1,127,170	-630.00	118	125.520	-7.520	735	1230
Ti ₂ O ₃	-1,520,900	-1,520,884	-16.00	77.3	77.237	0.063	772	1694
Ti₃O₅ (alpha)	-2,459,100	-2,459,146	46.00	129.4	129.369	0.031	786	1695
TiB ₂	-315,900	-323,800	7900.00	28.5	28.493	0.007	115	1669
TiBr ₃	-551,900	-550,196	-1704.00	176.6	176.565	0.035	207	1671
TiBr ₄	-619,700	-617,977	-1723.00	243.5	243.509	-0.009	215	1672
TiCl ₂	-515,500	-515,469	-310.00	87.3	87.362	-0.062	355	1676
TiCl ₃	-721,700	-721,740	40.00	139.8	139.746	0.054	380	1677

Table 6-39. Comparison of ΔH_f° and S° Values for Solid Species from Binnewies and Milke, and Barin and Platzki (Continued)

Solid Species	ΔH _f ° (J/mol) 99Bin/Mil ¹	ΔH _f ° (J/mol) 95Bar/Pla²	Difference in ΔH _f ° (J/mol)	S° (J/mol-K) 99Bin/Mil ¹	S° (J/mol-K) 95Bar/Pla ²	Difference in S° (J/mol-K)	Page Numbers 99Bin/Mil ¹	Page Numbers 95Bar/Pla ²
TiF ₃	-1,435,500	-1,435,530	30.00	87.9	87.864	0.036	509	1681
TiF ₄ (am)	-1,649,300	-1,649,333	33.00	134	133.972	0.028	520	1682
Til ₄	-375,700	-375,723	23.00	246.2	246.019	0.181	631	1687
TiO	-542,700	-542,665	-35.00	34.8	34.769	0.031	749	1690
Uranium U	0	0	0.00	50.3	50.292	0.008	888	1725
U(SO ₄) ₂	-2,318,000	-2,317,936	-64.00	164	161.084	2.916	794	1757
U_2S_3	-854,000	-854,000	0.00	199.2	199.200	0.000	843	1757
UBr ₃	-699,100	-699,146	46.00	192.5	192.464	0.036	208	1729
UBr₄	-802,500	-802,500	0.00	238.5	238.501	-0.001	216	1730
UCl ₃	-861,900	-861,904	4.00	159	158.992	0.008	381	1734
UCl₄	-1,018,800	-1,019,201	401.00	197.2	197.100	0.100	394	1735
UCl₅	-1,041,500	-1,059,000	17500.00	246.9	242.701	4.199	400	1736
UCI ₆	-1,068,200	-1,091,999	23799.00	285.8	285.801	-0.001	402	1737
UF ₃	-1,502,100	-1,508,750	6650.00	123.4	123.428	-0.028	510	1738
UF ₄	-1,914,200	-1,920,874	6674.00	151.7	151.670	0.030	520	1739
UF₅(beta)	-2,083,200	-2,083,214	14.00	179.5	179.494	0.006	527	1741
UF ₆	-2,197,000	-2,197,002	2.00	227.6	227.601	-0.001	531	1742
UI ₃	-460,700	-460,658	-42.00	222	222.170	-0.170	625	1743
UI ₄	-512,100	-512,122	22.00	263.6	263.592	0.008	632	1744
UO ₂ Br ₂	-1,137,600	-1,137,630	30.00	169.5	169.452	0.048	187	1749
UO ₂ Cl ₂	-1,243,500	-1,243,903	403.00	150.6	150.540	0.060	346	1751
UO ₂ F ₂	-1,651,400	-1,648,078	-3322.00	135.6	135.562	0.038	484	1752
UO ₂ SO ₄	-1,845,100	-1,845,102	2.00	154.8	154.808	-0.008	789	1754
UO₃(gamma)	-1,226,500	-1,222,983	-3517.00	98.8	96.107	2.693	774	1747
UOBr ₂	-973,600	-973,617	17.00	157.6	157.569	0.031	187	1748
UOBr₃	-954,000	-953,952	-48.00	205	205.016	-0.016	202	1749
UOCI	-833,900	-947,258	113358.00	102.5	102.926	-0.426	328	1750
UOCl ₂	-1,067,500	-1,066,920	-580.00	138.3	138.323	-0.023	345	1750
UOCI ₃	-1,151,600	-1,163,001	11401.00	170.7	171.498	-0.798	371	1751
WCl ₂ (s)	-260,300	-257,316	-2984.00	130.5	130.541	-0.041	356	1792
WCl ₄ (s)	-443,100	-443,086	-14.00	198.3	198.322	-0.022	395	1793
WCI ₅ (s)	-513,000	-512,958	-42.00	217.6	217.568	0.032	400	1794
WCI ₆ (s)	-593,700	-593,710	10.00	238.5	238.488	0.012	402	1795
WO ₂ Cl ₂ (s)	-780,300	-780,316	16.00	200.8	200.832	-0.032	347	1812
WOCl ₄ (s)	-671,100	-671,114	14.00	172.8	172.799	0.001	388	1811
WOF ₄ (s)	-1,406,900	-1,394,360	-12540.00	175.7	175.728	-0.028	516	1813

Sources: 1 Binnewies and Milke 1999 [DIRS 158955].

Output DTN: This table appears in output DTN: SN0410T0510404.001.

² Barin and Platzki 1995 [DIRS 157865].

^{*} The S° values for wollastonite and CoF₂ are switched in this table and in DTN: SN0410T0510404.001; the output values are equivalent, given the uncertainty of these results, and are thus qualified.

6.4 EVALUATION AND QUALIFICATION OF THERMODYNAMIC DATA FOR GASES AND ASSOCIATED AQUEOUS SPECIES

Data for dissociation of HF (aq) were taken from two sources. The values selected from Ellis and Mahon (1977 [DIRS 159230], Table 8.4, p. 288) are for the pK_a of HF between steam and water at various temperatures (25°C – 300°C). This source is an excellent compilation of data collected from geothermal wells in New Zealand. In addition to this, data found in Table 18-4 in Clark (1966 [DIRS 153163], pp. 407) are used, which corroborate many of the data points (250°C – 300°C) from Ellis and Mahon (1977 [DIRS 159230]). The data from Clark (1966 [DIRS 153163]) are considered handbook data. The eight log K grid points necessary for the EQ3/6 data blocks were extracted from a regression of this data in *HF Dissasoc.xls* (DTN: MO0302SPATHDYN.001 [DIRS 161886]) for the reaction:

$$HF(aq) = H^+ + F^-$$
 (Eq. 6-34)

Data for dissociation of HF₂⁻ (aq) were taken from data found in Table 18-4 in Clark (1966 [DIRS 153163], p. 407). The data from Clark (1966 [DIRS 153163]) are also considered handbook data. The log K grid points necessary for the EQ3/6 data block were extracted from a regression of this data in *HF2- Dissasoc.xls* (DTN: MO0302SPATHDYN.001 [DIRS 161886]) for the reaction:

$$HF(aq) + F^{-} = HF_{2}^{-}$$
 (Eq. 6-35)

In the current qualification effort it was found that the reaction delineated by Eq. 6-35 is wrongly implemented in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). The reaction in the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) is given by:

$$HF_2^- = H^+ + 2F^-$$
 (Eq. 6-36)

Moreover, the values given in the source for the reaction delineated by Eq. 6-35 are expressed as K as documented in the Spreadsheet HF2- Dissasoc.xls Therefore, the data block needs to be (DTN: MO0302SPATHDYN.001 [DIRS 161886]). corrected in accord with Eq. 6-36 using the retrieved log K data from for reactions given by Eqs. 6-34 and 6-35 with the data of Clark (1966 [DIRS 153163]) and Ellis and Mahon (1977 [DIRS 159230]) as presented above. The proper linear combination of reactions given by Eqs. 6-34 and 6-35 yields the log K value for Eq. 6-36 as function of temperature (see Spreadsheet HF2-_Dissoc1_CFJC_fix.xls; output DTN: SN0410T0510404.001). The data are compared values reported in the qualified database data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]) (Table 6-40). The comparison shows that the log K values for HF(aq) dissociation are in strong agreement to those reported in data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]). Thus, these values are considered qualified for intended use on the basis of corroborative data. However, the corrected log K values for the dissociation of HF₂⁻ show a similar trend of decreasing log K with increasing temperature when compared to data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]) but shifted to lower values by approximately 1.15 log units. For corroborative purposes, a log K value at 25°C for the reaction defined by Eq. 6-36 computed using handbook thermodynamic data (Wagman et al. 1982 [DIRS 159216]) is used to evaluate the difference

between the corrected values for $\mathrm{HF_2}^-$ dissociation described in this section and those from data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]). The difference between the corrected log K value using Clark (1966 [DIRS 153163]) data and that obtained from (Wagman et al. 1982 [DIRS 159216]) is relatively small (approximately 0.12 log K units.), therefore indicating a strong data corroboration between "established fact" sources. The difference in log K at 25°C between data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]) and Wagman et al. (1982 [DIRS 159216]) is relatively large (approximately 1 log K unit). The erroneous log K value for $\mathrm{HF_2}^-$ in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) should not be used for YMP work. The corrected log K values are listed in Table 6-41 and are included in the updated database file data0.ymp.R4 (output DTN: SN0410T0510404.002).

Table 6-40. Log K EQ3/6 Grids for Hydrogen Fluoride Species

T (°C)	0.01	25	60	100	150	200	250	300	Source
HF(aq)	-2.9654	-3.1791	-3.4948	-3.8477	-4.3264	-4.9345	-5.7479	-6.8164	1,2
HF(aq)	-2.9848	-3.1681	-3.4737	-3.8482	-	-	-	-	3
HF ₂ ⁻	4.2705	3.4048	4.2836	4.9121	5.2966	7.9085	-	-	4
HF ₂ ^{-a}	-3.4639	-3.7101	-4.1266	-4.5367	-5.0532	-5.8324	-	-	1,2
HF ₂ ⁻	-2.2376	-2.5509	-2.9600	-3.3848	-	-	-	-	3
HF ₂ ^{-b}	-	-3.5915	-	-	-	-	-	-	5

Sources: Output DTN: SN0410T0510404.001 (Spreadsheet HF2-_Dissoc1_CFJC_fix.xls).

DTN: MO0302SPATHDYN.001 ([DIRS 161886], Spreadsheets HF Dissasoc.xls and HF2- Dissasoc.xls).

- 1 Clark 1966 [DIRS 153163], p.407, Table 18-4.
- 2 Ellis and Mahon 1977 [DIRS 159230], Table 8.4, p.288.
- data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]) for the reaction given by Eq. 6-36.
- Incorrect value for the reaction delineated by Eq. 6-36 as entered in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). The data0.ymp.R2 file contains null values (500.00) for this species at temperatures 250°C and 300°C.
- 5 Wagman et al. 1982 [DIRS 159216], pp. 2-38, 2-45, and 2-46.

Log K values for other gas species computed using thermodynamic data from Barin and Platzki (1995 [DIRS 157865]) and Binnewies and Milke (1999 [DIRS 158955]) are listed in Table 6-41. In revising the heat capacity coefficient data in Table 4-17, an error was identified corresponding to the correct scaling of the "c" coefficient for the gas species shown in Table 6-42. The scaling difference between source and adopted values in this work is by factor of 10 and the corrected values are given in Table 6-42. The corrected log K values upon correction of this heat capacity term in the source spreadsheets are given in Table 6-43. The ΔLog K values (difference between incorrect and corrected values) are given in Table 6-44. Notice in this table that the maximum difference is on the order of 0.2 log K units at 300°C, which is considered negligible given the inherent uncertainties in the source data.

