DOC.20070619.0007

QA: QA

ANL-WIS-GS-000003 REV 01

June 2007

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

Prepared for:
U.S. Department of Energy
Office of Civilian Radioactive Waste Management
Office of Repository Development
1551 Hillshire Drive
Las Vegas, Nevada 89134-6321

Prepared by:
Sandia National Laboratories
OCRWM Lead Laboratory for Repository Systems
1180 Town Center Drive
Las Vegas, Nevada 89144

Under Contract Number
DE-AC04-94AL85000

QA: QA

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

ANL-WIS-GS-000003 REV 01

June 2007

Sandia National Laboratories

Scientific Analysis/Calculation Signature Page/Change History

Complete only applicable items.

1. Total Pages: 412

2. Document Title Qualification of Thermodynamic Data for Geochemical Modeling of Mineral–Water Interactions in Dilute Systems			
3. DI (including Rev. No.) ANL-WIS-GS-000003 REV 01			
	Printed Name	Signature	Date
4. Originator	Thomas J. Wolery Carlos F. Jove-Colon	Thomas J. Wolery	6/15/2007 6/15/2007
5. Checker	James L. Krumhansl	James L. Krumhansl	6/15/2007
6. QCS/Lead Lab QA Reviewer	Robert E. Spencer	Robert E Spencer	6/15/07
7. Responsible Manager/ Lead	Patrick V. Brady	Patrick V. Brady	6/15/2007
8. Responsible Manager	Geoff A. Freeze	Geoff Freeze	6/15/07

9. Remarks

This report draws heavily from Rev. 00 of this analysis report, which in turn drew heaviliy from an earlier document (Steinborn et al. 2003 [DIRS 161956]).

Change History

10. Revision No.	11. Description of Change
REV 00	Initial issue of this analysis report requalifies data developed in TDR-EBS-MD-000022, *Data Qualification: Update and Revision of the Geochemical Thermodynamic Database, Data0.ymp*, REV 00 (Steinborn et al. 2003 [DIRS 161956]) and provides supplementary information.
REV 01	This revision adds some additional data and corrects some data in the previous revision. Several Condition Reports (CRs) are addressed: CR 6489, CR 6731, CR 7542, and CR 7756. Notable changes include a general revision of phosphate data to achieve consistency with the CODATA recommendations (Cox. et al. 1989 [DIRS 150874]) for key data for the species HPO_4^{2-} and $H_2PO_4^-$ (part of CR 6731) and additions and corrections for uranium minerals (CR 7756).

ACKNOWLEDGMENTS

Tom Wolery and Carlos Jove-Colon are the co-originators of this report. We wish to acknowledge the contributions of many others. Joe Rard, Mark Sutton, Kate Helean, Bob Finch, and Jim Nowak contributed to the present revision (Rev. 01). The checking team consisted of Jim Krumhansl (lead), Emma Thomas, and James W. Johnson. This revision incorporates a substantial amount of material from the previous revision (Rev. 00). We acknowledge the efforts of the checking team for that revision: Russell Jarek (lead), Dave Shields, and Susan LeStrange. Rev. 00 in turn incorporated a substantial amount of material from an earlier report (Steinborn et al. 2003 [DIRS 161956]). That report included contributions from Terry Steinborn, Tom Wolery, Steve Alcorn, Sara Arthur, Trish Bernot, Pat Brady, Yueting Chen, Paul Domski, Darren Jolley, Rich Metcalf, and Emma Thomas.

The work presented in this document was supported by the Office of Repository Design as part of the Civilian Radioactive Waste Management Program, managed by the U.S. Department of Energy.

INTENTIONALLY LEFT BLANK

CONTENTS

CONTENTS (Continued)

CONTENTS (Continued)

INTENTIONALLY LEFT BLANK

TABLES

TABLES (Continued)

Page

TABLES (Continued)

Page

TABLES (Continued)

TABLES (Continued)

TABLES (Continued)

Page

ACRONYMS AND ABBREVIATIONS

(aq)	aqueous
CODATA	Committee on Data for Science and Technology
CR	Condition Report
(cr)	crystalline
CSH	calcium silicate hydrate
DIRS	Document Input Reference System
DTN	data tracking number
(ex)	exchange
(g)	gas
ICSU	International Council for Science
NBS	National Bureau of Standards (now NIST)
NEA	Nuclear Energy Agency
NIST	National Institute of Standards and Technology (formerly NBS)
OECD	Organisation for Economic Cooperation and Development
(s)	solid
YMP	Yucca Mountain Project

INTENTIONALLY LEFT BLANK

1. PURPOSE

This report is developed from *Technical Work Plan for: Thermodynamic Databases for Chemical Modeling* (BSC 2006 [DIRS 177885]). The purpose of this analysis report is to update the thermochemical database data0.ymp.R4 (Output DTN: SN0410T0510404.002). Various data have been added, corrected, or corroborated, partly in response to four Condition Reports (CRs): CR 6489, CR 6731, CR 7542, and CR 7756. The most notable changes are a general revision of phosphate data to achieve consistency with the recommendations from the Committee on Data for Science and Technology (CODATA) (Cox. et al. 1989 [DIRS 150874]) for key thermodynamic data for the aqueous species HPO_4^{2-} and $H_2PO_4^-$ (this action is in response to part of CR 6731) and additions and corrections for uranium minerals observed in UO_2 drip tests and natural analogues (CR 7756). The resulting principal product is the thermochemical database data0.ymp.R5 (Output DTN: SN0612T0502404.014).

The thermochemical databases in the data0.ymp.R* series are used with the computer software package EQ3/6 (e.g., EQ3/6 V8.0; see Section 3.1.1). These databases are used in predictive models for waste form and waste package corrosion, modeling of in-package and in-drift chemical conditions, and for prediction of dissolved radionuclide concentrations. They are also used to support criticality assessments and modeling of reactive transport of radionuclides in groundwater. The members of this database series support chemical modeling of solid–fluid interactions in systems with dilute aqueous solutions (ionic strengths of up to one molal) at temperatures of 0°C to 300°C along the liquid-vapor saturation curve of pure water. The limitation to dilute systems is tied to the support for model equations for thermodynamic activity coefficients of aqueous species. The databases in this series are suitable for use with either of two activity coefficient models, the B-dot equation (Helgeson 1969 [DIRS 137246]) and the Davies equation (Wolery 1992 [DIRS 100836], pp. 38 and 39). The B-dot equation requires a database of hard core diameters or "ion sizes" for aqueous species (see Section 6.5). The Davies equation requires no special data, only the electrical charge numbers of the aqueous ions. Both models are known to become inaccurate at high ionic strength.

For treating systems with concentrated or "high ionic strength" aqueous solutions, more sophisticated models with more extensive data requirements (typically for "interaction coefficients") are needed. For this, EQ3/6 and similar modeling codes typically employ Pitzer's equations (Wolery 1992 [DIRS 100836], pp. 44 to 64). Analogous thermochemical databases in the data0.ypf.R* series (e.g., data0.ypf.R1; DTN: SN0302T0510102.002 [DIRS 162572]) support EQ3/6 modeling using Pitzer's equations. "High ionic strength" activity coefficient models are perfectly applicable to instances of low ionic strength. However, a lack of necessary data for many chemical components and species restricts the present applicability of the Pitzer model and other "high ionic strength" models. Consequently, both types of thermochemical database retain their usefulness.

The present database update is the result of various corrections, additions, and other improvements to data0.ymp.R4 (Output DTN: SN0410T0510404.002). The database data0.ymp.R4 was in turn an update of data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). The purpose of the previous version (Rev. 00) of this analysis report was to qualify data0.ymp.R2 (qualifying an unqualified input) and develop data0.ymp.R4 (product output), as well as to describe the updates and improvements incorporated into the latter. For the present revision (Rev. 01), data0.ymp.R2 and data0.ymp.R4 are treated as before, and data0.ymp.R5 is developed as new product output. The database data0.ymp.R4 did not technically supersede data0.ymp.R2. The development of data0.ymp.R2 was originally to have been qualified by another report (Steinborn et al. 2003 [DIRS 161956]).

This report is in turn intended to support the qualified use of data0.ymp.R2, data0.ymp.R4, and data0.ymp.R5, with no supersession of the earlier thermochemical databases. However, access to data0.ymp.R4 (Output DTN: SN0410T0510404.002) and data0.ymp.R2 (Output DTN: MO0302SPATHDYN.00) through the Technical Data Management System is presently restricted and subject to management controls.

Thermochemical databases called data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]) and an intermediate database called data0.ymp.R1 (never entered in any DTN) preceded data0.ymp.R2. There was also a data0.ymp.R3 (DTN: MO0312SPATDMIF.000 [DIRS 167800]) which was not qualified. This was an update of data0.ymp.R2 that only incorporated a correction in the stoichiometry of the Pu phase $PuO_2(OH)_2{:}H_2O$. This correction was also incorporated in the database data0.ymp.R4. The database data0.ymp.R5 follows data0.ymp.R4.

The development of each qualified member in the data0.ymp.R* series has been associated with the creation of a supplementary calculations data package. For data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), the supporting calculations are located in DTN: MO0302SPATHDYN.001 [DIRS 161886]. It consists of a collection of Excel spreadsheets and a set of SUPCRT92 (SUPCRT92 V1.0; see Section 3.1.2) calculations. For data0.ymp.R4 (Output DTN: SN0410T0510404.002), a new supplementary calculations package located in Output DTN: SN0410T0510404.001 was developed for updates and changes only. This package contains only Excel spreadsheets. The newer supplementary calculations package did not supersede DTN: MO0302SPATHDYN.001 [DIRS 161886], and data0.ymp.R4 remains tied to both supplementary calculations packages. For data0.ymp.R5 (Output DTN: SN0612T0502404.014), a new supplementary data calculations package (Output DTN: SN0702T0502404.015) has been developed, again covering only updates and changes. It includes both Excel spreadsheets and SUPCRT92 calculations. Thus, data0.ymp.R5 is tied to all three supplementary calculations packages (DTN: MO0302SPATHDYN.001 [DIRS 161886], Output DTN: SN0410T0510404.001, and Output DTN: SN0702T0502404.015).

The organization of the present analysis report largely reflects the historical development and the need to keep multiple versions of the thermodynamic database qualified. To that end, the qualification of data for data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) that was first presented in Rev. 00 of this report is presented first, then changes and additions for data0.ymp.R4 (Output DTN: SN0410T0510404.002), and then changes and additions for data0.ymp.R5 (Output DTN: SN0612T0502404.014).

In a number of instances, qualified data have different values in different versions of the database addressed in this analysis report. All of these versions contain some data that are affected by known errors. The rationale for keeping qualified databases with known errors is as follows. All known errors are documented in this report, and corrected values have been calculated or the magnitudes of the errors are otherwise constrained. Most of the known errors are not significant, and there are no significant errors for any of the species/reactions anticipated to be important in Yucca Mountain Project (YMP) applications of these databases.

Known errors can be partly evaluated by comparing them with the expected uncertainties associated with the log K values used in the databases. Section 7.1.1 notes that in the best of circumstances, log K values carry an uncertainty of about 0.02 unit, while more typically the uncertainty is about 0.1 unit. The log K values used in the data0.ymp.R* series of databases are given to the nearest 0.0001 unit. This is done in order to facilitate smoothness in interpolating to temperatures not corresponding to the log K data grids. Unfortunately, it also facilitates errors at a purely "forensic" level. The majority of known errors are very small, less than the associated uncertainties. These errors are mainly due to transposition errors in transferring data or errors in entering certain data, especially heat capacity coefficients, into calculations. In some cases involving error in entering data into calculations, the output errors are less than the expected uncertainties only up to some temperature, which varies from one species/reaction to the next, but this is commonly in the range 150°C to 250°C.

Section 6.8 summarizes the known errors in the data0.ymp.R5 database (Output DTN: SN0612T0502404.014). The subject of known errors in the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) is more complex and difficult to deal with in a summary fashion. The relevant discussion in this report starts in Section 6.3.2 with errors in data for some zeolites. It concludes with a consideration of the changes made for data0.ymp.R4 (Output DTN: SN0410T0510404.002) and data0.ymp.R5 (Output DTN: SN0612T0502404.014).

At this point in time, usage of data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) and data0.ymp.R4 (Output DTN: SN0410T0510404.002) is subject to the limitations and proscriptions identified in Section 7.1. Therefore, use of the database data0.ymp.R5 (Output DTN: SN0612T0502404.014) is recommended.

This report cannot provide full impact assessments of the significant known errors or the effects of changes and deletion of chemical species for all possible applications scenarios. Therefore, responsibility falls to the originators of the downstream calculations.