^a Corrected log K value for the reaction delineated in Eq. 6-36 using data from 1 and 2 (see Spreadsheet HF2-_Dissoc1_CFJC_fix.xls; output DTN: SN0410T0510404.001).

^b Calculated using Gibbs free energy of formation data from Wagman et al. (1982 [DIRS 159216], pp. 2-38, 2-45, and 2-46) for the species HF₂⁻, F⁻, and H⁺.

The combined use of different sets of thermodynamic data could create discrepancies between the retrieved thermodynamic parameters generated by this study (e.g., ΔG_f° and log K). In this report, two types of thermodynamic data (ΔG_f° and ΔH_f° ; S° and Cp°) from two different sources (Barin and Platzki 1995 [DIRS 157865] and Binnewies and Milke 1999 [DIRS 158955]), respectively, were combined in the source spreadsheets. To anyone knowledgeable in the manipulation of thermodynamic parameters, such mixing of data could translate into some level of inconsistency that could affect the resulting log K value adopted in this report. That is, the retrieved log K value as obtained using reference-state thermodynamic data from two different sources can have some level of discrepancy due to differences in the standard-state thermodynamic data adopted by each source. In the case of the affected gas species given in Table 6-45, the ΔG_f° values were obtained from Barin and Platzki (1995 [DIRS 157865]) and the heat capacity data (Cp°) used to extrapolate the apparent Gibbs free energy of formation to temperatures other than 25°C were obtained from Binnewies and Milke (1999 [DIRS 158955]). This combination of data can be justified if the source thermodynamic data used to derive values of ΔG_f° (i.e., ΔH_f° and S°) are identical or at least very close within the uncertainty reported in each source. Table 6-45 shows a comparison of ΔH_f° and S° values given by Barin and Platzki (1995 [DIRS 157865]) and Binnewies and Milke (1999 [DIRS 158955]) for the affected gas species. As can be seen in this table, the overall maximum difference in ΔH_f° and S° values between the two sources do not exceed approximately 0.3 kJ/mol and 0.3 J/mol-K, respectively. These differences are deemed small, given the range of values observed for these thermodynamic parameters in multiple sources. Therefore, the combined use of these data should not generate large inconsistencies that could adversely affect the extrapolation of log K values at various temperatures.

Table 6-41. Log K EQ3/6 Grids for Gas Species

Data0 Species		log K							
Designation	Reaction	0.01	25	60	100	150	200	250	300
CoCl ₂ (g)	$CoCl_2(g) = Co^{++} + 2Cl^{-}$	41.4537	36.7471	31.1543	25.8597	20.4010	15.8084	11.7430	7.8795
CoF ₂ (g)	$CoCl_2(g) = Co^{++} + 2F^{-}$	49.3305	43.4386	36.4974	29.9939	23.3714	17.8778	13.0898	8.6294
CoCl ₃ (g)	$CoCl_3(g) = Co^{+++} + 3Cl^{-}$	22.2966	18.4912	13.8127	9.2301	4.3105	-0.0388	-4.1179	-8.2725
FeCl ₂ (g)	$FeCl_2(g) = Fe^{++} + 2Cl^{-}$	39.2745	34.7781	29.4270	24.3536	19.1135	14.6946	10.7712	7.0262
FeCl ₃ (g)	$FeCl_3(g) = Fe^{+++} + 3Cl^{-}$	33.2539	28.6029	22.9692	17.5297	11.7840	6.7987	2.2182	-2.3408
FeF ₂ (g)	$FeF_2(g) = Fe^{++} + 2F^{-}$	50.5720	44.6657	37.7009	31.1680	24.5078	18.9773	14.1542	9.6606
FeF ₃ (g)	$FeF_3(g) = Fe^{+++} + 3F^{-}$	12.3517	8.7062	4.2443	-0.0944	-4.7214	-8.8021	-12.6442	-16.5964
H ₂ O(g)	$H_2O(g) = H_2O(I)$	2.2146	1.4999	0.7020	-0.0003	-0.6614	-1.1562	-1.5353	-1.8314
N ₂ O(g)	$N_2O(g) + O_2(g) + H_2O = 2H^+ + 2NO_2^-$	-12.0018	-12.0141	-12.2146	-12.5775	-13.1546	-13.8444	-14.6712	-15.7404
$N_2O_3(g)$	$N_2O_3(g) + H_2O = 2H^+ + 2NO_2^-$	-5.8017	-5.8273	-6.0418	-6.4165	-7.0044	-7.7025	-8.5364	-9.6122
N ₂ O ₄ (g)	$N_2O_4(g) + H_2O = 2H^+ + NO_3^- + NO_2^-$	1.1380	0.6532	-0.0785	-0.9175	-1.9549	-3.0014	-4.1115	-5.4080
$N_2O_5(g)$	$N_2O_5(g) + H_2O = 2H^+ + 2NO_3^-$	20.1428	17.9824	15.3326	12.7454	9.9892	7.5886	5.3857	3.1923
NiCl ₂ (g)	$NiCl_2(g) = Ni^{++} + 2Cl^{-}$	44.3255	39.3145	33.3600	27.7233	21.9152	17.0361	12.7305	8.6624
NiF ₂ (g)	$NiF_2(g) = Ni^{++} + 2F^-$	51.9705	45.8142	38.5561	31.7502	24.8158	19.0640	14.0574	9.4092
NO(g)	$NO(g) + 0.25 O_2(g) + 0.5 H_2O = H^+ + NO_2^-$	0.8345	0.0394	-0.9685	-1.9803	-3.0873	-4.0781	-5.0142	-5.9801
NO ₂ (g)	$NO_2(g) + 0.5 H_2O = H^+ + 0.5 NO_3^- + 0.5 NO_2^-$	1.4420	0.7415	-0.1493	-1.0467	-2.0338	-2.9243	-3.7741	-4.6634
NO ₃ (g)	$NO_3(g) + 0.5 H_2O = H^+ + NO_{3^-} + 0.25 O_2(g)$	21.1117	18.9865	16.4496	14.0349	11.5358	9.4348	7.5903	5.8674
TiCl(g)	$TiCl(g) + 2.5H_2O + 0.75O_2 = Ti(OH)_4(aq) + Cl^- + H^+$	190.2907	172.3060	151.4823	132.3524	113.4126	98.3569	86.0287	75.6078
TiCl ₂ (g)	$TiCl_2(g) + 3H_2O + 0.5O_2 =$ $Ti(OH)_4(aq) + 2Cl^- + 2H^+$	122.2838	110.2269	96.1165	83.0195	69.8936	59.2891	50.4081	42.6156
TiCl ₃ (g)	$TiCl_3(g) + 3.5H_2O + 0.25O_2 =$ $Ti(OH)_4(aq) + 3CI^- + 3H^+$	70.9080	63.3449	54.2966	45.7197	36.9126	29.5752	23.1791	17.2172

Table 6-41. Log K EQ3/6 Grids for Gas Species (Continued)

Data0 Species Designation	Reaction	log K 0.01	log K 25	log K 60	log K 100	log K 150	log K 200	log K 250	log K 300
TiCl ₄ (g)	$TiCl_4(g) + 4H_2O = Ti(OH)_4(aq) + 4Cl^- + 4H^+$	34.5154	30.1919	24.7681	19.4016	13.6279	8.5467	3.8206	-0.9813
TiF(g)	$TiF(g) + 2.5H_2O + 0.75O_2 =$ $Ti(OH)_4(aq) + F^- + H^+$	177.1146	159.9794	140.1364	121.9117	103.8742	89.5369	77.7918	67.8510
TiF ₂ (g)	$TiF_2(g) + 3H_2O + 0.5O_2 =$ $Ti(OH)_4(aq) + 2F^- + 2H^+$	94.2707	84.0468	72.0515	60.9053	49.7216	40.6626	33.0352	26.2751
TiF ₃ (g)	$TiF_3(g) + 3.5H_2O + 0.25O_2 = Ti(OH)_4(aq) + 3F^- + 3H^+$	11.1332	7.6257	3.2298	-1.0933	-5.7082	-9.7432	-13.4825	-17.2709
TiF ₄ (g)	$TiF_4(g) + 4H_2O = Ti(OH)_4(aq) + 4F^-$ + $4H^+$	-0.0196	-2.5016	-5.7894	-9.1658	-12.9354	-16.4076	-19.8245	-23.5501
TiO(g)	$TiO(g) + 2H_2O + 0.5O_2 = Ti(OH)_4$ (aq)	168.9494	152.9154	134.4281	117.5315	100.9167	87.8313	77.2527	68.4955
WCl ₂ (g)	$WCl_2(g) + 2H_2O + O_2(g) = WO_4^{} + 2CI^- + 4H^+$	131.0808	118.0426	102.7000	88.3078	73.6569	61.5713	51.1828	41.7346
WCl ₄ (g)	$WCl_4(g) + 3H_2O + 0.5O_2 = WO_4^{} + 4Cl^- + 6H^+$	82.4091	73.8570	63.4710	53.4023	42.7497	33.5415	25.1672	16.9419
WCI ₆ (g)	$WCl_6(g) + 4H_2O = WO_4^{} + 6Cl^- + 8H^+$	66.9459	60.2282	51.7525	43.2240	33.8288	25.3346	17.2232	8.7737
WF(g)	WF(g) + 1.5H ₂ O + 1.25O ₂ = WO ₄ + F ⁻ + 3H ⁺	446.1868	406.2009	359.7610	316.8493	273.9572	239.3569	210.4069	185.0598
WF ₆ (g)	$WF_6(g) + 4H_2O = WO_4^{} + 6F^- + 8H^+$	7.3753	4.1500	-0.2826	-5.0591	-10.6927	-16.1771	-21.8419	-28.2782
WO ₂ Cl ₂ (g)	WO ₂ Cl ₂ (g) + 2H ₂ O = WO ₄ + 2Cl ⁻ + 4H ⁺	13.4668	10.9926	7.7737	4.4438	0.6700	-2.8458	-6.3093	-10.0460
WOCl ₄ (g)	$WOCl_4(g) + 3H_2O = WO_4^{} + 4Cl^- + 6H^+$	42.5106	37.7624	31.7416	25.6554	18.9179	12.7936	6.9105	0.7393
WOF ₄ (g)	$WOF_4(g) + 3H_2O = WO_4^{} + 4F^- + 6H^+$	12.8522	9.5474	5.2052	0.6912	-4.4534	-9.2934	-14.1299	-19.4418

DTN: MO0302SPATHDYN.001 ([DIRS 161886], Spreadsheets *Minerals_j_psd_1.xls*, *Minerals_j_psd_2.xls*, *Minerals_j_psd_3.xls*, *Minerals_j_psd_5.xls*, *Minerals_j_psd_6.xls*, and *Minerals_j_psd_7.xls*).

Table 6-42. Thermodynamic Data Input for Gas Phases with the Correct Scaling of the "c" Heat Capacity Coefficient

				Heat Capacity Coefficients ^a			
Gas Species	ΔG _f ° (J/mol)	ΔH _f ° (J/mol)	S° (J/mol-K)	a (J/mol-K)	b x 10 ³ (J/mol-K ²)	c x 10 ⁻⁶ (J-K/mol) ^b	Source
CoCl ₂ (g)	-107,220	-93,700	298.50	60.730	2.820	-0.170	1, 2
CoF ₂ (g)	-369,947	-356,500	278.00	55.410	2.680	-0.440	1, 2
CoCl ₃ (g)	-154,434	-163,600	334.20	87.610	-2.000	-0.960	1, 2
CrCl₄(g)	-395,322	-426,800	364.40	106.43	1.310	-0.950	1, 2
FeCl ₂ (g)	-155,571	-141,000	299.30	59.950	2.920	-0.290	1, 2
FeCl ₃ (g)	-247,843	-253,100	344.20	82.880	0.160	-0.460	1, 2
FeF ₂ (g)	-400,055	-389,500	265.20	70.540	-3.320	-1.230	1, 2
FeF ₃ (g)	-812,795	-820,900	304.20	78.590	2.800	-1.230	1, 2
NiCl ₂ (g)	-83,779	-70,200	298.20	68.290	-0.970	-0.660	1, 2
NiF ₂ (g)	-347,601	-335,600	273.10	64.310	1.040	-1.080	1, 2
TiCl(g)	122,516	154,400	249.20	43.940	0.250	-0.610	1, 2
TiCl ₂ (g)	-244,529	-237,200	278.30	60.120	2.220	-0.280	1, 2
TiCl ₃ (g)	-524,829	-539,300	316.90	87.260	-0.710	-1.290	1, 2
TiCl ₄ (g)	-726,764	-763,200	354.90	107.170	0.490	-1.050	1, 2
TiF(g)	-98,305	-66,900	237.30	43.480	0.340	-0.760	1, 2
TiF ₂ (g)	-694,886	-688,300	255.70	59.470	2.560	-0.650	1, 2
TiF ₃ (g)	-1,175,664	-1,188,200	291.20	86.280	-0.260	-2.070	1, 2
TiF ₄ (g)	-1,515,221	-1,551,400	314.90	104.250	1.980	-1.800	1, 2
TiO(g)	24,534	54,400	233.50	37.040	0.970	-0.490	1, 2
WCl ₂ (g)	-28,637	-12,600	309.40	58.170	4.510	-0.100	1, 2
WCl ₄ (g)	-306,245	-336,000	379.30	107.400	0.460	-0.780	1, 2
WCl ₆ (g)	-409,436	-493,700	419.20	157.540	0.190	-1.230	1, 2
WF(g)	351,397	386,200	251.10	37.810	2.900	-0.520	1, 2
WF ₆ (g)	-1,632,294	-1,721,700	341.10	152.650	2.750	-3.140	1, 2
$WO_2Cl_2(g)$	-639,675	-671,500	353.90	103.580	2.300	-1.570	1, 2
WOCl ₄ (g)	-512,272	-573,500	377.10	128.840	1.850	-2.230	1, 2
WOF ₄ (g)	-1,275,166	-1,336,600	334.70	125.690	4.140	-2.770	1, 2

Sources: 1

Barin and Platzki 1995 [DIRS 157865]. Binnewies and Milke 1999 [DIRS 158955].

^a Heat capacity coefficients a, b, and c defined in Eq. 4-1. ^b Scaling corrected from 10^{-5} to 10^{-6} in the formula used to calculate apparent Gibbs energies within the respective species spreadsheet.

Table 6-43. Log K EQ3/6 Grid for Corrected Gas Species in Table 6-41

			<u> </u>				<u> </u>		
Data0.ymp.R2		log K							
Species Name	Reaction	0.01°C	25°C	60°C	100°C	150°C	200°C	250°C	300°C
CoCl ₂ (g)	$CoCl_2(g) = Co^{++} + 2Cl^{-}$	41.4541	36.7471	31.1548	25.8615	20.4049	15.8145	11.7513	7.8899
CoF ₂ (g)*	$CoF_2(g) = Co^{++} + 2F^{-*}$	49.3315	43.4386	36.4987	29.9986	23.3815	17.8937	13.1113	8.6562
CoCl ₃ (g)	$CoCl_3(g) = Co^{+++} + 3Cl^{-}$	22.2987	18.4912	13.8155	9.2403	4.3327	-0.0040	-4.0710	-8.2141
CrCl ₄ (g)	$CrCl_4(g) + 0.5H_2O = Cr^{+++} + 4Cl^- + 0.25O_2(g) + H^+$	43.5477	38.1077	31.4658	24.9997	18.1084	12.0732	6.4784	0.8564
FeCl ₂ (g)	$FeCl_2(g) = Fe^{++} + 2Cl^-$	39.2751	34.7781	29.4278	24.3567	19.1202	14.7051	10.7854	7.0438
FeCl ₃ (g)	$FeCl_3(g) = Fe^{+++} + 3Cl^-$	33.2549	28.6029	22.9706	17.5346	11.7946	6.8153	2.2407	-2.3128
FeF ₂ (g)	$FeF_2(g) = Fe^{++} + 2F^{-}$	50.5747	44.6657	37.7045	31.1811	24.5361	19.0218	14.2144	9.7355
FeF ₃ (g)	$FeF_3(g) = Fe^{+++} + 3F^{-}$	12.3544	8.7062	4.2479	-0.0813	-4.6930	-8.7576	-12.5840	-16.5215
NiCl ₂ (g)	$NiCl_2(g) = Ni^{++} + 2Cl^-$	44.3269	39.3145	33.3619	27.7303	21.9304	17.0599	12.7627	8.7026
NiF ₂ (g)	$NiF_2(g) = Ni^{++} + 2F^-$	51.9729	45.8142	38.5592	31.7617	24.8407	19.1030	14.1102	9.4749
TiCl(g)	$TiCl(g) + 2.5H_2O + 0.75O_2 =$ $Ti(OH)_4(aq) + Cl^- + H^+$	190.2921	172.3060	151.4841	132.3589	113.4267	98.3790	86.0585	75.6449
TiCl ₂ (g)	$TiCl_2(g) + 3H_2O + 0.5O_2 =$ $Ti(OH)_4(aq) + 2Cl^- + 2H^+$	122.2844	110.2269	96.1173	83.0225	69.9000	59.2993	50.4218	42.6326
TiCl ₃ (g)	$TiCl_3(g) + 3.5H_2O + 0.25O_2 =$ $Ti(OH)_4(aq) + 3Cl^- + 3H^+$	70.9109	63.3449	54.3004	45.7335	36.9424	29.6218	23.2422	17.2958
TiCl ₄ (g)	$TiCl_4(g) + 4H_2O = Ti(OH)_4(aq) + 4Cl^-$ + 4H ⁺	34.5178	30.1919	24.7712	19.4128	13.6521	8.5847	3.8720	-0.9174
TiF(g)	$TiF(g) + 2.5H_2O + 0.75O_2 = Ti(OH)_4(aq) + F^- + H^+$	177.1163	159.9794	140.1386	121.9198	103.8917	89.5644	77.8289	67.8972
TiF ₂ (g)	$TiF_2(g) + 3H_2O + 0.5O_2 =$ $Ti(OH)_4(aq) + 2F^- + 2H^+$	94.2722	84.0468	72.0534	60.9123	49.7366	40.6861	33.0670	26.3146
TiF ₃ (g)	$TiF_3(g) + 3.5H_2O + 0.25O_2 =$ $Ti(OH)_4(aq) + 3F^- + 3H^+$	11.1378	7.6257	3.2358	-1.0712	-5.6604	-9.6683	-13.3812	-17.1449
TiF ₄ (g)	$TiF_4(g) + 4H_2O = Ti(OH)_4(aq) + 4F^-$ + 4H ⁺	-0.0156	-2.5016	-5.7841	-9.1466	-12.8939	-16.3425	-19.7364	-23.4406
TiO(g)	$TiO(g) + 2H_2O + 0.5O_2 = Ti(OH)_4$ (aq)	168.9505	152.9154	134.4295	117.5368	100.9280	87.8490	77.2766	68.5253

Qualification of the Thermodynamic Data for Geochemical Modeling of Mineral-Water Interactions in Dilute Systems

Table 6-43. Log K EQ3/6 Grid for Corrected Gas Species in Table 6-41 (Continued)

Data0.ymp.R2 Species Name	Reaction	log K 0.01°C	log K 25°C	log K 60°C	log K 100°C	log K 150°C	log K 200°C	log K 250°C	log K 300°C
WCl ₂ (g)	$WCl_2(g) + 2H_2O + O_2(g) = WO_4^{} + 2CI^- + 4H^+$	131.0810	118.0426	102.7003	88.3089	73.6592	61.5749	51.1877	41.7407
WCl ₄ (g)	$WCl_4(g) + 3H_2O + 0.5O_2 = WO_4^{} + 4Cl^- + 6H^+$	82.4109	73.8570	63.4733	53.4106	42.7677	33.5697	25.2054	16.9894
WCl ₆ (g)	$WCl_6(g) + 4H_2O = WO_4^{} + 6Cl^- + 8H^+$	66.9486	60.2282	51.7561	43.2371	33.8571	25.3791	17.2833	8.8486
WF(g)	WF(g) + $1.5H_2O$ + $1.25O_2$ = $WO_4^{}$ + F^- + $3H^+$	446.1880	406.2009	359.7625	316.8549	273.9692	239.3758	210.4323	185.0915
WF ₆ (g)	$WF_6(g) + 4H_2O = WO_4^{} + 6F^- + 8H^+$	7.3823	4.1500	-0.2735	-5.0256	-10.6202	-16.0635	-21.6883	-28.0870
WO ₂ Cl ₂ (g)	$WO_2Cl_2(g) + 2H_2O = WO_4^{} + 2Cl^- + 4H^+$	13.4703	10.9926	7.7783	4.4606	0.7062	-2.7890	-6.2325	-9.9504
WOCl ₄ (g)	$WOCl_4(g) + 3H_2O = WO_4^{} + 4Cl^- + 6H^+$	42.5155	37.7624	31.7481	25.6792	18.9694	12.8742	7.0196	0.8751
WOF₄(g)	$WOF_4(g) + 3H_2O = WO_4^{} + 4F^- + 6H^+$	12.8584	9.5474	5.2133	0.7208	-4.3895	-9.1932	-13.9944	-19.2731

^{*} The equation for CoF₂ is corrected from the data0.ymp.R2 file (DTN: MO0302SPATHDYN.000 [DIRS 161756]), which gives an equation for CoCl₂.