In summary, applications using data0.ymp.R2 must be evaluated against the changes and additions for data0.ymp.R4 and the changes and additions for data0.ymp.R5, and applications of data0.ymp.R4 must be evaluated against the changes and additions for data0.ymp.R5. There are some known errors in data0.ymp.R4 documented in this analysis report that remain uncorrected in data0.ymp.R5, and some other errors in data0.ymp.R5 that are also documented in this report. These errors are numerically small, less than the expected uncertainty, and are non-impacting for YMP applications. Section 7 notes a small number of exceptions.

1.1 BACKGROUND AND APPROACH

Thermochemical data can be divided into two categories, standard state data and activity coefficient data. Standard state data include equilibrium constants (*K*) and "standard state" forms of Gibbs energies, enthalpies, entropies, heat capacities, and compressibilities. Activity coefficient data include such parameters as Debye-Hückel parameters, the B-dot parameter, hard core diameters, and interaction coefficients. The standard state data contained in the thermochemical databases of the "data0" type at a minimum consist of log K values on a temperature grid. In the case of the data0.ymp.R* series, the only standard state data are the log K values, and the temperature grid is the "classic" one (for EQ3/6) of 0-25-60-100-150-200-250-300°C. The Debye-Hückel parameters A_γ and B_γ and the B-dot parameter are represented on the same grid. The only required remaining activity coefficient parameters are an array of hard core diameters. The data files in the data0.ypf.R* series are similar, but the single Debye-Hückel parameter represented is $A\varphi$, which is related to A_γ, and an extensive array of interaction coefficients replaces the B-dot parameter and hard core diameters.

Thermochemical data are used in many branches of physical science, including geochemistry, mineralogy, petrology, chemical engineering, physical chemistry, corrosion science, metallurgy, and materials science. There is an extensive literature on the development and application of such data, spanning the various disciplines. This includes many efforts to compile, evaluate, and standardize the data. Most of this effort focuses on standard state data. Some notable compilations include the *Critical Stability Constants* series (e.g., Smith and Martell 1976 [DIRS 127382]; Martell and Smith 1982 [DIRS 159196]), the *CODATA Key Values for Thermodynamics* (Cox et al. 1989 [DIRS 150874]), *The NBS Tables of Chemical Thermodynamic Properties, Selected Values for Inorganic and C_1 and C_2 Organic Substances in SI Units* (Wagman et al. 1982 [DIRS 159216]; Wagman et al. 1989 [DIRS 179315]), the *NIST-JANAF Thermochemical Tables* (Chase 1998 [DIRS 157874]), *Thermochemical Data of Pure Substances* (Barin and Platzki 1995 [DIRS 157865]), and the *Chemical Thermodynamics* series sponsored by the Nuclear Energy Agency (NEA) of the Organisation for Economic Co-operation and Development (OECD) (e.g., Grenthe et al. 1992 [DIRS 101671]; Silva et al. 1995 [DIRS 102087]; Rard et al. 1999 [DIRS 157912]).

The literature on thermochemical data is an active one and continues to grow. New papers focused on specific species or reactions or families of such appear monthly. Compilations and evaluations are extended and revised (the OECD/NEA series noted above is still continuing after producing nine volumes). Old data are re-evaluated, sometimes giving revised results. Practical applications are found to require data for species or reactions for which existing data are unavailable, generating new data needs. Also, experimental and field observations sometimes encounter previously unknown chemical species, also generating new data needs. New methods for evaluating, correlating, representing, predicting, and extrapolating thermodynamic data continue to evolve and be applied.

Thermochemical data present some problems that are not typically encountered with other kinds of data. For a discussion of the nature and use of thermochemical data, particularly in regard to geochemistry, see the work of Garrels and Christ (1990 [DIRS 144877]), Nordstrom and Munoz (1994 [DIRS 168480]), or Stumm and Morgan (1996 [DIRS 125332]). One problem is that thermochemical data can be obtained by a variety of means, including various forms of calorimetry, a few genres of phase equilibrium experiments (including solubility measurements), potentiometry, and spectrophotometry. The actual measurements are then made to yield tabulated thermodynamic data. Often this requires assuming other data which have been obtained elsewhere. For example, in obtaining standard Gibbs energies or enthalpies of formation, corresponding data for "key" species (e.g., Cox et al. 1989 [DIRS 150874]) are generally required. Obtaining a solubility product constant from solubility measurements requires an understanding of which if any aqueous complexes may form and the corresponding complexation constants. The "other data" could also include Pitzer interaction coefficients or alternative activity coefficient model parameters. Thus, the tabulated thermodynamic data are often in a form distinct from the original measured data, and they often depend on values assumed for still other data.

Compiled sources differ in terms of the transparency and traceability of their recommendations. *The NBS Tables of Chemical Thermodynamic Properties, Selected Values for Inorganic and C_1 and C_2 Organic Substances in SI Units* (Wagman et al. 1982 [DIRS 159216]; Wagman et al. 1989 [DIRS 179315]) remains highly influential among the major compilations, primarily because of its extensive breadth and because it was issued by a government standards agency, the National Bureau of Standards (NBS), now known as the National Institute of Standards and Technology (NIST). Yet this major work gives no sources, does not document how specific recommended values were arrived at (though a short introductory section does address general methodologies), and gives no estimates of associated uncertainties. At the other end of the spectrum, the OECD/NEA *Chemical Thermodynamics* series provides a thorough examination of data, well documents the process in each instance, and provides estimates of uncertainties. This series also adopts (and is consistent with) *CODATA Key Values for Thermodynamics* (Cox et al. 1989 [DIRS 150874]). This type of source is preferred. However, due to the extensive scope of coverage of the NBS tables (Wagman et al. 1982 [DIRS 159216]; Wagman et al. 1989 [DIRS 179315]) and the lack of coverage by alternative sources, it is still necessary to use this source for some chemical species. Furthermore, some other literature is based on data from this source (e.g., the NBS tables data are used in the calculation of other data). This is likely to be true in the case of key aqueous species not covered by the CODATA recommendations or the OECD/NEA volumes.

Because of the considerable activity in the field of thermochemical data, which as previously noted spans several scientific and engineering disciplines, thermochemical databases that support computerized modeling (e.g., those in the data0.ymp.R* series) tend to be dynamic. The thermochemical databases used on the YMP are perhaps somewhat unusual compared to other databases used on the Project to support modeling in that only a relatively small proportion of the included data are directly produced by the Project itself. Instead, the majority of data come from outside the YMP and are selected for use.

To maximize efficiency and credibility, the thermochemical databases in the data0.ymp.R* (and data0.ypf.R*) series rely heavily on existing compilations and evaluations. A principal source is the geochemical database associated with the computer code SUPCRT92 (Johnson et al. 1992 [DIRS 101632]). SUPCRT92 is based on the work of H.C. Helgeson and various students and coworkers (e.g., Helgeson et al. 1978 [DIRS 101596]; Helgeson and Kirkham 1974 [DIRS 157904]; Shock and Helgeson 1988 [DIRS 144817]; Shock et al. 1997 [DIRS 150770]; and Shock et al. 1997 [DIRS 127953]). The SUPCRT92 database contains standard Gibbs energies, enthalpies, and entropies of many mineral and aqueous species of geochemical interest. It also contains standard heat capacity coefficients and standard molar volumes for mineral species, and equation of state data for aqueous species, including equivalent data for water (H_2O liquid). The SUPCRT92 code can be used to calculate log K values (and other standard state thermochemical properties, and Debye-Huckel parameters) as functions of temperature.

The other principal source is the *Chemical Thermodynamics* series sponsored by OECD/NEA (e.g., Grenthe et al. 1992 [DIRS 101671]; Silva et al. 1995 [DIRS 102087]; Rard et al. 1999 [DIRS 157912]). The OECD/NEA volumes contain tabulations of recommended values for equilibrium constants and standard thermodynamic functions at 298.15 K, and heat capacity coefficients for solids. The data provided in the OECD/NEA volumes do not include representations of the thermodynamic data at elevated temperatures. This is also the case for the data provided by many other sources. Thus, it is necessary to provide a means for extrapolating data to elevated temperature.

The methodology of calculating the necessary thermodynamic data is discussed in Section 6.1. Briefly, it involves using the SUPCRT92 software (Johnson et al. 1992 [DIRS 101632]; SUPCRT92 V1.0; see Section 3.1.2) in combination with a set of workbook (spreadsheet) tools. SUPCRT92 is capable of calculating standard state thermodynamic data on a specified temperature grid, including the EQ3/6 temperature grid (0-25-60-100-150-200-250-300°C) used in the data0.ymp.R* series. It should be noted that the ability to treat the temperature dependence of the thermodynamic properties of aqueous species and complexes in this manner is fairly unique and generally superior to anything else presently available for this purpose. This is used for both providing data directly to a data0* file and also to provide support for the workbook tools through library worksheets (discussed below). A negative aspect of SUPCRT92 is that it works in obsolete calorie units. In order to put data in joule units into the SUPCRT92 database, it is necessary to convert them to calorie units (1 cal = 4.184 J; Weast and Astle 1981 [DIRS 100833], p. F-304). SUPCRT92 requires that input Gibbs energies and enthalpies be rounded to the nearest cal/mol. SUPCRT92 output data are generally converted back to joule units. Output log K data are unitless and pose no conversion issue.

The SUPCRT92 software and database are used for three purposes:

1. Calculation of log K (and Debye-Hückel A_γ and B_γ) values on the EQ3/6 temperature grid (0-25-60-100-150-200-250-300°C), for input to a data0* file. This provides a core of data for many aqueous species and minerals of geochemical interest.

2. Calculation of apparent standard molal Gibbs energies of aqueous *basis* species on the same temperature grid. Basis or *master* species are used as general "building blocks" in writing reactions: e.g., species including H_2O, Na^+, K^+, Cl^-, HCO_3^-, and UO_2^{2+}. These results (converted to joule units) are collected in a *BasisSpeciesLib_j*xls* file and organized into worksheets called "Basis Species 1," "Basis Species 2," etc. These *library* worksheets are then copied as needed into other workbooks described below. Some library worksheets in calorie units were directly added into certain workbook templates (now considered obsolete; see below). The contents of the most recent *BasisSpecies_j*.xls* file are presented in Appendix C of this report.

3. Calculation of apparent standard molal Gibbs energies of *reference* species on the same temperature grid. Reference species largely overlap basis species, but also include aqueous complexes representing various stoichiometries and charge types. A few simple oxides are also included. These results (converted to joule units) are collected in a *ReferenceSpecies_j*.xls* workbook. The data for the aqueous species in the set are organized onto worksheets called "Aq. Species 1," "Aq. Species 2," etc.,

and the few solids onto a single worksheet called “Misc Solids.” These are also *library* worksheets. Some library worksheets in calorie units were directly added into certain workbook templates (now considered obsolete; see below).

For additional information on SUPCRT92 and its application, see Section 6.1.2.

The workbook (spreadsheet) tools consist of a set of generic templates that support the calculation of apparent standard Gibbs energies and of log K values on the EQ3/6 temperature grid (0-25-60-100-150-200-250-300°C). These are basically temperature extrapolation tools. They work by means of cell formulas. In fitting heat capacity coefficients to tabulated heat capacity data, the built-in Excel “regression tool” is also used. No macros are employed. The following types of generic templates are used:

1. *Solids_j*.xls*: This is used to compute log K values on the EQ3/6 temperature grid for the dissolution reaction of a solid. The required input data are the Gibbs energy and entropy of the solid (at 298.15 K), and a set of corresponding heat capacity (C_p) coefficients. These coefficients must be consistent with the eleven-term generalized form represented by Equation 6-8 (usually only two to four terms are used for any given solid). Energy-related quantities are in joule (J) units. The Gibbs energy values of the solid are calculated on the EQ3/6 temperature grid using the “retrieval” Equation 6-3, using Equations 6-9 and 6-10 respectively for the $\int C_p\, dT$ and $\int C_p\, d\ln T$ terms. The log K values are calculated using these results in conjunction with Gibbs energy values on the same grid for the basis species, as obtained from the library worksheets in a *BasisSpeciesLib_j*xls* file. This is the preferred generic template for dealing with solids.

2. *Minerals_j*.xls*: This is used to compute log K values on the EQ3/6 temperature grid for the dissolution reaction of a solid. This is like *Solids_j*.xls*, except that the input heat capacity coefficients must be consistent with the Maier-Kelley equation (Equation 6-2). It is not much used, as the terms in the Maier-Kelley equation (Equation 6-2) appear in the generalized equation (Equation 6-8) used in *Solids_j*.xls*, so that template can be used instead. This template is essentially obsolete.

3. *Solids_cal*.xls*: This is used to compute log K values on the EQ3/6 temperature grid for the dissolution reaction of a solid. This is like *Solids_j*.xls*, except that energy-related quantities are in obsolete calorie units. This is an older template. It requires library worksheets for the basis species in calorie units. These are built-in worksheets that trace to SUPCRT92 calculations in DTN: MO0302SPATHDYN.001 [DIRS 161886]. These library worksheets are no longer maintained, and this template is essentially obsolete.