Table 6-44. Δ Log K (Difference Between Incorrect and Corrected Values) for Gas Species

Data0.ymp.R2		∆ log K	∆ log K	Δ log K	∆ log K				
Species Name	Reaction	0.01°C	25°C	60°C	100°C	150°C	200°C	250°C	300°C
CoCl ₂ (g)	$CoCl_2(g) = Co^{++} + 2Cl^-$	0.0004	0.0000	0.0005	0.0018	0.0039	0.0061	0.0083	0.0103
CoF ₂ (g)*	$CoF_2(g) = Co^{++} + 2F^{-*}$	0.0010	0.0000	0.0013	0.0047	0.0102	0.0159	0.0215	0.0268
CoCl ₃ (g)	$CoCl_3(g) = Co^{+++} + 3Cl^{-}$	0.0021	0.0000	0.0028	0.0103	0.0222	0.0347	0.0470	0.0584
CrCl₄ (g)	$CrCl_4(g) + 0.5H_2O = Cr^{+++} + 4Cl^- + 0.25O_2(g) + H^+$	0.0021	0.0000	0.0028	0.0101	0.0219	0.0344	0.0465	0.0578
FeCl ₂ (g)	$FeCl_2(g) = Fe^{++} + 2Cl^{-}$	0.0006	0.0000	0.0008	0.0031	0.0067	0.0105	0.0142	0.0177
FeCl ₃ (g)	FeCl ₃ (g) = Fe ⁺⁺⁺ + 3Cl ⁻	0.0010	0.0000	0.0013	0.0049	0.0106	0.0166	0.0225	0.0280
FeF ₂ (g)	$FeF_2(g) = Fe^{++} + 2F^{-}$	0.0027	0.0000	0.0036	0.0131	0.0284	0.0445	0.0602	0.0749
FeF ₃ (g)	$FeF_3(g) = Fe^{+++} + 3F^{-}$	0.0027	0.0000	0.0036	0.0131	0.0284	0.0445	0.0602	0.0749
NiCl ₂ (g)	$NiCl_2(g) = Ni^{++} + 2Cl^{-}$	0.0015	0.0000	0.0019	0.0071	0.0152	0.0239	0.0323	0.0402
NiF ₂ (g)	$NiF_2(g) = Ni^{++} + 2F^-$	0.0024	0.0000	0.0032	0.0115	0.0249	0.0391	0.0528	0.0657
TiCl(g)	$TiCl(g) + 2.5H_2O + 0.75O_2 = Ti(OH)_4(aq) + Cl^- + H^+$	0.0013	0.0000	0.0018	0.0065	0.0141	0.0221	0.0298	0.0371
TiCl ₂ (g)	$TiCl_2(g) + 3H_2O + 0.5O_2 = Ti(OH)_4(aq) + 2Cl^- + 2H^+$	0.0006	0.0000	0.0008	0.0030	0.0065	0.0101	0.0137	0.0170
TiCl ₃ (g)	$TiCl_3(g) + 3.5H_2O + 0.25O_2 = Ti(OH)_4(aq) + 3Cl^- + 3H^+$	0.0029	0.0000	0.0038	0.0138	0.0298	0.0467	0.0631	0.0785
TiCl ₄ (g)	$TiCl_4(g) + 4H_2O = Ti(OH)_4(aq) + 4Cl^- + 4H^+$	0.0023	0.0000	0.0031	0.0112	0.0242	0.0380	0.0514	0.0639
TiF(g)	TiF(g) + 2.5H2O + 0.75O2 = Ti(OH)4(aq) + F- + H+	0.0017	0.0000	0.0022	0.0081	0.0175	0.0275	0.0372	0.0463
TiF ₂ (g)	$TiF_2(g) + 3H_2O + 0.5O_2 = Ti(OH)_4(aq) + 2F^- + 2H^+$	0.0014	0.0000	0.0019	0.0069	0.0150	0.0235	0.0318	0.0396
TiF ₃ (g)	$TiF_3(g) + 3.5H_2O + 0.25O_2 = $ $Ti(OH)_4(aq) + 3F^- + 3H^+$	0.0046	0.0000	0.0060	0.0221	0.0478	0.0749	0.1012	0.1260
TiF ₄ (g)	$TiF_4(g) + 4H_2O = Ti(OH)_4(aq) + 4F^- + 4H^+$	0.0040	0.0000	0.0053	0.0192	0.0415	0.0651	0.0880	0.1096
TiO(g)	$TiO(g) + 2H_2O + 0.5O_2 = Ti(OH)_4$ (aq)	0.0011	0.0000	0.0014	0.0052	0.0113	0.0177	0.0240	0.0298

Table 6-44. △ Log K (Difference Between Incorrect and Corrected Values) for Gas Species (Continued)

Data0.ymp.R2 Species Name	Reaction	∆ log K 0.01°C	∆ log K 25°C	∆ log K 60°C	∆ log K 100°C	∆ log K 150°C	∆ log K 200°C	∆ log K 250°C	∆ log K 300°C
WCl ₂ (g)	$WCl_2(g) + 2H_2O + O_2(g) = WO_4^{} + 2Cl^{-} + 4H^{+}$	0.0002	0.0000	0.0003	0.0011	0.0023	0.0036	0.0049	0.0061
WCl ₄ (g)	$WCl_4(g) + 3H_2O + 0.5O_2 = WO_4^{} + 4Cl^- + 6H^+$	0.0017	0.0000	0.0023	0.0083	0.0180	0.0282	0.0382	0.0475
WCl ₆ (g)	$WCI_6(g) + 4H_2O = WO_4^{} + 6CI^{-} + 8H^{+}$	0.0027	0.0000	0.0036	0.0131	0.0284	0.0445	0.0602	0.0749
WF(g)	WF(g) + $1.5H_2O + 1.25O_2 = WO_4^{} + F^- + 3H^+$	0.0012	0.0000	0.0015	0.0056	0.0120	0.0188	0.0254	0.0317
WF ₆ (g)	$WF_6(g) + 4H_2O = WO_4^{} + 6F^-$ + $8H^+$	0.0069	0.0000	0.0092	0.0335	0.0725	0.1136	0.1536	0.1911
WO ₂ Cl ₂ (g)	$WO_2Cl_2(g) + 2H_2O = WO_4^{} + 2Cl^{-} + 4H^{+}$	0.0035	0.0000	0.0046	0.0168	0.0362	0.0568	0.0768	0.0956
WOCl ₄ (g)	$WOCl_4(g) + 3H_2O = WO_4^{} + 4Cl^- + 6H^+$	0.0049	0.0000	0.0065	0.0238	0.0515	0.0807	0.1091	0.1357
WOF₄(g)	$WOF_4(g) + 3H_2O = WO_4^{} + 4F^- + 6H^+$	0.0061	0.0000	0.0081	0.0296	0.0639	0.1002	0.1355	0.1686

^{*} The equation for CoF₂ is corrected from the data0.ymp.R2 file (DTN: MO0302SPATHDYN.000 [DIRS 161756]), which gives an equation for CoCl₂.

Table 6-45. Comparison of ΔH_f° and S° Values from Binnewies and Milke, and Barin and Platzki

Gas Species	ΔH _f ° (J/mol) 99Bin/Mil ¹	ΔH _f ° (J/mol) 95Bar/Pla ²	Difference in ∆H _f ° (J/mol)	S° (J/mol-K) 99Bin/Mil ¹	S° (J/mol-K) 95Bar/Pla ²	Difference in S° (J/mol-K)	Page Numbers 99Bin/Mil ¹	Page Numbers 95Bar/Pla ²
CoCl ₂ (g)	-93,700	-93,722	22	298.5	298.429	0.071	334	536
CoF ₂ (g)	-356,500	-356,477	-23	278	278.015	-0.015	407	541
CoCl ₃ (g)	-163,600	-163,594	-6	334.2	333.993	0.207	358	538
CrCl₄(g)	-426,800	-426,768	-32	364.4	364.402	-0.002	385	564
FeCl ₂ (g)	-141,000	-141,001	1	299.3	299.265	0.035	337	687
FeCl ₃ (g)	-253,100	-253,132	32	344.2	344.214	-0.014	363	688
FeF ₂ (g)	-389,500	-389,530	30	265.2	265.375	-0.175	475	692
FeF ₃ (g)	-820,900	-820,901	1	304.2	304.286	-0.086	493	693
NiCl ₂ (g)	-70,200	-70,291	91	298.2	298.228	-0.028	344	1208
NiF ₂ (g)	-335,600	-335,557	-43	273.1	273.065	0.035	483	1211
TiCl(g)	154,400	154,390	10	249.2	249.225	-0.025	331	1675
TiCl ₂ (g)	-237,200	-237,233	33	278.3	278.345	-0.045	355	1677
TiCl₃(g)	-539,300	-539,318	18	316.9	316.838	0.062	380	1678
TiCl₄(g)	-763,200	-763,162	-38	354.9	354.913	-0.013	394	1679
TiF(g)	-66,900	-66,944	44	237.3	237.342	-0.042	472	1680
TiF ₂ (g)	-688,300	-688,268	-32	255.7	255.752	-0.052	490	1681
TiF₃(g)	-1,188,200	-1,188,674	474	291.2	291.316	-0.116	509	1682
TiF ₄ (g)	-1,551,400	-1,551,427	27	314.9	314.914	-0.014	520	1683
TiO(g)	54,400	54,392	8	233.5	233.476	0.024	750	1691
WCl ₂ (g)	-12,600	-12,552	-48	309.4	309.725	-0.325	356	1792
WCl ₄ (g)	-336,000	-335,975	-25	379.3	379.180	0.120	395	1793
WCl ₆ (g)	-493,700	-493,712	12	419.2	419.346	-0.146	404	1796
WF(g)	386,200	386,183	17	251.1	250.731	0.369	474	1798
WF ₆ (g)	-1,721,700	-1,721,716	16	341.1	341.122	-0.022	532	1799
$WO_2Cl_2(g)$	-671,500	-671,532	32	353.9	354.076	-0.176	347	1813
WOCl₄(g)	-573,500	-573,208	-292	377.1	377.088	0.012	388	1812
WOF ₄ (g)	-1,336,600	-1,336,621	21	334.7	334.704	-0.004	516	1814

Sources: 1 Binnewies and Milke 1999 [DIRS 158955]. 2 Barin and Platzki 1995 [DIRS 157865].

6.5 "AZERO" ION SIZE PARAMETERS

The "azero" parameters appear in the B-dot equation (Helgeson 1969 [DIRS 137246]), which is used to calculate activity coefficients of aqueous species in dilute solution. The equation is given by:

$$\log \gamma_{i} = -\frac{A_{\gamma,10} z_{i}^{2} \sqrt{I}}{1 + B_{\gamma} \mathring{a}_{i} \sqrt{I}} + \mathring{B}I$$
 (Eq. 6-37)

where γ_i is the activity coefficient of the i-th solute species, $A_{\gamma,10}$ and B_{γ} are the relevant Debye-Hückel parameters, B is the B-dot parameter, I is the ionic strength, Z_i is the electrical charge number of the species, and a_i is the corresponding ionic diameter or "azero" parameter. The "azero" parameter is more properly described as the hard core diameter. It is also known as the "ion size" parameter. The above equation, less the second term on the right-hand side, is known as the extended Debye-Hückel equation. That is to distinguish it from the Debye-Hückel limiting law, which is obtained by further setting the denominator in the right-hand-side term to unity.

The B-dot equation is an EQ3/6 option (Wolery 1992 [DIRS 100836], pp. 39-41) for determining aqueous activity coefficients. Values for the "azero" parameters are contained in a non-Pitzer EQ3/6 data file (data0.ymp.R2; DTN: MO0302SPATHDYN.000 [DIRS 161756]) and data0.ymp.R4 (output DTN: SN0410T0510404.002) in a block that is headed by the somewhat misleading label of "bdot parameters." This block contains lines, each of which includes a species name and a corresponding "azero" parameter value. If the data file contains a normal species block for a species that is not represented by an entry in the "azero" section, the software assigns a default "azero" value of 4.0 angstroms.

In the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), little effort was made to provide "azero" values for species added to the file. This is by design (the intent is to use the default value assigned by EQ3/6).

The B-dot equation is only an approximate relationship whose nominal validity extends to an ionic strength of about one molal (Wolery 1992 [DIRS 100836], p. 38). However, that is intended only as a suggested practical limit for calculations that do not require high accuracy. If accuracy matching that of physical measurements is required, the ionic strength limit is much less, the more so for higher magnitudes of the electrical charge number. In the case of monovalent ions, this limit is closer to 0.3–0.4 molal. For divalent ions, it is more like 0.1–0.2 molal. For more highly charged ions, the high accuracy limit is generally even smaller. What is the exact high accuracy limit depends on both the ions in question and the measurement accuracies associated with the physical measurement techniques. Nevertheless, these numbers are illustrative.

The approximate nature of the B-dot equation is highlighted by the fact that it does not satisfy a key thermodynamic consistency equation (e.g., Wolery 1990 [DIRS 159223], p. 313–315):

$$\frac{\partial \log \gamma_i}{\partial n_i} = \frac{\partial \log \gamma_j}{\partial n_i}$$
 (Eq. 6-38)

There is a violation in the B-dot (second) term, unless I there is replaced by Σm , the sum of solute molalities. There is another in the first term, which can only be resolved if all ions have the same value for the "azero" parameter.

Historically, the B-dot equation was developed in Helgeson (1969 [DIRS 137246], pp. 742-752) by fitting the B-dot parameter itself to mean activity coefficient data for aqueous sodium chloride. The effective ion size parameter for the electrolyte (both ions) was estimated in Helgeson (1969 [DIRS 137246], pp. 748-749) using an entirely different theory. The resulting parameter varied with temperature (Helgeson 1969 [DIRS 137246], p. 746, Table 2) but was 3.89 angstroms at 25°C and ranged from 3.22 to 4.4 angstroms over the temperature range of 25°C to 300°C. For comparison, Kielland (1937 [DIRS 151237], p. 1677, Table 2) gives a value of 4.0-4.5 angstroms for Na⁺ and 3.0 for Cl⁻. In the subsequent application of the B-dot equation, fixed ion sizes have generally been employed, roughly following the values recommended by Kielland. Such data have never been fitted or optimized for use with the B-dot equation itself.

Kielland's table of ion sizes (Kielland 1937 [DIRS 151237], p. 1676, Table 1, and p. 1677, Table 2) is limited to only a few dozen species. That table has been reproduced in many physical chemistry, geochemistry, chemical engineering, and metallurgy texts, commonly with both omissions and undocumented additions (e.g., Table 7-4 in Nordstrom and Munoz 1986 [DIRS 153965], pp. 200-201). The extended Debye-Hückel model represented by the first term in the B-dot equation has also been incorporated into other activity coefficient models. Even in that context, there have been very few attempts to fit or to optimize any of the ion size parameters to one or another set of physical data. Other theories that treat the ion size as an important fitting parameter do exist (e.g., Triolo et al. 1976 [DIRS 159210]); however, the values obtained must be viewed as specific to those theories.

Even in the earlier EQ3/6 database development, the number of aqueous species far exceeded those in Kielland (1937 [DIRS 151237], Table 2). The data in Kielland's table roughly correlate with electrical charge numbers. The correlation in Table 4-4 was used at one time to estimate "azero" values for species not in Kielland's table that were added to the EQ3/6 database. However, this was only intended as a guideline and many exceptions may be found in the set of values in, for example, data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]).

Because the intrinsically approximate nature of the B-dot equation, any attempt to optimize the ion size parameters beyond the scope of Kielland (1937 [DIRS 151237], Table 1) is considered unwarranted. Instead, it is preferable to use the EQ3/6 default value of 4.0 angstroms. In fact, one of the few species for which such a value would definitely not be appropriate is H⁺, which is in Kielland's table with an ion size of 9.0 angstroms. The large size is associated with water of hydration.

The Spreadsheet *Azero_sensitivity_TJW.xls* (DTN: MO0302SPATHDYN.001 [DIRS 161886]) contains calculations of sensitivity of calculated activity coefficients to the "azero" parameter. In general, assuming "azero" values in the range of 3.0-5.0 angstroms (likely the case in the vast majority of instances), there is not much sensitivity to the exact value in the limited ionic strength ranges in which the B-dot equation is truly accurate. High sensitivity is seen at higher ionic strengths. However, B-dot equation results there can not be made generally accurate by any meaningful optimization of "azero" parameters.

The "azero" parameter can be avoided by using either of two other options for aqueous activity coefficients in EQ3/6. The Davies equation (Wolery 1992 [DIRS 100836], pp. 38-39) is valid for use in the same concentration range as the B-dot equation. Pitzer's equations (Wolery 1992 [DIRS 100836], pp. 44-64) can be used in both dilute and concentrated solutions. Neither of these options uses the "azero" parameter.

6.6 EVALUATION OF MINERAL MOLAR VOLUME DATA

This section documents the qualification of molar volume data given in Section 4.1, that were added when the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) was developed. Previously qualified molar volume data in the data0.ymp.R0 database (DTN: MO0009THRMODYN.001 [DIRS 152576]), which are included in the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), are not considered for qualification here with the exception of schoepite as discussed below.

Qualification of molar volume data for clays is discussed in Section 6.3.1. The mineral volume sources are mainly the *Encyclopedia of Minerals* (Roberts et al. 1990 [DIRS 107105]), Gaines et al. (1997 [DIRS 172360]), and the internet resource website www.webmineral.com. The latter is an extensive compilation of mineral data that includes crystallographic (cell) parameters from recognized resources such as peer-reviewed mineralogical journals.

Table 6-46 lists the molar volume estimates or ranges, developed in this qualification report for comparison to values from the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]). Molar volume estimates based on information from alternate sources are used to qualify the data0.ymp.R2 values (DTN: MO0302SPATHDYN.000 [DIRS 161756]) through data corroboration. Most of the mineral species in Table 6-46 are clays and zeolites.

The qualification effort focuses on literature sources and established-fact sources for density and mineral volume data. Calculations of mineral volumes based on mineral density and volume data Spreadsheet Volume Q DS 11-17-04.xls given in DTN: SN0410T0510404.001). Most of the mineral volumes (not to be confused with molar volume) obtained from the corroborative sources are derived from mineral crystallographic data. In many cases, the density data given in handbook sources (e.g., Gaines et al. 1997 [DIRS 172360]) appear to be based on mineral volumes. In the spreadsheet, the computed molar compared from data0.ymp.R2 volume values are to those the (DTN: MO0302SPATHDYN.000 [DIRS 161756]). Overall, the calculated molar volumes in Table 6-46 are typically within 5 to 15% of those in the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), and within approximately 50% for clays (discussed below). These differences are satisfactory considering that molar volume is not a parameter in the application of EQ3/6 modeling to repository simulation, because pressure changes in the repository are too small to significantly affect chemical equilibria. Volume changes associated with chemical reactions simulated using EQ3/6 must be calculated externally to the code, with attention to the applicability of molar volume data. Accordingly, the molar volume data in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) are qualified by corroboration with data from other sources, subject to the stated uncertainties.

Corroborating molar volume estimates for many clay minerals differ from those in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) by as much as 50% for some species (Table 6-46). Such differences between reported measurements and estimates are reasonable because the volumes occupied by clays depend on the physical state, especially moisture content. Clays experience substantial changes in unit-cell volume depending on the hydration state and the type of cation occupying exchangeable sites in the mineral structure. The amount of inter-layer water is a function of composition and the physical characteristics of the clay minerals (Deer et al. 1992 [DIRS 163286]). For example, Brindley and Brown (1980 [DIRS 105235], Chapter 3, p. 205-206, Figure 3.3-3.4) shows changes in basal spacing (d001) distance as a function of relative humidity for various clay phases, including montmorillonite and beidellite. These differences in basal spacings for beidellite range from approximately 9.8 angstroms at low relative humidities (e.g., 0 to 10%) to 15.5 angstroms at elevated relative humidities (e.g., 70 to 100%). Because clay mineral volumes estimated from crystallographic data are usually obtained for well-hydrated conditions or after induced swelling of the clay (e.g., using ethylene glycol), differences in reported molar volumes of 50% should be expected. Accordingly, these ranges in molar volume (and density) for clays are realistic and acceptable, and the values developed for data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) are qualified.

For one phase (Ni₃(PO₄)₂), corroborative data for molar volume were not found in the literature. These data are considered qualified because the first author (Calvo and Faggiani 1975 [DIRS 172265]) has authored a substantial number of articles related to the characterization and refinement of crystal structures for various types of chemical compounds including phosphates (Ng et al. 1978 [DIRS 172385]; Shannon and Calvo 1973 [DIRS 172386]; Krishnamachari and Calvo 1972 [DIRS 172387]). The expertise and publishing record of the authors justify confidence in the data obtained from their source.

A molar volume value of 66.080 cm³/mol is reported for schoepite in the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]). On recalculation for this report, the correct value is found to be 66.70 cm³/mol, or approximately one percent greater. This difference is well within the corroborative comparisons made for other minerals above, and the original value from data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) is therefore qualified. The original value of 66.080 cm³/mol is used in the new database data0.ymp.R4 (output DTN: SN0410T0510404.002).

Table 6-46. Mineral Phase Molar Volume and Density Data

Mineral Phase	Molar Volume from R2 Database (cm³/mol)	Calculated Molar Volume (Crystal Parameter) (cm³/mol)	Calculated Molar Volume (Density) (cm ³ /mol) ^a	Density Min. (g/cm³)	Density Max. (g/cm³) ^b	Z1°	Mineral Volume (cm³) ^d	Molar Volume (cm³/mol) ^e	Present in R0?	Sources Used for Corroboration	Page Number
Amesite-7A	103.00	98.48	-	2.83	-	-	-	-	n	Gaines et al. 1997 [DIRS 172360]	1422
Beidellite-Ca	129.77	184.89	160.77	2	2.3	2.00	6.79E-22	204.45	n	Barthelmy 2004 [DIRS 172415]	-
Beidellite-H	128.91	180.13	156.64	2	2.3	2.00	6.79E-22	204.45	n	Barthelmy 2004 [DIRS 172415]	1
Beidellite-K	134.15	189.66	164.92	2	2.3	2.00	6.79E-22	204.45	n	Barthelmy 2004 [DIRS 172415]	1
Beidellite-Mg	128.73	189.00	164.34	2	2.3	2.00	6.79E-22	204.45	n	Barthelmy 2004 [DIRS 172415]	-
Beidellite-Na	130.73	185.63	161.42	2	2.3	2.00	6.79E-22	204.45	n	Barthelmy 2004 [DIRS 172415]	-
CaUO₄	45.93	-	-	-	-	1.00	7.62E-23	45.87 ⁿ	y ^f	Pialoux and Touzelin 1998 [DIRS 172359]	18
Chabazite	499.40	494.11	471.13	2.05	2.15	1.00	8.34E-22	502.33	n	Barthelmy 2004 [DIRS 172410]	-
Cr-ferrihydrite	129.00	134.07 ^h	-	3.8	-	1.00	-	-	n	Roberts et al. 1990 [DIRS 107105]	273
Cronstedtite- 7A	110.90	111.28	-	3.59	-	2.00	1.85E-22	55.68	y ^f	Gaines et al. 1997 [DIRS 172360]	1427
Erionite	672.00	683.67	670.83	2.09	2.13	2.00	2.27E-21	684.95	n	Barthelmy 2004 [DIRS 172414]	-
Fe ₂ (MoO ₄) ₃	131.85 ⁱ	147.88 ⁱ	131.45	4	4.5	-	-	-	n	Barthelmy 2004 [DIRS 172412]	-
Ferro-aluminoc eladonite	153.68	146.17	-	2.93	-	2.00	4.78E-22	143.96	n	Barthelmy 2004 [DIRS 172407]	-
Ferroceladonite	156.72	149.88	-	3.05	-	2.00	4.78E-22	143.96	n	Barthelmy 2004 [DIRS 172408]	-
Illite	139.35	152.61	141.24	2.61	2.82	2.00	4.70E-22	141.48	n	Gaines et al. 1997 [DIRS 172360]	1472
Laumontite	406.40	438.10	-	2.12	-	4.00	2.76E-21	415.07	y ^g	Gaines et al. 1997 [DIRS 172360]	1650