4. *Minerals_cal*.xls*: This is used to compute log K values on the EQ3/6 temperature grid for the dissolution reaction of a solid. This is like *Solids_cal*.xls*, except that the input heat capacity coefficients must be consistent with the Maier-Kelley equation (Equation 6-2). This template is essentially obsolete.

5. *Cp_Solids_j*.xls*: This is used to fit the Maier-Kelley equation (Equation 6-2) to heat capacity data that are tabulated as a function of temperature. The input and output data are in joule units.

6. *Cp_Solids_cal*.xls*: This is used to fit the Maier-Kelley equation (Equation 6-2) to heat capacity data that are tabulated as a function of temperature. The input and output data are in obsolete calorie units. This template is essentially obsolete.

7. *AqueousSpecies_j*.xls*: This is used to compute log K values on the EQ3/6 temperature grid for the reaction of an aqueous species that is destroyed in that reaction. Usually this is the dissociation reaction of an aqueous complex. The required input data are the Gibbs energy and entropy (at 298.15 K) of the aqueous species. Energy-related quantities are in joule units. The isocoulombic/isoelectric method (Section 6.1.3) is used to extrapolate the Gibbs energy of the aqueous species of interest over the EQ3/6 temperature grid. This requires the user to define an isocoulombic or isoelectric reaction (which is generally not the desired reaction) and to use 298.15 K Gibbs energy and entropy data for the other species in that reaction (these are called the *reference* species). These data for the reference species are taken from library worksheets in a *ReferenceSpecies_j*.xls* file. The isocoulombic/isoelectric method in essence extrapolates the calculated Gibbs energy of reaction over the temperature grid assuming a constant entropy of reaction. The Gibbs energy grid for the species of interest is then extracted using similar grids for the reference species obtained from the library worksheets. The log K values (for the desired reaction) are then calculated using these results in conjunction with Gibbs energy values on the same grid for the basis species, as obtained from the library worksheets in a *BasisSpeciesLib*xls* file. This is the preferred generic template for dealing with aqueous species.

8. *AqueousSpecies_cal*.xls*: This is a now obsolete variant of the generic template *AqueousSpecies_j*.xls*. It uses obsolete calorie units.

For additional description of these generic templates, see Section 6.1.3.

Other spreadsheets are used in developing the data. These are used to help accommodate the full variety of possible forms of input thermodynamic data, to estimate thermodynamic properties from measured data, to apply various estimation techniques based on correlation relations (see Section 6.1.4), and to perform other supporting analyses, including data comparisons. These tend to be one-of-a-kind in nature. Some workbooks are hybrid in character, including one or more elements of the template functionality described above, but also including other calculational elements. Workbook *Clays_TJW_1_Rev1b.xls* (in folder *\CD\Spreadsheets\Solids* of DTN: MO0302SPATHDYN.001 [DIRS 161886]) is an example of a spreadsheet used to estimate thermodynamic data from correlation relations (it is used to estimate data for certain clay minerals).

SUPCRT92 and its data file were adopted because they provide access to a core of data for significant aqueous species and solids (minerals) that are of geochemical interest. This body of data is widely used and accepted in the geochemical community. A notable feature is an equation of state model for aqueous species (Shock and Helgeson 1988 [DIRS 144817]; Shock et al. 1997 [DIRS 150770]; Shock et al. 1997 [DIRS 127953]) that permits calculation of standard thermodynamic properties of such species over a very wide range of temperature and pressure (well exceeding what is required for the databases in the data0.ymp.R* series). This capability is essential to support the use of isocoulombic/isoelectric method calculations for aqueous species that are not included in the SUPCRT92 data file.

Other thermodynamic data are taken from a broad array of sources. For the most part, these data are processed through Excel workbooks that follow the generic templates discussed previously. Some equilibrium constant (log K) data are directly incorporated into the data0.ymp.R* file. This generally occurs only when the only data available are log K data for 25°C.

As noted previously, a major source of the non-SUPCRT92 data is the *Chemical Thermodynamics* series sponsored by OECD/NEA (e.g., Grenthe et al. 1992 [DIRS 101671]; Silva et al. 1995 [DIRS 102087]; Rard et al. 1999 [DIRS 157912]). The data given in these volumes is sufficient to make temperature extrapolations. However, such extrapolations are generally not included in the OECD/NEA volumes themselves. Hence, Excel workbooks based on the previously described generic templates are used to process the OECD/NEA data.

Other sources of data are similarly processed. Noteworthy sources include the *Critical Stability Constants* series (e.g., Smith and Martell 1976 [DIRS 127382]; Martell and Smith 1982 [DIRS 159196]), *CODATA Key Values for Thermodynamics* (Cox et al. 1989 [DIRS 150874]), *The NBS Tables of Chemical Thermodynamic Properties, Selected Values for Inorganic and* C_1 *and* C_2 *Organic Substances in SI Units* (Wagman et al. 1982 [DIRS 159216]; Wagman et al. 1989 [DIRS 179315]), *NIST-JANAF Thermochemical Tables* (Chase 1998 [DIRS 157874]), *Thermochemical Data of Pure Substances* (Barin and Platzki 1995 [DIRS 157865]), *Thermochemical Data of Elements and Compounds* (Binnewies and Milke 1999 [DIRS 158955]), and *Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (*10^5 *Pascals) Pressure and at Higher Temperatures* (Robie and Hemingway 1995 [DIRS 153683]). Still other sources include various journal articles and reports that deal with a single solid, gas, or aqueous species, or with groups of related species.

Levels of transparency and traceability of the sources described above vary tremendously. At the high end of the scale are the OECD/NEA volumes. These volumes provide detailed information concerning their own sources, how they evaluated and processed the data, and discussion of alternative data considered. The SUPCRT92 data are also well-documented in the associated literature, though there is less discussion of alternative data. Reports and journal articles of more restricted scope are also generally well-documented. Many of the compilation sources, including the *Critical Stability Constants* series (e.g., Smith and Martell 1976 [DIRS 127382]; Martell and Smith 1982 [DIRS 159196]), *Thermochemical Data of Pure Substances* (Barin and Platzki 1995 [DIRS 157865]), *Thermochemical Data of Elements and Compounds* (Binnewies and Milke 1999 [DIRS 158955]), and *Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (*10^5 *Pascals) Pressure and at Higher Temperatures* (Robie and Hemingway 1995 [DIRS 153683]) identify specific data sources, but do not provide information on how the source data were evaluated and processed or address possible alternative data. The low end is typified by *The NBS Tables of Chemical Thermodynamic Properties, Selected Values for Inorganic and* C_1 *and* C_2 *Organic Substances in SI Units* (Wagman et al.

1982 [DIRS 159216]; Wagman et al. 1989 [DIRS 179315]), which basically gives nothing beyond a set of recommended values. In constructing the thermochemical databases in the data0.ymp.R* series, sources with higher levels of transparency and traceability are preferred. However, sources with lower levels are sometimes used when no other data are available.

As used in this report, SUPCRT92 refers to the associated data files *slop98.dat*, *sprons98.dat*, *speq02.dat*, and *speq06.dat* (these files form a chronological series). The file *slop98.dat* is archived in DTN: MO0106MWDTDG01.035 [DIRS 161791]; *sprons98.dat* and *speq02.dat* are in the folder *\cd\SUPCRT_runs_TJW\SUPCRT_datafiles* of DTN: MO0302SPATHDYN.001 [DIRS 161886]. The files *slop98.dat* and *sprons98.dat* are very nearly identical. They differ only in that the latter corrects a sign error in the Gibbs energy of formation of the non-key aqueous species $AuCl_4^-$. For the purposes of this report, any further reference to "slop98.dat" should be considered equivalent to one to *sprons98.dat*. The file *speq02.dat* is exactly duplicated in DTN: MO0303SPASPEQ2.000 [DIRS 162278], which is a data package that is associated with a cancelled document (Steinborn et al. 2003 [DIRS 161956]). This data package was frequently cited as the source for *speq02.dat* in Rev. 00 of this report. In the present revision (Rev. 01), only DTN: MO0302SPATHDYN.001 [DIRS 161886] is used for this purpose. References to DTN: MO0303SPASPEQ2.000 [DIRS 162278] (outside this paragraph) are replaced by references to DTN: MO0302SPATHDYN.001 [DIRS 161886]. The data file *speq06.dat* is a later, modified form of *speq02.dat* that is described below.

The file *speq02.dat* was developed from *sprons98.dat* as part of the development of the data0.ymp.R* series (Steinborn et al. 2003 [DIRS 161956]; see also Section 6.1.2 of the present report). The species names in *speq02.dat* were revised for consistency with EQ3/6 naming conventions (e.g., *CORUNDUM* was changed to *Corundum*; *Al+3* to *Al+++*; and *CaSO4,aq* to *CaSO4(aq)*). The file *speq02.dat* contains very slightly different data for the mineral quartz (SiO_2) and notably different data for the key aqueous species SiO_2(aq), reflecting a change to the "Rimstidt" paradigm (e.g., Rimstidt 1997 [DIRS 101709]; Stefánsson 2001 DIRS [159208]) from the older "Fournier" paradigm. This change increases the thermodynamic stability of SiO_2(aq) and is associated with an increased solubility of quartz (see Section 6.1.5 of this report). The file *speq02.dat* was used in support of the development of data0.ymp.R0 through data0.ymp.R4. The more recently modified file *speq06.dat* is used in developing data0.ymp.R5. The file *speq06.dat* will be briefly discussed in Section 1.2 below.

Log K data for various cement phases present in the thermochemical database data0.ymp.R4 (Output DTN: SN0410T0510404.002) are carried over into the data0.ymp.R5 database (Output DTN: SN0612T0502404.014). These data 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 the data0.ymp.R4 and data0.ymp.R5 databases, but the thermodynamic information in the comments, and the discussion of these data in this report, are available for possible use in applications.

This document was prepared in accordance with SCI-PRO-005, *Scientific Analyses and Calculations*, and SCI-PRO-001, *Qualification of Unqualified Data*. This report is both a scientific analysis report and a data qualification report. The technical work plan (TWP) (BSC 2006 [DIRS 177885]) was written to follow the corresponding Bechtel SAIC Company (BSC) procedures applicable at the time (AP-SIII.9Q, *Scientific Analyses*, and AP-SIII.2Q, *Qualification of Unqualified Data*). The data qualification report aspect of this report is limited to the qualification of the database data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), although that qualification also invokes elements of a scientific analysis report in some of the methodologies used. The qualification of the more recent databases data0.ymp.R4 (Output DTN: SN0410T0510404.002) and data0.ymp.R5 (Output DTN: SN0612T0502404.014) is conducted using only the methods of a scientific analysis report.

Although this report invokes SCI-PRO-001 for data qualification, the only relevant data qualification function in the present revision (Rev. 01) is to reiterate and document the qualification activity that was carried out in Rev. 00 of this report, and to preserve the relevant data qualification report material from Rev. 00 (in fact, that material has been expanded in response to the discovery of a few deficiencies that will be noted later in this report). There is no new documentation plan and no new data qualification team. The data qualification plan is given in Appendix A of the TWP for Rev. 00 of this report (BSC 2004 [DIRS 172402]). The chairman of the team was Dr. Carlos F. Jove-Colon. The other technical team members were Dr. Charles Bryan and Dr. Russell Jarek. Their qualifications are given in the data qualification plan, and are reproduced in Appendix E of the present revision (Rev. 01) of this report.

It is noted that there are no major differences between the AP-SIII.2Q used in the original data0.ymp.R2 data qualification and the present SCI-PRO-001. The original requirements and terminology are essentially preserved. The chosen methods for the this data qualification activity (see Appendix A of BSC 2004 [DIRS 172402]) were Method 2 (Corroborating Data) and Method 5 (Technical Assessment). These are the two principal methods used by the technical community at large to evaluate thermodynamic data. It is appropriate to use the methods generally accepted and used in the cognizant technical community at large. Also, it is generally necessary to follow these methods as nearly all the input data for the databases in the data0.ymp.R* series originate from outside the YMP. No Attachment 4 qualification process attributes were deemed appropriate.

The selected methods are described in Attachment 3 of SCI-PRO-001 (and are nearly identical to those of AP-SIII.2Q, Rev. 1, ICN 2):

> ***Method 2—Corroborating Data***. *The Corroborating Data approach may be used when data comparisons can be shown to substantiate or confirm parameter values. The corroborating data qualification process may include comparisons of unqualified to unqualified data, as well as unqualified to qualified data with appropriate compliance documentation as defined in this procedure.*
>
> *The following are conditions for the use of corroborating data:*
>
> a. *Corroborating data are available for comparison with the unqualified data set(s).*
>
> b. *Inferences drawn to corroborate the unqualified data can be clearly identified, justified, and documented.*

***Action to be Taken**: Identify the data set(s) that will be used to corroborate the unqualified data set(s). Identify, justify, and document the rationale for using these data set(s) and the inferences drawn to corroborate the unqualified data.*

***Method 5—Technical Assessment**. The Technical Assessment approach may be used when it is determined that an independent evaluation of the data by a subject matter expert is needed to raise the confidence of the data to a proper level for the intended use. Either of the following conditions could require using the Technical Assessment approach:*

a. The confidence in the data is in question because data collection procedures are unavailable for review, or the procedures used are not adequate.

b. Documentation or proof of proper data acquisition is unavailable for review.