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Table 6-46. Mineral Phase Molar Volume and Density Data (Continued)

Mineral Phase	Molar Volume from R2 Database (cm ³ /mol)	Calculated Molar Volume (Crystal Parameter) (cm ³ /mol)	Calculated Molar Volume (Density) (cm ³ /mol) ^a	Density Min. (g/cm³)	Density Max. (g/cm³) ^b	Z1°	Mineral Volume (cm³) ^d	Molar Volume (cm³/mol) ^e	Present in R0?	Sources Used for Corroboration	Page Number
Montmorillonite -Ca	133.07	181.72	134.61	2	2.7	2.00	4.53E-22	136.41	n	Barthelmy 2004 [DIRS 172413]	-
Montmorillonite -H	132.22	179.82	133.20	2	2.7	2.00	4.53E-22	136.41	n	Barthelmy 2004 [DIRS 172413]	-
Montmorillonite -K	137.46	183.63	136.02	2	2.7	2.00	4.53E-22	136.41	n	Barthelmy 2004 [DIRS 172413]	-
Montmorillonite -Mg	132.03	179.96	133.30	2	2.7	2.00	4.53E-22	136.41	n	Barthelmy 2004 [DIRS 172413]	-
Montmorillonite -Na	134.03	182.01	134.83	2	2.7	2.00	4.53E-22	136.41	n	Barthelmy 2004 [DIRS 172413]	-
Ni ₃ (PO ₄) ₂ ^j	83.36	-	-	-	-	-	-	-	y ^f	-	-
Na ₄ UO ₂ (CO ₃) ₃ ^k	149.31	147.69	-	3.67	-	4.00	9.65E-22	145.30	y ^f	Ralph n.d. [DIRS 172416]	-
Nontronite-Ca	135.85	185.28	179.78	2.29	2.36	2.00	7.23E-22	217.58	n	Gaines et al. 1997 [DIRS 172360]	1485
Nontronite-K	140.24	188.03	182.45	2.29	2.36	2.00	7.23E-22	217.58	n	Gaines et al. 1997 [DIRS 172360]	1485
Nontronite-Mg	134.81	184.14	178.68	2.29	2.36	2.00	7.23E-22	217.58	n	Gaines et al. 1997 [DIRS 172360]	1485
Nontronite-Na	136.81	185.70	180.20	2.29	2.36	2.00	7.23E-22	217.58	n	Gaines et al. 1997 [DIRS 172360]	1485
Phillipsite	609.20	581.15	-	2.17	-	1.00	9.93E-22	598.15	n	Gaines et al. 1997 [DIRS 172360]	1665
Ripidolite-14A	209.63	225.02 ^m	192.99 ^m	2.47	2.88	2.00	7.00E-22	210.65	n	Gaines et al. 1997 [DIRS 172360]	1501
Ripidolite-7A	215.38	225.02 ^m	192.99 ^m	2.47	2.88	2.00	7.00E-22	210.65	n	Gaines et al. 1997 [DIRS 172360]	1501
Saponite-Ca	134.36	183.58	169.83	2.1	2.27	2.00	7.00E-22	210.65	n		
Saponite-H	133.51	180.59	167.06	2.1	2.27	2.00	7.00E-22	210.65	n	Gaines et al. 1997	1489
Saponite-K	138.75	186.57	172.60	2.1	2.27	2.00	7.00E-22	210.65	n	[DIRS 172360] Roberts et al. 1990	(Gaines) 756
Saponite-Mg	132.60	182.34	168.68	2.1	2.27	2.00	7.00E-22	210.65	n	[DIRS 107105]	(Roberts)
Saponite-Na	135.32	184.04	170.26	2.1	2.27	2.00	7.00E-22	210.65	n		

Qualification of Thermodynamic Data for Geochemical Modeling of Mineral-Water Interactions in Dilute Systems

Table 6-46. Mineral Phase Molar Volume and Density Data (Continued)

Mineral Phase	Molar Volume from R2 Database (cm³/mol)	Calculated Molar Volume (Crystal Parameter) (cm³/mol)	Calculated Molar Volume (Density) (cm ³ /mol) ^a	Density Min. (g/cm³)	Density Max. (g/cm³) ^b	Z1°	Mineral Volume (cm³) ^d	Molar Volume (cm³/mol)°	Present in R0?	Sources Used for Corroboration	Page Number
Smectite- Reykjanes ^l	142.85	-	-	2	2.7	2.00	4.53E-22	136.41	n	Barthelmy 2004 [DIRS 172413]	-
Smectite high-Fe-Mg ^l	139.51	-	-	2	2.7	2.00	4.53E-22	136.41	n	Barthelmy 2004 [DIRS 172413]	-
Smectite low-Fe-Mg ^l	139.60	-	-	2	2.7	2.00	4.53E-22	136.41	n	Barthelmy 2004 [DIRS 172413]	-
Stellerite	665.50	664.85	-	2.12	-	4.00	4.38E-21	659.70	n	Gaines et al. 1997 [DIRS 172360]	1676
Uranophane (alpha)	251.34	226.56	-	3.78	-	3.00	7.39E-22	148.38	n	Gaines et al. 1997 [DIRS 172360]	1111
Weeksite-Na	246.04	270.78	-	3.71	-	16.00	7.26E-21	273.32	n	Gaines et al. 1997 [DIRS 172360]	1114

Qualification of Thermodynamic Data for Geochemical Modeling of Mineral-Water Interactions in Dilute Systems

Output DTN: SN0410T0510404.001 (All calculated values reported in this table are generated in Spreadsheet Volume Q DS 11-17-04.xls).

^a Molar volume calculated only when a range of densities (lower value and upper value; Columns 5 and 6, respectively) given in the source.

^b Density Max., given only when the source gives a lower and upper value for density.

^c Number of formula units used in defining cell parameters.

Based on crystollographic data as given in source (cm³).

Based on crystollographic data as given in source (cm³/mol).
In data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]) but no molar volume or mineral volume data available.

⁹ Present in data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]), but there is a slight difference in chemical formula.

Molar volume calculated using density and molecular weight of ferrihydrite (not Cr-ferrihydrite), because no data available for this mineral phase.

Molar volume calculated using density value of the phase Fe₂(MoO₄)₃·8H₂O, because no data for Fe₂(MoO₄)₃ available.

See text for qualification argument.

Density and molecular weight for volume calculation from the mineral Cejkaite, which has the same chemical formula. Density values are from Montmorillonite, because no data available for this smectite.

^m Molar volume calculated using the formula for Ripidolite as Mg₃(Mg₂Al)(Si₃AlO₁₀)(OH)₈. Volume in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) calculated using the formula Mg₃Fe₂(Al₂Si₃O₁₀)(OH)₈

The volume data from various sources given in Pialoux and Touzelin (1998 [DIRS 172359]) is for a hexagonal transformation of the true rhombohedral structure of this phase. The conversion from rhombohedral to hexagonal for the volume relation is V hexa = 3V rhomb. Therefore, the values tabulated by Pialoux and Touzelin (1998 [DIRS 172359]) need to be divided by 3.

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7. CONCLUSIONS

The data sets listed in Table 7-1 were qualified or generated in the course of this evaluation. data0.ymp.R2 database and include input supporting (DTN: MO0302SPATHDYN.000 [DIRS 161756], qualified by this report; DTN: MO0302SPATHDYN.001 [DIRS 161886], and DTN: MO0303SPASPEO2.000 [DIRS 162278]), and the corrected data0.ymp.R4 database and supporting files (output DTNs: SN0410T0510404.002 and SN0410T0510404.001). Similarly, the sources used to develop the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), as listed in Table 1-1, were evaluated, and justification provided for the appropriateness of these sources. Errors were found related to some of these sources, and substitutions for the data are included in the new data0.ymp.R4 database (output DTN: SN0410T0510404.002).

Title	Preliminary DTN	Status*	Description
Data0.ymp.R2	MO0302SPATHDYN.000 [DIRS 161756]	Qualified	Thermodynamic database (input)
Speq02.dat	MO0303SPASPEQ2.000 [DIRS 162278]	Qualified	Updated SUPCRT92 database file used to develop data0.ymp.R2 (input)
Supporting Files	MO0302SPATHDYN.001 [DIRS 161886]	Qualified	Spreadsheets and SUPCRT92 files used to develop data0.ymp.R2 (input)
Data0.ymp.R4	SN0410T0510404.002	Qualified	Corrected thermodynamic database (output)
Additional Supporting Files	SN0410T0510404.001	Qualified	Additional spreadsheets supporting data0.ymp.R4 (output)

Table 7-1. Summary of Qualification Recommendations

In addition to the criteria discussed in Section 4.2, development of a thermodynamic database in this report includes the following considerations:

A. Are the data reasonable in terms of compatibility with other existing data (thermodynamic consistency)?

The data have been cross-checked within the database to ensure that the data are internally consistent. The change to the "Rimstidt" paradigm for quartz solubility (Section 6.1.5) required that all silicate species (with some exceptions) be checked for consistency, including the recalculation of these species that was performed for development of the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]). Although multiple sources of input data were used in the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), the development process prevented any significant departure from overall internal consistency. Some discrepancies were noted during qualification, including transcription errors, and these are summarized below and explained in detail in Section 6.

^{*} Recommended as a result of this report.

B. Are the qualifications of the personnel or organizations generating the data comparable to qualification requirements of personnel generating similar data under the approved 10 CFR 63, Subpart G [DIRS 156605] quality assurance program?

The data used to update the data0.ymp.R0 database (DTN: MO0009THRMODYN.001 [DIRS 152576]) creating the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), were generated in internationally recognized laboratories in North America and Europe. They were published either in internationally recognized handbooks or in peer-reviewed international journals and national laboratory reports. The data selected for the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) are selected from sources that are widely accepted by the geochemical modeling community. Most of the chemical data for transuranic elements were generated in national laboratories or their international equivalents.

C. Does analysis of comparable qualified and unqualified data indicate a reasonable level of accuracy for the fundamental thermodynamic data?

The data used to implement changes to the data0.ymp.R0 database (DTN: MO0009THRMODYN.001 [DIRS 152576]), creating the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), are compatible with the previous data0.ymp.R0 database (DTN: MO0009THRMODYN.001 [DIRS 152576]) that has been in use for several years and is qualified for use by the YMP. The additional data and the methodology used for the update are comparable in accuracy to the original basis for the data0.ymp.R0 database (DTN: MO0009THRMODYN.001 [DIRS 152576]). In some cases, newer data were available and replaced previous values reflecting the evolving nature of thermodynamic data. These changes used to create the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), and the justification for those changes, are documented in this report.

As a result of the data evaluation described in Section 6, various errors and discrepancies were identified in this qualification effort. The errors are mostly from errors in transcription of data from original sources to the spreadsheets used to adjust and calculate log K values for data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). Other errors are related to implementation of log K values in the database and representation of chemical reactions relative to the reactions given in the sources. The errors found in qualification of data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) are summarized as follows:

• Log K Values for Certain Zeolites (Section 6.3.2) – Transcription errors, mainly in heat capacity data for zeolite species which were added in creation of the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), caused potentially significant differences in the log K values after the correction in the data0.ymp.R4 database (output DTN: SN0410T0510404.002). These differences are larger at higher temperatures. The problem was remedied for the data0.ymp.R4 database (output DTN: SN0410T0510404.002) by correcting the scaling for heat capacity coefficients and recalculating the log K values. Section 6.3.2 provides further details including tabulation of corrected log K

values and listing of the differences (Δ log K) between corrected and uncorrected log K values. The significance of these changes increases with temperature: at 25°C there is no effect, at 100°C the maximum difference for any affected zeolite is 1.7 log K units (analcime, erionite, and stellerite in Table 6-22), and at 300°C the maximum difference is 15 log K units (analcime, erionite, phillipsite, and stellerite in Table 6-22). Accordingly, data for the affected zeolites in the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) should not be used above 100°C. The corrected data are included in data0.ymp.R4 (output DTN: SN0410T0510404.002), which should be used instead.