***Actions to be Taken**: Conduct an independent evaluation of the data and available documentation by a subject matter expert who is independent from the data collection or data reduction process. It is required that documentation be traceable to the original source of the data (it is noted that the original source can be a scientific journal, publication, etc.) and that checking, review, and approval of the data (and data use) can be conducted without recourse to the subject matter expert that is qualifying the data. The Technical Assessment should include one or a combination of the following:*

a. Determination that the employed methodology is acceptable. A discussion and justification that the data collection methodology used was appropriate for the type of data under consideration (used appropriate equipment, typical of scientific and industry collection methods, etc.).

b. Determination that confidence in the data acquisition or developmental results is warranted. A discussion and justification that the data acquisition and/or subsequent data development (e.g., reduction or extrapolation) discussed in source documentation was appropriate for the type of data under consideration. This could include assurances that processes were conducted by qualified professionals; data were collected under proper environmental conditions; collected results and/or data development are appropriate, reasonable, and suitable for their intended use; etc.

c. Confirmation that the data have been used in similar applications. A discussion and documentation that the data have been used in applications that are similar to those for which the data will be used. Past applications could include data used by the U.S. Nuclear Regulatory Commission or Environmental Protection Agency (or their subcontractors) in technical evaluation reports, licensing proceedings, or safety evaluation reports; by nationally/internationally recognized scientific organizations (International Atomic Energy Agency, International Radioactive Waste consortiums, etc.); or by the scientific community, including publications, peer reviews, etc.

Section 6.1.2.D.2 of SCI-PRO-001 requires addressing the qualification process attributes listed in its Attachment 4. This requirement was also part of AP-SIII.2Q. No attributes were deemed appropriate in the data qualification plan (Appendix A of BSC 2004 [DIRS 172402]). However, the following attributes are germane both to the qualification of data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) and to subsequent database development under the scientific analysis approach:

2. The technical adequacy of equipment and procedures used to collect and analyze the data
3. The extent to which the data demonstrate the properties of interest (e.g., physical, chemical, geologic, mechanical)
4. The environmental conditions under which the data were obtained if germane to the quality of data
7. Prior uses of the data and associated verification processes
8. Prior peer or other professional reviews of the data and their results
9. Extent and reliability of the documentation associated with the data
10. Extent and quality of corroborating data or confirmatory testing results
12. The importance of the data to showing that the proposed U.S. Department of Energy repository design meets the performance objectives of the QA program that supports the YMP License Application process or post closure science.

The methods adopted for correction and/or updating of thermodynamic data parameters mainly involve reviewing and/or corroboration with literature data: e.g., examining reported studies of solubilities and associated thermodynamic data, examining reported comparisons of thermodynamic data from different sources, and making original comparisons of adopted data with alternate data.

1.2 CHANGES FOR DATA0.YMP.R5

The present revision of this report is developed from *Technical Work Plan for: Thermodynamic Databases for Chemical Modeling* (BSC 2006 [DIRS 177885]). That TWP documents the changes to be implemented in the development of the data0.ymp.R5 thermochemical database (Output DTN: SN0612T0502404.014) from the data0.ymp.R4 database (Output DTN: SN0410T0510404.002). Some of the changes described in the plan are relevant to the data0.ypf.R* series and changes to the IDPS model (SNL 2007 [DIRS 177411]). Some changes affect both the data0.ymp.R* series and the data0.ypf.R* series. Some of the changes are associated with actions to resolve CRs. Others are not. Looked at another way, some of the changes are being made to correct errors; others are being made only as opportunities for improvement (a CR may involve both types of changes).

Most of the changes made for data0.ymp.R5 are relatively minor. An exception concerns corrections to resolve discrepancies in key thermochemical data for aqueous phosphate species (Appendices A and B of this analysis report; see also CR 6731 noted below). A comparison of key thermodynamic data for a large set of phosphate ions from commonly referenced tabulations of key thermodynamic data indicates a discrepancy in the recommended thermochemical properties of the HPO_4^{2-} and $H_2PO_4^-$ aqueous species. The data for HPO_4^{2-} and $H_2PO_4^-$ in *speq02.dat* are consistent (see Appendix A) with *The NBS Tables of Chemical Thermodynamic Properties, Selected Values for Inorganic and C_1 and C_2 Organic Substances in SI Units* (Wagman et al. 1982 [DIRS 159216]). The data for phosphate compounds and species in the *Chemical Thermodynamics* series sponsored by OECD/NEA (e.g., Grenthe et al. 1992 [DIRS 101671]) are not consistent with the data from the *NBS Tables*. This discrepancy is ~7 kJ/mol and should be considered important in effecting geochemical calculations. The data for HPO_4^{2-} and $H_2PO_4^-$ in the OECD/NEA volumes are taken from *CODATA Key Values for Thermodynamics* (Cox et al. 1989 [DIRS 150874]). This indicates a major discrepancy between the recommendations of two sanctioning bodies (CODATA and NBS, now NIST). Appendix A of this report documents this discrepancy. Appendix B evaluates the discrepancy, documents an apparent error in the NBS/NIST data, and recommends that the CODATA data be used instead. The SUPCRT92 data file *speq06.dat* is a modification of *speq02.dat* that implements the CODATA data for these phosphate species. This file is used in the present revision of this analysis report to correct affected data in the *BasisSpeciesLib_j*.xls* and *ReferenceSpecies_j.xls* library workbooks. The resulting updated are used in turn in Excel workbooks to correct other data for phosphate compounds and species.

The updates implemented in development of the data0.ymp.R5 database (Output DTN: SN0612T0502404.014) are in part a result of several Condition Reports (CR 6489, CR 6731, CR 7542, CR 7756) described in the TWP (BSC 2006 [DIRS 177885]). Text from the relevant CRs is presented below in its original form, with any modifications indicated in square brackets:

- **CR 6489: Sensitivity Studies on Form of Sepiolite Used in ANL-EBS-MD-000074, Rev. 01**.

  Description: The IDPS model (EQ3/6 simulations) is used in the Analysis of Dust Deliquescence for FEP Screening, ANL-EBS-MD-000074 Rev 00. The IDPS model uses the precipitation of the mineral, sepiolite as the primary mechanism controlling magnesium concentrations in brines. The thermodynamic data base, data0.ypf.R0 contains the log K value for crystalline sepiolite. Validation of the IDPS model in In-Drift Precipitates/Salt Model, ANL-EBS-MD-000045 REV 02, Section 7.1.1, required changing the log K value for sepiolite by 6 log units to match experimental data. The modified log K represents an amorphous form of sepiolite rather than the crystalline form…Modifying the IDPS model with the revised log K for amorphous sepiolite and running the simulations of the brine formed by evaporation would improve the confidence in the results of the model as it applied to dust deliquescence.

- **CR 6731: Discrepancy in thermodynamic data for phosphate species**.

  Description: [the originator has identified]….discrepancies in key thermodynamic data used to develop the data0.ymp.R0 and successor data0.ymp.R2 thermochemical databases (see ANL-WIS-GS-000003 Rev. 00). The data0.ymp.R0 database is used as a starting point for a Pitzer database in the In-Drift Precipitates/Salts AMR (ANL-EBS-MD-000045 Rev. 02) which is applied in the seepage evaporation abstraction for TSPA (ANL-EBS-MD-000033 Rev. 05). Phosphate species are not included in these models, and are likely to be very scarce in the EBS chemical environment. In other models, however, phosphate may be a significant reactant. Because phosphate forms insoluble precipitates with certain actinides (e.g., U) and other important elements (e.g., Gd), discrepant thermodynamic data for phosphate species may be significant to TSPA abstractions or FEP exclusion (see ANL-EBS-MD-000037 Rev. 04)…[in addition, we are] unable to verify the stoichiometry of $GdPO_4{:}10H_2O$ from the source cited in the data0.ymp.R2 database (ANL-WIS-GS-000003 Rev. 00). This is a different but related issue to the one identified in the attachment, and the two issues should be evaluated together.

- **CR 7542: Thermodynamic database *data0.ymp.R4* (Output DTN: SN0410T0510404.002) update [$NiCO_3$ solid].**

  Description: The solid mineral $NiCO_3$ (nickel carbonate) has been identified as needing an update in the data0.ymp.R4 thermodynamic database(DTN: SN0410T0510404.002). The ymp.R4 data leads to a very high nickel solubility and is realized in the in-package chemistry calculations (ANL-EBS-MD-000037 REV 04). A recent NAGRA 2002 report (02-16; TIC 253421) states how previous databases commonly contained this incorrect solubility product…The updated value from NAGRA is already contained within data0.ypf.R2 (DTN: SN0504T0502205.008).

- **CR 7756**: **Add mineral phases observed in UO_2 drip tests and natural analogue to EQ3/6 databases**.

  Description: A number of secondary minerals observed in UO_2 dissolution experiments and/or at the Pena Blanca uraninite deposit are not included in YMP thermodynamic databases such as data0.ymp.R4 used in TSPA. They include [the following listed species]: haiweeite, dehydrated schoepite ($UO_3{:}0.8\text{-}1.0H_2O$), becquerelite, compreignacite, sklodowskite, boltwoodite ($KH(UO_2)SiO_4{:}1.5H_2O$), beta-uranophane (same formula as uranophane), palygorskite, ianthinite, and weeksite ($K_2(UO_2)_2Si_6O_{15}{:}4H_2O$). Because these minerals are observed to form under conditions similar to conditions that could develop at the repository, they should be added to the databases, if data are available. Without these phases in the databases, one cannot predict their potential formation and accumulation nor their potential effects on water composition.

Additional changes to be made for the data0.ymp.R5 database as described in the TWP (BSC 2006 [DIRS 177885]) consist mainly of updates and corrections to log K values for dissociation reactions over the appropriate temperature ranges. Some changes affect both the data0.ymp.R* series and the data0.ypf.R* series. Descriptions of these changes from the TWP are as follows:

- **Consistent Application of log K Values in the Pitzer and "B-dot" Databases**. There is a need to address consistent application of "infinite dilution" log K values for dissociation reactions for actinides and transition metal solids and aqueous species common to data0.ymp.R4 (Output DTN: SN0410T0510404.002) and data0.ypf.R1 (DTN: SN0302T0510102.002 [DIRS 162572]). Consistency does not necessarily mean that identical values for parameters will be used in different databases but their evaluation with respect to how these were obtained and consistency with the adopted activity coefficient model needs to be assessed.

- **New Data for Se(VI) and Sn(IV) Species**. The base data0.ymp.R4 database adopts the "B-dot" activity coefficient model and has thermodynamic data for aqueous and solid species involving these two components, but additional data are needed to expand the stability range and number of possible solid and aqueous species that could occur in this system. The application will be in radionuclide transport for certain scenarios of system performance. Solubility data has been reported for the solid SnO_2(am) and the aqueous species.

- **Update log K Values for Silica Species**. This task affecting data for high-pH aqueous silica species was planned in the TWP (BSC 2006 [DIRS 177885], Section 1.2.2). This task was cut from the scope of this report because the technical basis for making the planned changes was found to be insufficiently developed and documented to justify making them. In particular, a credible explanation was lacking for why the sources currently cited and used would be in error. This appears to be a case where there are discrepancies in the data reported by different sources.

- **Addition of the Phase $NiMoO_4$(s)**. Thermodynamic data for this Ni-bearing phase have recently been determined by Morishita and Navrotsky (2003 [DIRS 176846]). Thermodynamic data for this phase as a function of temperature will be combined with its constituents as aqueous species already in the current database to calculate a log K value for the hydrolysis reaction.

- **Review of Complexation Data for the Species $Th(CO_3)_5^{6-}$**. Consistency of the current value adopted in the Pitzer database (which is from data0.ymp.R4; Output DTN: SN0410T0510404.002) with the Pitzer parameters obtained for this species needs to be reevaluated. This evaluation is directed to more defensible solubility calculations, since the activity model for highly charged species can have a strong effect on solubility, particularly where there is a high concentration of dissolved carbonate in solution.

- **Add Kogarkoite (Na_3SO_4F) to the Databases**. This phase has been identified as a product of the experimental evaporation of synthetic seepage solutions. Thermodynamic properties for this phase have been determined by Gurevich et al. (1999 [DIRS 176845]). Solubility relations for kogarkoite have been evaluated by Felmy and MacLean (2001 [DIRS 177660]), and thermodynamic parameter data will be considered in the solubility evaluation of this phase.

- **Changes Involving Reactions for Some Cr Species**. The reactions for the solids eskolaite (Cr_2O_3) and CrO_2 and the aqueous species CrO_3Cl^- are currently written as redox reactions. Cr(III) or Cr(IV) is oxidized to Cr(VI), represented by the basis species CrO_4^{2-}. The reactions for eskolate and CrO_3Cl^- are changed to non-redox reactions (Cr(III) goes to Cr(III), represented by the basis species Cr^{3+}). In the case of CrO_2, the oxidation state cannot be exactly preserved, because there is no basis species for Cr(IV). The reaction is changed to the type Cr(IV) goes to Cr(III), again using Cr^{3+}. This minimizes the oxidation state change as much as possible. These changes facilitate suppressions in the problem definition in the computer software package EQ3/6 input file.

- **Changes involving some other Cr Species**. Changes are made for some Cr species to obtain better consistency with the solubility of $Cr(OH)_3$(am) as a function of pH (Rai et al. 1987 [DIRS 163369]; Ball and Nordstrom 1998 [DIRS 163015]; Rai et al. (2004 [DIRS 179582]). The species $Cr_3(OH)_4^{5+}$ and $Cr_2(OH)_2^{4+}$ are deleted, and the data for $CrOH^{2+}$, $Cr(OH)_3$(aq), and $Cr(OH)_3$(am) are changed.

- **Incorporate Tabulated Data Corrections**. This issue involves incorporation of the corrections for log K values noted in the previous version of this report (BSC 2005 [DIRS 171916], Section 7; Output DTN: SN0410T0510404.002) but not implemented into the updated version of the data0.ymp.R5 database file.

- **CR 6752**. The TWP (BSC 2006 [DIRS 177885]) states that changes associated with CR 6752 will be documented in several reports, including this one. However, it was not necessary to document the changes associated with CR 6752 in this report because they did not apply to the data0.ymp.R* series of databases.

INTENTIONALLY LEFT BLANK

2. QUALITY ASSURANCE

The quality assurance program used for the development of this activity and document is discussed in *Technical Work Plan for: Thermodynamic Databases for Chemical Modeling* (BSC 2006 [DIRS 177885]). In accordance with the TWP, 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 LS-PRO-0203, *Q-List and Classification of Structures, Systems, and Components*) that are important to the demonstration of compliance with the postclosure performance objectives prescribed in 10 CFR 63.113:

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

These barriers are classified as Safety Category (SC) with regard to importance to waste isolation as defined in LS-PRO-0203. 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 were applied as required by IM-PRO-002, *Control of the Electronic Management of Information.* This document was prepared in accordance with SCI-PRO-005, *Scientific Analyses and Calculations*, and SCI-PRO-001, *Qualification of Unqualified Data*. Software usage discussed in Section 3 was conducted in accordance with IM-PRO-003, *Software Management*.

Planning and preparation of this report was initiated under the BSC Quality Assurance Program. Therefore, forms and associated documentation (primarily the TWP) prepared prior to October 2, 2006, the date this work transitioned to the Lead Laboratory, were completed in accordance with BSC procedures.

INTENTIONALLY LEFT BLANK

3. USE OF SOFTWARE

3.1 QUALIFIED SOFTWARE

All qualified software discussed in this document was obtained from Software Configuration Management in accordance with IM-PRO-003, *Software Management*. This software was used in the operating environments for which it was baselined. There are no limitations of the software within the range of application. This software is appropriate for the application and was used only within the range of model validation in accordance with IM-PRO-003.

3.1.1 EQ3/6 Version 8.0

EQ3/6 Version 8.0 (EQ3/6 V8.0 [DIRS 162228], STN: 10813-8.0-00) was installed and used on IBM-compatible computers using the Microsoft Windows 2000 operating system. This software was selected because it was the best software available for implementing the database developed in this report. EQ3/6 is the software that the data0.ymp.R* series of thermochemical databases is designed to support. Its usage in this report is relatively minor. The EQPT data file pre-processor that is part of EQ3/6 performs certain error-checking functions and is used in part to verify that a data0.ymp.R* file is suitable for use. Also, EQ3/6 can be used to check computed solubilities. It can also be used to calculate adjustments to equilibrium constants to satisfy solubility data. This is done only in rare instances.

3.1.2 SUPCRT92

SUPCRT92 Version 1.0 (SUPCRT92 V1.0 [DIRS 153218], STN: 10058-1.0-00) is used to calculate thermodynamic data from input thermodynamic data and equation of state parameters. SUPCRT92 was installed and used on IBM-compatible computers using the Microsoft Windows 98 operating system The output thermodynamic data are generally apparent standard Gibbs energies of formation of mineral and aqueous species on the EQ3/6 temperature grid (0-25-60-100-150-200-250-300°C), or equilibrium constants (log K) for specified reactions, again on the same temperature grid.

3.2 EXEMPT SOFTWARE

The exempt software Microsoft Excel, a commercially available spreadsheet software package, was installed and used on IBM-compatible computers using the Microsoft Windows operating system. Excel is part of the Microsoft Office package, of which the following versions were used: *Office 97 Professional* (STN: 610236-97-00); *Office 2000 Professional* (STN: 610236-2000-00); *Office XP* (STN: 610236-XP-00); *Office 2003 Professional* (STN: 610236-2000STD-00); and *Office 2003 SP1 & SP2* (STN: 610236-2003SP1SP2-00). This software is exempt in accordance with Section 2.0 of IM-PRO-003. The software was also 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 is presented in Section 6.2. The regression tool intrinsic to Microsoft Excel (all versions noted above) was used in many cases. No Excel macros or other non-standard functions were developed or used in this effort.

INTENTIONALLY LEFT BLANK

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: Thermodynamic Databases for Chemical Modeling* (BSC 2006 [DIRS 177885]). All source data are summarized in Table 4-1. These data are taken from a variety of reference materials.

Standard reference volumes (handbooks) are extensively used. Some of these carry the weight of sanctioning bodies such as CODATA and NIST (formerly NBS). For example, sources include *CODATA Key Values for Thermodynamics* (Cox et al. 1989 [DIRS 150874]) and *The NBS Tables of Chemical Thermodynamic Properties, Selected Values for Inorganic and* C_1 *and* C_2 *Organic Substances in SI Units* (Wagman et al. 1982 [DIRS 159216]; Wagman et al. 1989 [DIRS 179315]). As noted in Section 1, a principal source of input data is the OECD/NEA-sponsored series *Chemical Thermodynamics* (e.g., Grenthe et al. 1992 [DIRS 101671]; Silva et al. 1995 [DIRS 102087]).

Scientific journal articles, including review articles, are also extensively used. As noted in Section 1, a main source of data is a geochemical database associated with the computer code SUPCRT92 (Johnson et al. 1992 [DIRS 101632]). The associated database file *sprons98.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886]) that was originally adopted for this project is founded on a series of journal articles (e.g., Helgeson et al. 1978 [DIRS 101596]; Shock and Helgeson 1988 [DIRS 144817]; Shock et al. 1997 [DIRS 150770]; Shock et al. 1997 [DIRS 127953]). For YMP use, this data file was modified to add many new chemical species (solids, gases, and aqueous species) and to update the thermodynamic data for many of the existing species.

The input sources also include a product previously developed for use on the YMP: the qualified database data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]). This was qualified in an earlier data qualification report (CRWMS M&O 2000 [DIRS 152575]). This database is input to the development of the thermochemical databases data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) and data0.ymp.R4 (Output DTN: SN0410T0510404.002) in Rev. 00 of this report. It remains as such in the present Rev. 01, and is also input to the development of data0.ymp.R5 (Output DTN: SN0612T0502404.014). The database data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) and its supporting calculations package (DTN: MO0302SPATHDYN.001 [DIRS 161886], including among other elements the *sprons98.dat* and *speq02.dat* SUPCRT92 data files) are also inputs to the development of data0.ymp.R4 (Output DTN: SN0410T0510404.002) and were qualified in Rev. 00 of this report as a data qualification activity under AP-SIII.2Q-BSC (the BSC equivalent of SCI-PRO-001). In the present revision, they are also inputs to the development of data0.ymp.R5 (Output DTN: SN0612T0502404.014). The thermochemical database data0.ymp.R4 (Output DTN: SN0410T0510404.002) and its supporting calculations package (Output DTN: SN0410T0510404.001) are also inputs to the development of data0.ymp.R5 (Output DTN: SN0612T0502404.014) in the present revision of this report.

These relationships among the various output products are somewhat complicated. For example, data0.ymp.R4 (Output DTN: SN0410T0510404.002) is treated as a product of the present revision of this report, but is also treated as an input for the purpose of developing data0.ymp.R5 (Output DTN: SN0612T0502404.014). The present revision of this report describes the qualification of all of the data contained in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), data0.ymp.R4 (Output DTN: SN0410T0510404.002), and data0.ymp.R5 (Output DTN: SN0612T0502404.014). It is noted that there are examples of using a data0.ymp.R* file as a direct input to calculations producing data for a later file in the series. These are largely trivial and include: using such a file as a convenient source of atomic weights or as a source of equilibrium constants for use in combining the corresponding reactions (e.g., $OH^- + H^+ = H_2O$) with other reactions (e.g., $Th^{4+} + 4\ OH = Th(OH)_4(aq)$) to recast the latter into a desired form (e.g., $Th(OH)_4(aq) + 4H^+ = Th^{4+}$). Some effort has been made in the present revision of this report to minimize such usages; however, some remain.

The situation for the two previous supporting calculations data packages (DTN: MO0302SPATHDYN.001 [DIRS 161886] and Output DTN: SN0410T0510404.001) is analogous in terms of using a previous data package as an input. This practice, while not optimal, has some justification in that a particular datum or set of data taken from such a data package for use as an input may depend in a complex manner on a wider array of original input data. Consequently, this practice in a number of instances improves transparency and traceability. It is noted that within any of these supporting calculations data packages, there are a number of elements of "intermediate" output that support other output elements. An optimal solution would be to combine all the supporting calculations into a single data package, with removal of all results that have subsequently been updated. However, doing so would only support the qualification of a single member of the data0.ymp.R* series of thermochemical databases.

The original SUPCRT92 data file *sprons98.dat* contained in DTN: MO0302SPATHDYN.001 [DIRS 161886] was subsequently modified to produce a data file called *speq02.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886]). This incorporates corrections associated with the implementation of the "Rimstidt" paradigm for silica solubility (Section 6.1.5). This SUPCRT92 data file was initially used as an input in the development of data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) and data0.ymp.R4 (Output DTN: SN0410T0510404.002) in Rev. 00 of this report. It is also used as an input to the development of data0.ymp.R5 (Output DTN: SN0612T0502404.014) in the present revision of this report.

The following is a listing of the items referred to in this report:

- The data0.ymp.R* items:
  - data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576])
  - data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756])
  - data0.ymp.R4 (Output DTN: SN0410T0510404.002)
  - data0.ymp.R5 (Output DTN: SN0612T0502404.014).
- The associated supporting calculations data package:
  - R2: DTN: MO0302SPATHDYN.001 [DIRS 161886]

  - R4: Output DTN: SN0410T0510404.001
  - R5: Output DTN: SN0702T0502404.015.

- SUPCRT92 data files:

  - *sprons98.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886], folder: *\cd\SUPCRT_runs_ TJW\SUPCRT_datafiles*)

  - *speq02.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886], folder: *\cd\SUPCRT_runs_TJW\SUPCRT_ datafiles*)

  - *speq06.dat* (Output DTN: SN0702T0502404.015, folder: *\SUPCRT Work\Speq06_db*).

The qualification status of each input is documented in the Document Input Reference System (DIRS) and is summarized in Table 4-1. The input data are presented in more detail in Section 4.1.

Potential data sources were identified by searching the on-line catalogs of the University of New Mexico and Sandia National Laboratories technical libraries. Handbooks identified and reviewed as potential data sources began with the works by Barin and Knacke (1973 [DIRS 160926]) and Binnewies and Milke (1999 [DIRS 158955]). The Binnewies and Milke (1999 [DIRS 158955]) handbook does not contain entropy data on the elements, but the Barin and Platzki (1995 [DIRS 157865]) handbook does contain those data, and was used as the source for this parameter. Other sources of handbook data include works by Cox et al. (1989 [DIRS 150874]) and Smith and Martell (1976 [DIRS 127382]). 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 development of the data0.ymp.R4 database (Output DTN: SN0410T0510404.002), thermodynamic data for 86 chemical elements, 1,209 aqueous species, 1,140 pure solids, 10 solids solutions, 3 pure liquids, and 128 gas species were collected for use in calculations of in-package chemical reactions and reactions involving corrosion of materials and ambient environmental conditions relevant to the YMP. 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:

log K	Log equilibrium constant of chemical reaction (dimensionless)

$\Delta H^\circ_{f,298}$	Standard enthalpy of formation at 298.15 K (kJ/mol or kcal/mol)
$\Delta G^\circ_{f,298}$	Standard Gibbs energy of formation at 298.15 K (kJ/mol or kcal/mol)
S°	Standard entropy at 298.15 K (also referred to as S°_{298}) (J/mol-K or cal/mol-K)
C_p°	Standard heat capacity at constant pressure, at 298.15 K (J/mol-K or cal/mol-K)
a, b, c	For solids and gases only: temperature-dependent C_p° coefficients (see Equation 4-1) for use in extrapolating the database to elevated temperatures, using the Maier-Kelly equation (Equation 4-1) as defined by Johnson et al. (1992 [DIRS 101632], p. 910) for the standard heat capacity C_p°, as explained in Section 6.1.1.