- Discrepancies in Thermodynamic Data for Cement Minerals Na- and Ca-Gismondine, Syngenite, and "Friedl Salt" (Sections 6.3.3.3 and 6.3.3.9) Corroborating thermodynamic data for Ca-gismondine (but not Na-gismondine) are available in the literature. Technical assessment (this report) of the data used in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) is based on data comparison with respect to this phase. The ΔG°_{f} value estimated in technical assessment generates a log K value (see Table 6-28) that is significantly different from the data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) value computed using data from Atkins et al. (1993 [DIRS 131758]. Also, comparison of ΔH°_{f} for Ca-gismondine reported in another literature source (Section 6.3.3.3) also indicates a discrepancy. These results show that the data adopted for data0.ymp.R2 (DTN: MO0302SPATHDYN.000 Ca-gismondine in [DIRS 161756]) are incorrect. No corroborating data are available for Na-gismondine, but the same conclusion is drawn by analogy to The data block for the cement phase "Friedl salt" Ca-gismondine. (Section 6.3.3.4) data0.ymp.R2 is inactive in the (DTN: MO0302SPATHDYN.000 [DIRS 161756]); the data for this phase in data0.ymp.R2 were also found to be incorrect. No corrections to the Na- and Ca-gismondine species or the inactive "Friedl salt" species were made to the data0.ymp.R4 database (output DTN: SN0410T0510404.002); these species appear in the data0.ymp.R4 database the same as in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). The log K value for syngenite at 25°C present in data0.ymp.R2 cannot be duplicated using the available data given in Harvie et al. (1984 [DIRS 118163]) and no documentation on how it was estimated is available. As explained in Section 6.3.3.9, an alternative log K value from the qualified Pitzer (DTN: SN0302T0510102.002 thermodynamic database. data0.ypf [DIRS 162572]) was identified. The difference between the value in data0.ymp.R2 and this alternative value (0.15 log units) is insignificant.
- Correction of Stoichiometry for the Pu Phase PuO₂(OH)₂·H₂O − A modification of the Pu solid PuO₂(OH)₂:H₂O was made to correct an error found in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) related to the stoichiometry of this species (the incorrect PuO₂(OH)₂:2H₂O was

corrected to PuO₂(OH)₂:H₂O). This correction is consistent with the usage in Lemire (2001 [DIRS 159027], Section 17.2.2.1) and was made originally in data0.ymp.R3 (DTN: MO0312SPATDMIF.000 [DIRS 167800]). This correction is carried into the new data0.ymp.R4 database (output DTN: SN0410T0510404.002).

- Correction to Log K Values for HF₂⁻ Dissociation (Section 6.4) Two errors were identified for this species: 1) incorrect transcription of solubility constants from the source related to scaling of log values, and 2) incorrect representation of the chemical reaction as entered in the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) with respect to the one given in the source. The protonated form of hydrofluoric acid (HF) is related to the formation of HF₂⁻ (Eq. 6-36). Aqueous dissociation of hydrofluoric acid (HF) occurs at approximately pH 3.85 at 100°C, and at higher pH values with increasing temperature (Ellis and Mahon 1977 [DIRS 159230], Table 8.4). The error is present for calculations at all pH levels, but can produce a quantitatively significant result only for acidic conditions (e.g., pH < 3.85 at 100°C) with abundant fluoride. The correction is included in the updated database data0.ymp.R4 (output DTN: SN0410T0510404.002).
- Log K Values for Np and Pu Solids (Section 6.3.4.5) Similar transcription errors were identified for these actinides. The errors are: 1) a factor of 1000 on the "b" parameter for the Maier-Kelley equation, 2) the "c" parameter was ignored in many cases for this same equation, and 3) for certain species $(NpC_{0.91}(cr), Pu_2C_3(cr), PuC_{0.84}(cr), PuOI(cr), PuOF(cr), and PuO_2(cr);$ Tables 6-33 and 6-34), the adopted coefficients were inappropriately applied as Maier-Kelly parameters. For listed items 1) and 2) the problem was remedied by correcting the scaling for heat capacity coefficients and recalculating the data0.ymp.R4 log K values, for the corrected database (output DTN: SN0410T0510404.002). Overall, the differences are not significant and the maximum difference was restricted to the upper temperature limit of 300°C. For the two species in listed item 3) above, the errors were not corrected in the data0.ymp.R4 database (output DTN: SN0410T0510404.002), and the log K values for temperatures other than 25°C should not be used. Section 6.3.4.5 details the errors and associated corrections plus tabulation of corrected log K values, including a listing of the differences (or $\Delta \log K$) between the corrected and uncorrected log K values.
- Log K Values for Metal Gas Species and Solids (Section 6.3.4.5) Similar transcription errors were identified for metal-bearing gas and solid species. Transcription errors related to scaling of the "c" Maier-Kelly heat capacity coefficient for several solids and gas species from the source Binnewies and Milke (1999 [DIRS 158955]) were found in the spreadsheets supporting the data0.ymp.R2 database development (DTN: MO0302SPATHDYN.001 [DIRS 161886]). For the gas and solid species, the "c" heat capacity coefficient is off by a factor of 10. As with the other transcription errors, the problem was

remedied by correcting the scaling for the heat capacity coefficients and recalculating the log K values. Overall, the differences are not significant (within the uncertainty of the available thermodynamic data) and the maximum differences are restricted to the upper temperature limit of 300° C. The corrected values are reported in Section 6.3.4.5, along with the differences (Δ log K), but the corrected values are not included in the updated database data0.ymp.R4 (output DTN: SN0410T0510404.002).

users of the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), given these discrepancies, uncertainties, and transcription errors, this data0.vmp.R4 report provides corrected database (output a DTN: SN0410T0510404.002) plus tabulation of the log K differences for all affected data0.ymp.R4 included species not in the database DTN: SN0410T0510404.002). As explained above, the most substantial errors for active data blocks in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) pertain to the zeolites, the gismondine cement species (Na and Ca), and the corrected stoichiometry of the Pu phase PuO₂(OH)₂·H₂O. The error associated with HF₂⁻ is potentially significant depending on the pH range and fluoride activity.

Molar volume data for many phases were included in the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) but no details on qualification were given in the original data qualification report (Steinborn et al. 2003 [DIRS 161956]). These data were assessed in this report (Section 6.6). For all phases for which molar volume data were not available in the original data0.ymp.R0 database (DTN: MO0009THRMODYN.001 [DIRS 152576]), and for which molar volume data were added to the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), the values are corroborated (within 5 to 15%) by alternate sources or comparison with analogous species. For certain clays there is substantial uncertainty (50%) in molar volume estimates from different sources (Section 6.3.1). As explained in Section 6.6, such difference are expected because of the variable hydration condition of measured clay mineral samples, which affects the unit-cell structure data.

7.1 EVALUATION OF UNCERTAINTY AND RECOMMENDED USE OF THE DATABASE

The chemical thermodynamic data needed for geochemical modeling of processes of importance to the YMP have been compiled, developed, and evaluated. The data sets qualified or created during the evaluation process are listed in Table 7-1. The following text provides additional discussion on the evaluated uncertainties and recommended use of the data.

Extrapolation of log K data for clays up to 300°C should be treated with caution since equilibrium between solution and clay minerals at elevated temperatures has been experimentally observed for only a few species. At temperatures above 250°C, mica-like phases may be more stable. The argument needed to establish which clay or mica phase is more or less stable as a function of pressure and temperature goes beyond the scope of this report. Therefore, it is up to the user of the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) (and the updated data0.ymp.R4 database; output DTN: SN0410T0510404.002) to determine the

appropriate assemblage of clay minerals (e.g., minerals to include or suppress) for the system of interest. The same statement applies to every solid species tabulated in these databases and is an important principle of geochemical modeling.

In addition to the qualification findings summarized in the previous section, a number of other assumptions and approximations were identified in the data0.ymp.R2 development (DTN: MO0302SPATHDYN.000 [DIRS 161756]), which may affect use of the database:

- Thermodynamic data for steam (Section 6.1.2) should not be retrieved from the SUPCRT92 database files, which are calibrated for ranges of temperature and pressure outside the range of interest to YMP. Rather, handbook values should be used.
- Reevaluation of SUPCRT92 properties was not performed for aqueous silica reactions (Section 6.1.5) because these reactions are generally unimportant for pH less than 9 to 10. However, for more alkaline pH these reactions should be reexamined and the thermodynamic properties reevaluated as appropriate.
- About 100 silicate minerals were not corrected to the Rimstidt paradigm (Section 6.1.5). The difference in log K units is generally less than 1 unit, and typically less than 0.5 log units. For close comparison of equilibria involving different silicate minerals, this aspect should be taken into account.
- The thermodynamic data for clays have some additional uncertainties (Section 6.3.1) because: clay species in the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) have idealized formulae, and the mineralogical compositions of clays can be uncertain, especially in nature; and the temperature dependence of Gibbs free energies for exchangeable components are approximate.
- Extrapolation of thermodynamic parameters for zeolites beyond the experimental range of temperature for heat capacity data from Viani and Bruton (1992 [DIRS 101407]) is not recommended (Section 6.3.2). The temperature ranges of these experiments varied, for example clinoptilolite was measured up to 500K (except for NH₄-clinoptilolite, which was measured only at 25°C).
- Transcription errors were discovered in the development of log K values for uranium silicates soddyite, uranophane, Na-weeksite, and Na-boltwoodite (Section 6.3.4). These errors were found to be insignificant and the log K values for these minerals in the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) are qualified.

Additional detailed information on uncertainty associated with thermodynamic properties of clay minerals is provided in Section 6.3.1.

7.1.1 Uncertainty in Thermodynamic Data

Uncertainties in thermodynamics are challenging to describe quantitatively because they do not propagate linearly. Uncertainties in thermodynamic parameters are often correlated so that simplistic representations of propagation overestimate the uncertainty. The problem is

compounded by the fact that thermodynamic calculations have variable inputs (e.g., pH, solubilities, and Gibbs free energies) and these same parameters can also be outputs. The mathematical structure of thermodynamics is a contributing factor because it allows different kinds of physical measurements to be used to solve the same problem (e.g., "second law" vs. "third law" approaches). It is an example of both the predictive power of thermodynamics and the difficulty in describing uncertainty, that one can, for example calculate the solubility of a solid in water when the relevant solubility equilibrium has never been measured or even observed. The log K data for crystalline PuO₂ and NpO₂ in the current EQ3/6 database are examples of this.

Reflecting this situation, a common dictum in dealing with thermodynamic data is that "consistency is more important than accuracy." This means that the treatment of thermodynamic data (e.g., reduction into a standard, relatively compact form for inclusion in a database) must be such that the constraining measurements can be faithfully recovered. All standard thermodynamic relations must be satisfied, both in data reduction and in subsequent usage. These include basic relations such as G = H - TS, $-S = \delta G/\delta T$, and $V = \delta G/\delta P$, where G is Gibbs free energy, H is enthalpy, T is absolute temperature, S is entropy, V is volume, and P is pressure. They also include "solution" consistency relations such as $\delta^2 G/\delta n_i \delta n_j = \delta^2 G/\delta n_j \delta n_i$, where n is the number of moles of a component.