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

where T is absolute temperature in Kelvin units. In some cases, log K data based on measured mineral solubilities measurements were extracted from the literature and used directly. 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. Equation 4-1 is generally only applied to solids and gases. For aqueous species that are represented in SUPCRT92 databases (for example, *sprons98.dat*; DTN: MO0302SPATHDYN.001 [DIRS 161886]), an equation of state representation (see Shock and Helgeson 1988 [DIRS 144817] and Shock et al. 1997 [DIRS 127953]) represents heat capacity effects. For other aqueous species, the heat capacity effects are estimated using the isocoulombic/isoelectric approximation (Section 6.1.3).

The standard entropy S° was also compiled for the elements. This is occasionally needed to compute the corresponding standard entropy of formation (ΔS_f°) at 298.15 K, which is required to relate standard Gibbs energies of formation to standard enthalpies of formation ($\Delta G_f^\circ = \Delta H_f^\circ - T\Delta S_f^\circ$). Corresponding heat capacity data for the elements are generally unnecessary, due to use of the apparent Gibbs energy of formation and apparent enthalpy of formation (e.g., described by Helgeson et al. 1978 [DIRS 101596]), unless the apparent standard properties of interest of elemental chemical species, such as O_2(g), are themselves required.

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 to develop the thermochemical databases data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) and data0.ymp.R4 (Output DTN: SN0410T0510404.002). These data are given in Section A of Table 4-1. Some data missing from that set (not noted in Table 4-1 of Rev. 00 of this report) are listed in Section A' ("A-prime") of Table 4-1 and are discussed at the end of this main part of Section 4.1, after Table 4-1 (and before the Section 4.1.1). Data used only for the development of data0.ymp.R5 (Output DTN: SN0612T0502404.014) are given in Section B of Table 4-1. Some input sources may appear in both sections. If so, this indicates a different usage in Section B of Table 4-1. Many of the direct input data listed in Table 4-1 require substantial reduction and transformation for qualification and use in the developed thermochemical databases. The reduction, transformation, and qualification processes are discussed in Sections 6.2 through 6.4.

The purpose of this report as stated in Section 1 is to qualify the thermochemical database data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) and to develop data0.ymp.R4 (Output DTN: SN0410T0510404.002) and data0.ymp.R5 (Output DTN: SN0612T0502404.014). The two older thermochemical databases data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) and data0.ymp.R4 (Output DTN: SN0410T0510404.002) were originally qualified or developed in Rev. 00 of this report and this revision also supports that outcome. Qualification frequently involves evaluation and re-evaluation of the original sources of the information used to develop the products. This is particularly true of thermodynamic data, where the relationships among the data may be unusually complex, and new results may affect the interpretation and use of older results.

This section of the report is structured to directly subsume the corresponding elements of the previous revision (Rev. 00). It was noted above that the contents of the Rev. 00 version of Table 4-1 comprise what is Section A of the corresponding table in the present revision. Sections 4.1.1 through 4.1.9 of the previous revision (Rev. 00) are carried over into the present revision with only minor editing and formatting changes. The new material pertinent to data0.ymp.R5 (Output DTN: SN0612T0502404.014) starts in Section 4.1.10 and continues through Section 4.1.19.

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

Table 4-1. Direct Input Data

Description	Source	Status	Where Discussed in Section 4.1
Section A. Input data for data0.ymp.R2 and data0.ymp.R4 (same as Table 4-1 of Rev. 00 of this report)			
Thermodynamic and volume data from data0.ymp.R2	DTN: MO0302SPATHDYN.000 [DIRS 161756]	Qualified in this report [a]	All
Supporting calculations for developing data0.ymp.R2 (includes the SUPCRT92 data files sprons98.dat and speq02.dat)	DTN: MO0302SPATHDYN.001 [DIRS 161886]	Qualified in this report [a]	All
Thermodynamic and volume data from data0.ymp.R0	DTN: MO0009THRMODYN.001 [DIRS 152576]	Qualified data	All
Thermodynamic data for various mineral phases	Robie et al. 1979 [DIRS 107109]	Established Fact	4.1.7
Thermodynamic data and updated stoichiometry for $PuO_2(OH)_2{:}H_2O$	Lemire 2001 [DIRS 159027]	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	Qualified product output	4.1.4
Handbook thermodynamic data	Binnewies and Milke 1999 [DIRS 158955]	Established Fact	4.1.7 4.1.8

Table 4-1. Direct Input Data (Continued)

Description	Source	Status	Where Discussed in Section 4.1
Handbook thermodynamic data	Barin and Platzki 1995 [DIRS 157865]	Established Fact	4.1.7 4.1.8
Handbook solubility data (Mo species)	Martell and Smith 1982 [DIRS 159196]	Established Fact	4.1.2
Volume data for $CaUO_4$	Loopstra and Rietveld 1969 [DIRS 172264]	Qualified for intended use in this report	4.1.9 [b]
Volume data for Cr-ferrihydrite	Towe and Bradley 1967 [DIRS 155334]	Qualified for intended use in this report	4.1.9 [b]
Volume data for $Fe_2(MoO_4)_3$	Johnson et al. 1992 [DIRS 101632]	Qualified for intended use in this report	4.1.9 [b]
Volume data for $Ni_3(PO_4)_2$	Calvo and Faggiani 1975 [DIRS 172265]	Qualified for intended use in this report	4.1.9 [b]
Volume data for $Na_4UO_2(CO_3)_3$	Douglass 1956 [DIRS 172266]	Qualified for intended use in this report	4.1.9
Volume data for uranophane (alpha)	Hemingway 1982 [DIRS 157905]	Qualified for intended use in this Report	4.1.9
Volume data for Na-weeksite	Hemingway 1982 [DIRS 157905]	Qualified for intended use in this report	4.1.9
Np and Pu thermodynamic data	Lemire 2001 [DIRS 159027]	Established Fact	4.1.1 4.1.2 4.1.7
Soddyite log K data	Moll et al. 1996 [DIRS 106349]	Qualified for intended use in this report	4.1.7
Uranophane log K data	Pérez et al. 2000 [DIRS 157910]	Qualified for intended use in this report	4.1.7
Na-Weeksite log K data	Nguyen et al. 1992 [DIRS 100809]	Qualified for intended use in this report	4.1.7
Na-Boltwoodite log K data	Nguyen et al. 1992 [DIRS 100809]	Qualified for intended use in this report	4.1.7
Zeolite thermodynamic and volume data	Chipera et al. 1995 [DIRS 100025], Table 1	Qualified for intended use in this report	4.1.5 4.1.9
Zeolite thermodynamic data (above 100°C)	Viani and Bruton 1992 [DIRS 101407]	Qualified for intended use in this report	4.1.5
Thermodynamic data for calcium silicates, aluminates, and ferrites	Babushkin et al. 1985 [DIRS 116981], Appendix 1	Established Fact	4.1.6
Calcium silicate hydrate data	Fujii and Kondo 1983 [DIRS 144876]	Qualified for intended use in this report	4.1.6

Table 4-1. Direct Input Data (Continued)

Description	Source	Status	Where Discussed in Section 4.1
Cr-ettringite data	Perkins and Palmer 2000 [DIRS 153349]	Qualified for intended use in this report	4.1.6
$CaCl_2$ data	Chase 1998 [DIRS 157874], p. 711	Established Fact	4.1.6
Gehlenite Hydrate	Atkins et al. 1992 [DIRS 100700]	Qualified for intended use in this report	4.1.6
Hydrotalcite	Bennett et al. 1992 [DIRS 116990]	Qualified for intended use in this report	4.1.6
Monocarboaluminate and Hemicarboaluminate	Damidot et al. 1994 [DIRS 144866], Appendix 1	Qualified for intended use in this report	4.1.6
Syngenite (updated)	DTN: SN0302T0510102.002 [DIRS 162572]	Qualified data	4.1.6
Gismondine	Atkins et al. 1993 [DIRS 131758]	Qualified for intended use 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]	Qualified for intended use in this report	4.1.2
Am^{3+} data	Silva et al. 1995 [DIRS 102087], p. 37	Established Fact	4.1.2
β-UO_3 data	Grenthe et al. 1992 [DIRS 101671], Tables III.1 and III.3	Established Fact	4.1.7
Mineral data used for estimation of thermodynamic properties of clays and other silicate minerals	Helgeson et al. 1978 [DIRS 101596]	Qualified for intended use in this report	4.1.4 4.1.6 4.1.9
HF_2^- and HF data	Clark 1966 [DIRS 153163], Table 18-4	Established Fact	4.1.8
HF data	Ellis and Mahon 1977 [DIRS 159230], Table 8.4	Qualified for intended use in this report	4.1.8
R Constant value of 1.9872 cal/mol-K	Weast and Astle 1979 [DIRS 102865], p. F-108	Established Fact	All
Conversion factor: 1 calorie = 4.184 Joules	Weast and Astle 1979 [DIRS 102865]	Established Fact	All
Section A' ("A-prime"). Input data for data0.ymp.R2 and data0.ymp.R4 (Missing from Table 4-1 of Rev. 00 of this report)			
R Constant value of 1.98719 cal/mol-K	Helgeson and Kirkham 1974 [DIRS [DIRS 157904], Table 1, p. 1095	Qualified for intended use in this report	4.1 (Main)
Mineral data used for extrapolation of thermodynamic properties of some uranium silicates, uranium phosphates, and americium phosphates	Helgeson et al. 1978 [DIRS 101596]	Qualified for intended use in this report	4.1 (Main)

Table 4-1. Direct Input Data (Continued)

Description	Source	Status	Where Discussed in Section 4.1
Solids data used for extrapolation of thermodynamic properties of some uranium minerals	Grenthe et al. 1992 [DIRS 101671]	Qualified for intended use in this report	4.1 (Main)
Solids data used for extrapolation of thermodynamic properties of some americium minerals	Silva et al. 1995 [DIRS 102087]	Qualified for intended use in this report	4.1 (Main)
Cr-ferrihydrrite [$Fe_4(OH)_{10}CrO_4$] data	Anthony et al. 2000 [DIRS 153209]	Qualified for intended use in this report	4.1 (Main)
$Fe_2(MoO_4)_3$ data	Titley 1963 [DIRS 153213] [c]	Qualified in this report, but now not recommended [c]	4.1 (Main)
Volume data for $Cu_3(PO_4)_2$	Shoemaker et al. 1977 [DIRS 180793]	Qualified for intended use in this report	4.1 (Main)
Handbook thermodynamic data	Wagman et al. 1982 [DIRS 159216]	Established Fact	4.1 (Main)
Handbook mineral volumetric data	Roberts et al. 1990 [DIRS 107105]	Established Fact	4.1 (Main)
Handbook mineral volumetric data	Gaines et al. 1997 [DIRS 172360]	Established Fact	4.1 (Main)
Mineral volumetric data for various silicates	www.webmineral.com: Barthelmy 2004 [DIRS 172407]; Barthelmy 2004 [DIRS 172408]; Barthelmy 2004 [DIRS 172410]; Barthelmy 2004 [DIRS 172412]; Barthelmy 2004 [DIRS 172413]; Barthelmy 2004 [DIRS 172414]; Barthelmy 2004 [DIRS 172415]	Qualified for intended use in this report	4.1 (Main)
Volumetric data for $CaUO_4$	Pialoux and Touzelin 1998 [DIRS 172359]	Qualified for intended use in this report	4.1 (Main)
Section B. Additional or Revised Inputs for data0.ymp.R5			
Thermodynamic data from data0.ymp.R0	DTN: MO0009THRMODYN.001 [DIRS 152576]	Qualified Data	All
Supporting calculations for developing data0.ymp.R2 (includes the SUPCRT92 data files sprons98.dat and speq02.dat)	DTN: MO0302SPATHDYN.001 [DIRS 161886]	Qualified in this report [a]	All
Handbook thermodynamic data	Barin and Platzki 1995 [DIRS 157865]	Established Fact	4.1.10, 4.1.17
$CaSeO_4{:}2H_2O$and $CaSeO_4(aq)$	Olin et al. 2005 [DIRS 177640]	Established Fact	4.1.11
Kogarkoite data	Gurevich et al. 1999 [DIRS 176845]; Felmy and MacLean 2001 [DIRS 177660]	Qualified for intended use in this report	4.1.12
$SnO_2(am)$, $Sn(OH)_4(aq)$, $Sn(OH)_5^-$, $Sn(OH)_6^-$	Amaya et al. 1997 [DIRS 176843]	Qualified for intended use in this report	4.1.13

Table 4-1. Direct Input Data (Continued)

Description	Source	Status	Where Discussed in Section 4.1
$NiMoO_4$ data	Morishita and Navrotsky 2003 [DIRS 176846]	Qualified for intended use in this report	4.1.14
Th(IV) aqueous and solid species data	Altmaier et al. 2005 [DIRS 173048]	Qualified for intended use in this report	4.1.15
$NiCO_3$ aqueous and solid species	Hummel et al. 2002 [DIRS 161904]	Qualified for intended use in this report	4.1.16
$NiCO_3$ aqueous and solid species	Gamsjäger et al. 2005 [DIRS 178266]	Established Fact	4.1.16
Handbook of key thermodynamic data	Cox et al. 1989 [DIRS 150874]	Established Fact	4.1.17
Handbook aqueous complexation and solubility data	Smith and Martell 1976 [DIRS 127382]	Established Fact	4.1.17
Handbook thermodynamic data	Guillaumont et al. 2003 [DIRS 168382]	Established Fact	4.1.17, 4.1.19
Handbook thermodynamic data	Wagman et al. 1982 [DIRS 159216]	Established Fact	4.1.17
Fluorophosphate aqueous species data	Larson and Su 1994 [DIRS 179363]	Qualified for intended use in this report	4.1.17
Rare earth aqueous phosphate complexes	Spahiu and Bruno 1995 [DIRS 103804]	Qualified for intended use in this report	4.1.17
Thermodynamic data for $PbH_2PO_4^+$	Nriagu 1972 [DIRS 151244]	Qualified for intended use in this report	4.1.17
Thermodynamic data for $UO_2PO_4^-$	Rai et al. 2005 [DIRS 181002]	Qualified for intended use in this report	4.1.17
Densities of Am_2O_3 and AmO_2	Lide 2006 [DIRS 178081]	Established Fact	4.1.17
Fluorapatite data	Westrich and Navrotksy 1981 [DIRS 178567]	Qualified in this report	4.1.17
Fluorapatite data	Egan et al. 1951 [DIRS 178570]	Qualified for intended use in this report	4.1.17
Handbook thermodynamic data	Robie and Hemingway 1995 [DIRS 153683]	Established Fact	4.1.17
Rare earth phosphate compositions	Hezel and Ross 1966 [DIRS 177990]; Hezel and Ross 1967 [DIRS 178227]; Assaaoudi et al. 1997 [DIRS 177936]; Assaaoudi et al. 2000 [DIRS 177992]; Assaaoudi et al. 2001 [DIRS 179602].	Qualified for intended use in this report	4.1.17

Table 4-1. Direct Input Data (Continued)

Description	Source	Status	Where Discussed in Section 4.1
magnesium silicates palygorskite	Birsoy 2002 [DIRS 178220]	Qualified in this report	4.1.18
Amorphous sepiolite	Wollast et al. 1968 [DIRS 162340]	Qualified for intended use in this report	4.1.18
Poorly crystalline antigorite	Gunnarsson et al. 2005 [DIRS 176844]	Qualified for intended use in this report	4.1.18
Handbook thermodynamic data	Grenthe et al. 1992 DIRS 101671]	Established Fact	4.1.19
Uranium Oxy-Hydrates and Silicates (Misc. Sources)	Chen et al. 1999 [DIRS 123270]; Perez et al. 2000 [DIRS 157910]; Möll et al. 1996 [DIRS 106349]; Ilton et al. 2006 [DIRS 178810]; Kubatko et al. 2003 [DIRS 173070]; Burns 1998 [DIRS 127210]; Guillaumont et al. 2003 [DIRS 168382]	Qualified for intended use in this report	4.1.19
Misc. chromium solid and aqueous species	Ball and Nordstrom 1998 [DIRS 163015]	Qualified for intended use in this report	4.1.20
Misc. chromium solid and aqueous species	Rai et al. 1987 [DIRS 163369]	Qualified for intended use in this report	4.1.20
Misc. chromium solid and aqueous species	Rai et al. 2004 [DIRS 179582]	Qualified for intended use in this report	4.1.20
R Constant value of 8.31441 J/mol-K	Weast and Astle 1981 [DIRS 100833], p. F-203	Established Fact	All
Conversion factor: 1 calorie = 4.1840 Joules	Weast and Astle 1981 [DIRS 100833], p. F-304	Established Fact	All

[a] Also qualified in Rev. 00 of this report.

[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 161886]). These data are tabulated in Table 4-21 and qualified in Section 6.6.

[c] This source was used as an input to data0.ymp.R2 (DTN: MO0302SPATHDYN.001 [DIRS 161886]). However, it has more recently been determined that the source data cannot be justified for use on the Yucca Mountain Project (see text addressing "Previously Missing Inputs").

<u>Discussion of Previously Missing Inputs (Listed in Section A' of Table 4-1</u>. Inputs that were not addressed in Rev. 00 of this report are discussed here. Some of these inputs were introduced as sources to data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), while others were introduced as sources to data0.ymp.R4 (Output DTN: SN0410T0510404.002). The former are taken to be qualified by implication by the data qualification activity for data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]).

Several entries appear in Section A' of Table 4-1. The gas constant value of 1.98719 cal/mol-K from Helgeson and Kirkham (1974 [DIRS 157904]) was extensively used in supporting calculations spreadsheets. This may be compared with the handbook value of 1.9872 cal/mol-K from Weast and Astle (1979 [DIRS 102865]). The difference is not significant.

It is noted that mineral data from Helgeson et al. (1978 [DIRS 101596]), Grenthe et al. (1992 [DIRS 101671]), and Silva et al. (1995 [DIRS 102087]) were used in estimating thermodynamic data (primarily standard molar entropies and heat capacity coefficients for some uranium oxy-hydrates and silicates, uranium phosphates, and americium phosphates. These sources should have been noted as inputs for Section 4.1.7. These data will not be listed in Section 4 owing to their number.

Anthony et al. (2000 [DIRS 153209]) performed a study of the solubility of $FeOHCrO_4$. For the reaction $FeOHCrO_4 + H^+ = Fe^{3+} + CrO_4^{2-} + H_2O$ they determined a log K value of −7.1 ± 0.2 (assumed for 25°C). At pH values above 2, they found that $FeOHCrO_4$ is unstable relative to an amorphous product they identified as $Fe_4(OH)_{10}CrO_4$ (here referred to as Cr-ferrihydrite). They determined for the reaction $Fe_4(OH)_{10}CrO_4 + 10\ H^+ = 4\ Fe^{3+} + CrO_4^{2-} + 10\ H_2O$ a log K value of 0.7 ± 0.8. This result is directly incorporated into data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) and is retained in data0.ymp.R4 (Output DTN: SN0410T0510404.002) and data0.ymp.R5 (Output DTN: SN0612T0502404.014). The use of this datum is justified because the methodology (precipitation from solution, measurement of solution chemistry) is sufficient to establish the solubility of an amorphous precipitate. It is understood that this provides a realistic upper bound on dissolved CrO_4^{2-}, as long as pH is known. The data for $FeOHCrO_4$ are not used in any of these databases owing to the limited region of stability in pH space.

Titley (1963 [DIRS 153213]) performed a study of the solubility of ferrimolybdite ($Fe_2(MoO_4)_3$) by adding crushed solid to water and measuring the pH response. Dissolution of ferrimolybite appeared to cause the precipitation of “limonite” (hydrous ferric oxide, but most likely amorphous $Fe(OH)_3$). The reaction $Fe_2(MoO_4)_3 + 6\ H_2O = 2\ Fe(OH)_3 + 3\ HMoO_4^- + 3\ H^+$ was assigned a log K value of −31.1. The database data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) contains the reaction $Fe_2(MoO_4)_3 = 2\ Fe^{3+} + 3\ MoO_4^{2-}$ and a log K value of −38.5200. No documentation concerning the derivation of the database datum from the source could be located. Attempts to reconstruct this derivation all failed to produce the database value. In addition, the methodology used by Titley (1963 [DIRS 153213]) is insufficient to justify the result given in his paper. No measurements were made of dissolved iron or dissolved molybdate, and neither the starting product (“ferrimolybdite”) or the experimentally produced solids were appropriately characterized. It is also noted that this work was severely criticized by Cloke (1964 [DIRS 180863]) in a comment-and-reply discussion in the original journal (the reply is given by Titley 1964 [DIRS 181154]). Titley’s results were also later described as “unreliable” by Lindsay (2001 [DIRS 153210], p. 369). Therefore, it is recommended that this datum not be used. At present, it is found in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), data0.ymp.R4 (Output DTN: SN0410T0510404.002), and data0.ymp.R5 (Output DTN: SN0612T0502404.014). Section 6.8 provides further discussion of this issue.

Shoemaker et al. (1977 [DIRS 180793]) performed an x-ray crystallography study of $Cu_3(PO_4)_2$ and determined a density D_x of 4.503 g/cm^3. The database data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]), a qualified source, gives the molecular weight as 380.581 g/mol. Therefore the molar volume would be 380.581 g/mol ÷ 4.503 g/cm^3 = 84.517 cm^3/mol, which exactly matches the datum in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). The use of the source datum is justified because (a) the methodology employed (x-ray crystallography) is the best method determining volumetric data for a crystalline solid and (b) the data were published in a peer-reviewed journal (*Acta Crystallographica*) which is a respected source for this kind of data.

Spencer (1981 [DIRS 180749]) reviewed the thermodynamic properties of solid species containing the element hafnium. These data were used in constructing the database data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]), which is a qualified data source to this report. Therefore, on technical grounds, Spencer (1981 [DIRS 180749]) is not a direct input to this report, and it is not listed in Table 4-1.

A noteworthy omission in the Rev. 00 of this report was the failure to list among the direct input sources *The NBS Tables of Chemical Thermodynamic Properties, Selected Values for Inorganic and C_1 and C_2 Organic Substances in SI Units* (Wagman et al. 1982 [DIRS 159216]). This handbook source produced by a U.S. government agency qualifies as Established Fact. This work was used as the source of data for dozens of aqueous, solid, and gas species in the data0.ymp.R* series from data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]) to data0.ymp.R4 (Output DTN: SN0410T0510404.002). Technically speaking, many of the affected data come from the declared direct input source data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]). However, others come from subsequent development. In these instances, the source from Wagman et al. (1982 [DIRS 159216]) is a direct input. These instances are locatable in the associated supporting calculations (DTN: MO0302SPATHDYN.001 [DIRS 161886]; Output DTN: SN0410T0510404.001). They are also tagged ("82wag/eva") in the datafiles in the data0.ymp.R* series. With few exceptions, individual data from this source are not listed in Section 4 owing to the large quantity. It is noted here that the "errata" (Wagman et al. 1989 [DIRS 179315]) have not been used as a direct input for any datafile in the data0.ymp.R* series work relevant to Rev. 00 or the present revision of this report. It is used as an indirect input to the present revision of this report (to check that certain recommended data had not changed). It is noted that the *NBS Tables* (Wagman et al. 1982 [DIRS 159216]; Wagman et al. 1989 [DIRS 179315]) is a handbook source from a U.S. government standards agency, and that data taken from it are considered Established Fact. However, it is known to contain some errors (see Section 4.1.17 and Appendices A and B). It also does not meet modern standards of transparency and traceability, in that no sources are given and no information beyond gross generalities exists regarding consideration and selection of data. However, it contains many useful data and remains widely cited in the technical literature. It is thus still used in this report, but alternative sources are now preferred when available.

The remaining entries in Section A' of Table 4-1 all deal with volumetric data (molar volumes and densities). These are used in Section 6.6. A chief source is the *Encyclopedia of Minerals* (Roberts et al. 1990 [DIRS 107105]). Another important source is *Dana's New Mineralogy* (Gaines et al. 1997 [DIRS 172360]). These are handbook sources. Additional data for some silicates are drawn from 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. The specific citations are listed in the entry in Table 4-1. It is noted that many of the volumetric data available from www.webmineral.com are taken from Roberts et al. (1990 [DIRS 107105]). Also used are volumetric data for $CaUO_4$ from Pialoux and Touzelin (1998 [DIRS 172359]). These data are published in a peer-reviewed international journal.