In reducing thermodynamic data, especially from a tabulated database, it is important that the starting data often are not original measurements but are values calculated from measurements. The ability to create a compact database from data in standardized form and then use this for a wide range of applications is one of the great powers of thermodynamics. Typically, there is some variation in the types of tabulated data, but standard Gibbs free energies of formation, standard enthalpies of formation, entropies, and heat capacities are most common. There are also data tabulations specific to log K values for reactions and to solubilities in simple chemical systems. Although tabulated solubilities are generally actual measurements, standard Gibbs free energies of formation, for example, are calculated.

Unfortunately, the uncertainties that go with the data can not generally be treated like the data. The uncertainty assigned to a tabulated value that is not a measurement reflects both the uncertainty in the original measured parameter and the uncertainties in any other parameters used to obtain the tabulated value. It may also reflect additional uncertainties in the use of thermodynamic models for solution behavior (e.g., ionic strength corrections). Not only do such models introduce additional parameters with their own uncertainties, the approximate nature of such models may add additional uncertainty. Also, failing to recognize how uncertainties are correlated, a much larger uncertainty than the one actually associated with the measurement could be calculated.

Many tabulations of thermodynamic data, particularly Gibbs free energies, do not include associated uncertainties. Furthermore, estimates of uncertainties in thermodynamic data often do not take a standard form such as the standard deviation. Even when replicates are used, it can be difficult to calculate a standard deviation with any statistical rigor. Apparent bounds or an informally defined scale of measurement are the approaches most likely to be encountered.

As a consequence, the exact uncertainties associated with a thermodynamic database depend on the history of the data. If uncertainties are small to begin with, there may be no significant consequences from the use of simplistic propagation calculations that tend to overstate the uncertainty. However, it is important to know the larger uncertainties associated with factors like sluggish kinetics, poorly crystallized or poorly defined phases (e.g., colloids), precise composition of the solid phase, radiation effects, low solubilities, and chemical systems that are difficult to control in the laboratory (e.g., plutonium). Uncertainties may also result from lack of published information (e.g., Cr(VI) solids).

A common approach to characterizing uncertainty in thermodynamic data is to estimate uncertainty for classes of thermodynamic data that share commonality in type and method of origin. This approach is used whenever uncertainty is estimated using analogies. The best tabulated log K values for complexation reactions, for example, tend to have an uncertainty of about 0.02 log unit or less, and many such values have an uncertainty within 0.1 log unit. The best calorimetrically determined standard Gibbs free energies of formation at 298.15K of clay minerals have uncertainties of about 4 to 6 kJ/mol. Reported solubilities of soluble salt minerals are probably uncertain to within about 1 percent, or higher for less soluble minerals.

For a detailed discussion of the treatment of uncertainties in thermodynamic data, refer to the NEA guidelines on the subject (Wanner and Osthols 1999 [DIRS 159222]). The NEA-sponsored volumes on the thermodynamics of radionuclide elements (e.g., Grenthe et al. 1992 [DIRS 101671], on uranium; Silva et al. 1995 [DIRS 102087], on americium; Lemire 2001 [DIRS 159027], on neptunium and plutonium) are excellent examples of expert treatment of thermodynamic data and uncertainties.

The remainder of this section addresses uncertainties associated with the use of the isocoulombic/isoelectric method for extrapolating thermodynamic data to higher temperature. This method is the only "new" temperature extrapolation method introduced in the development of the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) and is therefore of special interest. With regard to other methods, which have been used previously, refer to sources cited elsewhere in the present and previous reports, particularly the NEA guidelines on temperature extrapolations (Puigdomenech et al. 1997 [DIRS 159204], 1999 [DIRS 159205]). The latter source recommends use of the isocoulombic/isoelectric method to about 275°C.

The isocoulombic/isoelectric method requires as inputs Gibbs free energies (or log K values) and entropies, normally for 298.15K. The method utilizes an isocoulombic/isoelectric reference reaction together with the assumption that the corresponding heat capacity of reaction is zero. Rarely, the heat capacity of reaction is assumed to be a non-zero constant. Here the focus is on uncertainty in the method itself by examining the use of different reference reactions and how the results vary. One case is examined below, involving extrapolation of the apparent Gibbs free energy of formation for Am⁺⁺⁺, which is a basis species for this element in the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]). While the example is limited, the comparison is instructive.

Calculation of the apparent Gibbs free energy of formation using the isocoulombic/isoelectric method is addressed, given a choice of different reference reactions. The Am⁺⁺⁺ ion is not in the

SUPCRT92 database, so the Gibbs free energy grid was calculated for the normal library worksheets. The basic 25°C data (Gibbs free energy of formation and entropy) for the Am⁺⁺⁺ were taken from Silva et al. (1995 [DIRS 102087], p. 37). All other data were taken from the SUPCRT92 database. Calculations were done in the Spreadsheet *BasisSpecies_j_TJW_1.xls* (DTN: MO0302SPATHDYN.001 ([DIRS 161886]). The following reference reactions were considered:

$$2Am^{+++} + Cr_2O_3 = 2Cr^{+++} + Am_2O_3$$
 (Eq. 7-1)

$$2Am^{+++} + Fe_2O_3 = 2Fe^{+++} + Am_2O_3$$
 (Eq. 7-2)

$$2Am^{+++} + Ce_2O_3 = 2Ce^{+++} + Am_2O_3$$
 (Eq. 7-3)

$$2Am^{+++} + Gd_2O_3 = 2Gd^{+++} + Am_2O_3$$
 (Eq. 7-4)

$$2Am^{+++} + Lu_2O_3 = 2Lu^{+++} + Am_2O_3$$
 (Eq. 7-5)

$$2Am^{+++} + UO_2 = 2U^{+++} + AmO_2$$
 (Eq. 7-6)

The results are shown in Table 7-2. They suggest an uncertainty at 200°C of about 1 to 2 kJ/mol. The cerium data here led to the greatest deviations from the mean. For the database, it was decided to use the chromium extrapolation, on the basis that the reference data are more likely to be accurate than the other analogs considered here. The properties of Fe⁺⁺⁺, U⁺⁺⁺ and the trivalent rare earths are difficult to obtain because ferric iron is rather insoluble; those of U⁺⁺⁺ because this represents a difficult species to maintain, and those of the trivalent rare earths due to potential problems with sample purity.

This discussion shows the range of Gibbs free energy values that can be obtained, using the isocoulombic/isoelectric method with different reference reactions. The results shown can be considered typical for those species in the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) for which this method is relied upon. Smaller uncertainties pertain for reactions that have extensive laboratory measurement basis, and larger uncertainties may pertain for species with a paucity of reference data.

Table 7-2. Isocoulombic Extrapolation of the Calculated Apparent Gibbs Free Energy Grids of Am⁺⁺⁺, Comparing Extrapolations Using Various Reference Reactions

T (00)	Cr ⁺⁺⁺	Fe ⁺⁺⁺	Ce ⁺⁺⁺	Gd ⁺⁺⁺	Lu ⁺⁺⁺	U***	
T (°C)	Analog	Analog	Analog	Analog	Analog	Analog	Mean
0	-603601.4	-603624.0	-603467.9	-603534.6	-603552.8	-603527.4	-603551.4
25	-598698.0	-598698.0	-598698.0	-598698.0	-598698.0	-598698.0	-598698.0
60	-591510.4	-591542.7	-591314.3	-591414.2	-591440.8	-591405.2	-591437.9
100	-582964.5	-583097.4	-582164.8	-582580.4	-582685.5	-582548.1	-582673.5
150	-571700.5	-572043.7	-569734.4	-570785.7	-571035.2	-570727.5	-571004.5
200	-559550.7	-560195.0	-556082.7	-557995.7	-558418.7	-557931.8	-558362.4
250	-546146.8	-547186.9	-540934.0	-543904.0	-544512.6	-543875.0	-544426.6
300	-531053.9	-532560.9	-523855.0	-528053.1	-528867.2	-528115.7	-528751.0

DTN: MO0302SPATHDYN.001 ([DIRS 161886], Spreadsheet BasisSpecies_j_TJW_1.xls).

NOTE: Characterized by analogues; see text for details. Units are Joules/mole.

Table 7-3. Isocoulombic Extrapolation of the Calculated Apparent Gibbs Free Energy Deviations from Mean of Am***

T (°C)	Cr ⁺⁺⁺ Analog	Fe ⁺⁺⁺ Analog	Ce ⁺⁺⁺ Analog	Gd ⁺⁺⁺ Analog	Lu ⁺⁺⁺ Analog	U ⁺⁺⁺ Analog
0	-50.1	-72.7	83.4	16.8	-1.4	23.9
25	0.0	0.0	0.0	0.0	0.0	0.0
60	-72.4	-104.7	123.7	23.7	-2.9	32.7
100	-291.0	-424.0	508.6	93.0	-12.0	125.4
150	-696.0	-1039.2	1270.2	218.8	-30.7	277.0
200	-1188.3	-1832.6	2279.7	366.7	-56.3	430.6
250	-1720.2	-2760.4	3492.5	522.6	-86.0	551.5
300	-2302.9	-3809.9	4896.0	697.8	-116.2	635.3

DTN: MO0302SPATHDYN.001 ([DIRS 161886], Spreadsheet BasisSpecies_j_TJW_1.xls).

NOTE: Characterized by analogues; see text for details. Units are Joules/mole.

7.1.2 Use of Cement Data

Many of the cement mineral phases (e.g., portlandite, tobermorite, and gyrolite) included in the final data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) and the data0.ymp.R4 database (output DTN: SN0410T0510404.002) are naturally occurring minerals and could be formed if thermodynamically or kinetically possible. However, other cement phases in the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) are not likely to form in nature, and a modeler should use only those minerals that could be expected to form in the environment being modeled.

Cement phase minerals form from the alteration of cement used in the repository, and minerals such as gyrolite and tobermorite can also form as alteration products on nuclear waste glass (Gong et al. 1998 [DIRS 158976]) and from the alteration of host rock if conditions are sufficiently alkaline. Cement minerals that are not naturally occurring (not observed in rocks outside of cements and grouts) should not be considered in a non-cement model or set of calculations. Often when included in a calculation, the use of the data will cause the model run to precipitate cement mineral phases like hydrogarnet and Friedl salt. These phases are only relevant to calculations directly associated with cements and grouts. Finally, the reader is reminded that the CSH:1.7, Friedl salt, and hydrogarnet phases in the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) are inactive (i.e., they are "commented out" and not accessible to the EQ3/6 software) and the associated thermodynamic data in the file are not considered qualified.

8. INPUTS AND REFERENCES

The following is a list of the references cited in this document. Column 2 represents the unique six-digit numerical identifiers (the DIRS numbers), which are placed in the text following the reference callout (e.g., Atkins et al. 1992 [DIRS 100700]). The purpose of these numbers is to assist in locating a specific reference. Multiple sources by the same author (e.g., BSC 2004) are sorted alphabetically by title.

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8.2 CODES, STANDARDS, REGULATIONS, AND PROCEDURES

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8.3 SOURCE DATA, LISTED BY DATA TRACKING NUMBER

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MO0302SPATHDYN.000. Thermodynamic Data Input Files - Data0.YMP.R2. Submittal date: 02/05/2003.	161756
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8.4 OUTPUT DATA, LISTED BY DATA TRACKING NUMBER

SN0410T0510404.001. Corrections to Erros in the Data0.ymp.R2 Thermodynamic Database. Submittal date: 11/01/2004.

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8.5 SOFTWARE CODES

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