4.1.1 Compilation of Thermodynamic Data for Np and Pu Species

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 (originally, 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 functions 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 $PuO_2(OH)_2{:}H_2O$ 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 $PuO_2(OH)_2{:}2H_2O$ was corrected to $PuO_2(OH)_2{:}H_2O$). This correction is consistent with the usage of Lemire (2001 [DIRS 159027], Section 17.2.2.1) and was made originally in the data0.ymp.R4 database (Output DTN: SN0410T0510404.002).

Table 4-2. Np and Pu Species for Which Thermodynamic Data Were Added, or Existing Data Were Modified, in the data0.ymp.R2 Database

Data0 Species Designation	Change	$\Delta G_f°$ (J/mol)	$\Delta H_f°$ (J/mol)	$S°$ (J/mol-K)	Source
$(NpO_2)_2(OH)_2^{++}$	New	−2,030,400	—	—	1
$(NpO_2)_2CO_3(OH)_3^{-}$	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
$NpO_2(CO_3)_2OH^{----}$	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

Table 4-2. Np and Pu Species for Which Thermodynamic Data Were Added, or Existing Data Were Modified, in the data0.ymp.R2 Database (Continued)

Data0 Species Designation	Change	$\Delta G_f°$ (J/mol)	$\Delta H_f°$ (J/mol)	$S°$ (J/mol-K)	Source
$NpO_2(OH)_2CO_3^{---}$	Removed	—	—	—	—
$NpO_2OH(CO_3)_2^{----}$	Removed	—	—	—	—
$NpO_2(SO_4)_2^{--}$	New	–2,310,775	–2,653,413	121.798	1
NpO_2Cl^{+}	New	–929,440	—	—	1
$NpO_2CO_3^{-}$	Updated	–1,464,000	—	—	1
$NpO_2CO_3(aq)$	New	–1,377,000	—	—	1
$NpO_2F(aq)$	Updated	–1,196,100	—	—	1
NpO_2F^{+}	New	–1,103,600	—	—	1
$NpO_2F_2(aq)$	New	–1,402,400	—	—	1
$NpO_2H_2PO_4^{+}$	New	–1,952,000	—	—	1
$NpO_2HPO_4^{-}$	New	–2,020,600	—	—	1
$NpO_2HPO_4(aq)$	New	–1,927,300	—	—	1
$NpO_2IO_3(aq)$	New	–1,037,000	—	—	1
$NpO_2IO_3^{+}$	New	–929,130	—	—	1
$NpO_2OH(aq)$	Updated	–1,080,405	–1,199,226	25.000	1
NpO_2OH^{+}	New	–1,004,000	-	-	1
$NpO_2SO_4^{-}$	New	–1,654,281	–1,864,321	58.833	1
$NpO_2SO_4(aq)$	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
$Np(SO_4)_2(aq)$	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
$PuCl^{+++}$	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
$PuH_3PO_4^{++++}$	New	–1,641,050	—	—	2
PuI^{++}	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

Table 4-2. Np and Pu Species for Which Thermodynamic Data Were Added, or Existing Data Were Modified, in the data0.ymp.R2 Database (Continued)

Data0 Species Designation	Change	ΔG_f° (J/mol)	ΔH_f° (J/mol)	S° (J/mol-K)	Source
$Pu(CO_3)_5^{(-6)}$	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_2Cl^+	New	−897,566	—	—	2
$PuO_2Cl_2(aq)$	New	−1,021,360	—	—	2
$PuO_2CO_3^-$	Updated	−1,409,771	—	—	2
$PuO_2CO_3(aq)$	Updated	−1,356,466	—	—	2
PuO_2F^+	Updated	−1,069,900	—	—	2
$PuO_2F_2(aq)$	Updated	−1,366,780	—	—	2
$PuO_2OH(aq)$	Updated	−1,034,250	—	—	2
$Pu(OH)_4(aq)$	Removed	—	—	—	—
PuO_2OH^+	Updated	−968,099	−1,079,866	−12.680	2
$PuO_2SO_4(aq)$	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 energy grids for 15 species not previously defined strictly as basis species in data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]). These basis species are Am^{2+}, Am^{3+}, Am^{4+}, AmO_2^+, AmO_2^{2+}, Np^{3+}, Np^{4+}, NpO_2^+, NpO_2^{2+}, Pu^{3+}, Pu^{4+}, PuO_2^+, PuO_2^{2+}, 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 EQ3/6 reaction). The Am data were taken from the work by 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 source from Martell and Smith (1982 [DIRS 159196]) 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 thermodynamic data for the solid phase rutile (TiO_2) are from data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]), which also corresponds to the values reported by Robie et al. (1979 [DIRS 107109]), an Established Fact source.

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

Species	$\Delta G_f°$ (J/mol)	$\Delta H_f°$ (J/mol)	$S°$ (J/ mol-K)	Source
Basis Species				
Am^{3+}	–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	—	39.207	4
Secondary Basis Species (Redox)				
Am^{2+}	–376,780	–354,633	–1.000	1
Am^{4+}	–346,358	–406,000	–406.000	1
AmO_2^+	–739,796	–804,260	–21.000	1
AmO_2^{2+}	–585,801	–650,760	–88.000	1
Np^{3+}	–512,866	–527,184	–193.584	2
Np^{4+}	–491,774	–556,022	–426.390	2
NpO_2^{2+}	–795,939	–860,733	–92.387	2
Pu^{3+}	–578,984	–591,790	–184.510	3
Pu^{4+}	–477,988	–539,895	–414.535	3
PuO_2^{2+}	–762,353	–822,036	–71.246	3
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**	**Reaction**		**Source**
$H_2MoO_4(aq)$	4.00	$H^+ + HMoO_4^- = H_2MoO_4(aq)$		6
$HMoO_4^-$	4.24	$H^+ + MoO_4^{2-} = HMoO_4^-$		6

Sources:
1. Silva et al. 1995 [DIRS 102087], Table III.1, pp. 37 and 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.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) and subsequent data0.ymp.R* series thermochemical databases.

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

Source: 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 $\Delta G_f°$, $S°$, 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 (Equation 4-1) are included.

The $\Delta G_f°$ data for oxides summarized in Table 4-5 were taken from Helgeson et al. (1978 [DIRS 101596], Table 8, pp. 120 and 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 $\Delta G_f°$ and $S°$ values for SiO_2, which was selected for consistency with revision to the Rimstidt paradigm discussed in Section 6.1.5, as documented in *Data Qualification for Thermodynamic Data Used to Support THC Calculations* (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 $\Delta G_f°$ 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	**$\Delta G_f°$ (cal/mol)**	**$V°$ (cm^3/mol)**	**$S°$ (cal/mol-K)**	**a (cal/mol-K)**	**b × 10^3 (cal/mol-K^2)**	**c × 10^{-5} (cal-K/mol)**
Al_2O_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_2O_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
K_2O	–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
Na_2O	–89883.0	25.000	17.935	18.250	4.890	2.890
SiO_2	–204646.0[c]	22.688	9.88[c]	11.220	8.200	2.700

Sources: $\Delta G_f°$ from Helgeson et al. 1978 [DIRS 101596], Table 8, pp. 120 and 121; all other data from Helgeson et al. 1978 [DIRS 101596], Table 2, p. 48.

[a] Heat capacity coefficients a, b, and c defined in Equation 4-1.

[b] Values not used in any calculations.

[c] Value of –204656.0 cal/mol for $\Delta G_f°$, and 9.904 cal/mol-K for $S°$, from *Data Qualification for Thermodynamic Data Used to Support THC Calculations* (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.

The $\Delta G_f°$ 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 to 125) (Table 4-6). However, there are exceptions to this source including several Ca-bearing silicate phases present in *sprons98.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886]) and in data0.ymp.R0 (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 to 56, and Table 8, pp. 120 to 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 listed (Table 4-7). The source of these thermodynamic data is Helgeson et al. (1978 [DIRS 101596], Table 8, pp. 120 to 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° (cm^3/mol)
14A-Amesite	$Mg_4Al_4Si_2O_{10}(OH)_8$	— [a]	205.400
14A-Clinochlore	$Mg_5Al_2Si_3O_{10}(OH)_8$	−1961703	207.110
14A-Daphnite	$Fe_5Al_2Si_3O_{10}(OH)_8$	— [a]	213.420
7A-Amesite	$Mg_2Al_2SiO_5(OH)_4$	— [a]	103.000
7A-Chamosite	$Fe_2Al_2SiO_5(OH)_4$	— [a]	106.200
7A-Clinochlore	$Mg_5Al_2Si_3O_{10}(OH)_8$	−1957101	211.500
7A-Cronstedtite	$Fe^{2+}{}_2Fe^{3+}{}_2SiO_5(OH)_4$	— [a]	110.900
7A-Daphnite	$Fe_5Al_2Si_3O_{10}(OH)_8$	— [a]	221.200
Annite	$KFe_3AlSi_3O_{10}(OH)_2$	−1147156	154.320
Antigorite	$Mg_{48}Si_{34}O_{85}(OH)_{62}$	−15808020	1749.130
Celadonite	$KMgAlSi_4O_{10}(OH)_2$	— [a]	157.100
Chrysotile	$Mg_3Si_2O_5(OH)_4$	−964871	108.500
Greenalite	$Fe_3Si_2O_5(OH)_4$	— [a]	115.000
Hematite	Fe_2O_3	−178155	— [a]
Kaolinite	$Al_2Si_2O_5(OH)_4$	−905614	99.520
Margarite	$CaAl_4Si_2O_{10}(OH)_2$	−1394370[b]	129.400
Minnesotaite	$Fe_3Si_4O_{10}(OH)_2$	— [a]	147.860
Muscovite	$KAl_3Si_3O_{10}(OH)_2$	−1336301	140.710
Paragonite	$NaAl_3Si_3O_{10}(OH)_2$	−1326012	132.530
Phlogopite	$KAlMg_3Si_3O_{10}(OH)_2$	−1396187	149.660
Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$	−1255997	126.600
Quartz	SiO_2	−204646	22.688
Sepiolite	$Mg_4Si_6O_{15}(OH)_2{:}6H_2O$	— [a]	285.600
Talc	$Mg_3Si_4O_{10}(OH)_2$	−1320188	136.250

Sources: Column 3: Helgeson et al. 1978 [DIRS 101596], Table 8, pp. 120 to 125.
Column 4: Helgeson et al. 1978 [DIRS 101596], Table 3, pp. 53 to 56, and Table 8, pp. 120 to 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 energies and enthalpies consistent with updated values of Gibbs energies of Ca^{2+} (Shock and Helgeson 1988 [DIRS 144817]). Margarite properties are included in the SUPCRT92 data file *sprons98.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886]).

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 Coefficients[a]		
Reference Mineral	**Formula**	***S°*** **(cm^3/mol-K)**	***V°*** **(cm^3/mol)**	**a (cal/mol-K)**	**b × 10^3 (cal/mol-K^2)**	**c × 10^{-5} (cal-K/mol)**
7A-Clinochlore	$Mg_5Al_2Si_3O_{10}(OH)_8$	106.500	211.500	162.820	50.620	40.880
14A-Clinochlore	$Mg_5Al_2Si_3O_{10}(OH)_8$	111.200	207.110	166.500	42.100	37.470
Chrysotile	$Mg_3Si_2O_5(OH)_4$	52.900	108.500	75.820	31.600	17.580
Muscovite	$KAl_3Si_3O_{10}(OH)_2$	—[b]	—[b]	97.560	26.380	25.440
Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$	57.200	126.600	79.432	39.214	17.282
Talc	$Mg_3Si_4O_{10}(OH)_2$	62.340	136.250	82.480	41.610	13.340

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

[a] Coefficients defined in Equation 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	$Ca_{0.165}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2$
Ca-Nontronite	$Ca_{0.165}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$
Ca-Saponite	$Ca_{0.165}Mg_3Al_{0.33}Si_{3.67}O_{10}(OH)_2$
Ferroaluminoceladonite	$KFeAlSi_4O_{10}(OH)_2$
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	$H_{0.33}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2$
H-Nontronite	$H_{0.33}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$
H-Saponite	$H_{0.33}Mg_3Al_{0.33}Si_{3.67}O_{10}(OH)_2$
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	$K_{0.33}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2$
K-Nontronite	$K_{0.33}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$
K-Saponite	$K_{0.33}Mg_3Al_{0.33}Si_{3.67}O_{10}(OH)_2$
Low Fe-Mg Smectite	$Na_{0.15}K_{0.2}Ca_{0.02}(Mg_{0.9}Fe^{+++}_{0.16}Fe^{++}_{0.29}Al)(Al_{0.25}Si_{3.75})O_{10}(OH)_2$
Mg-Beidellite	$Mg_{0.165}Al_{2.33}Si_{3.67}O_{10}(OH)_2$
Mg-Montmorillonite	$Mg_{0.495}Al_{1.67}Si_4O_{10}(OH)_2$
Mg-Nontronite	$Mg_{0.165}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$
Mg-Saponite	$Mg_{0.165}Mg_3Al_{0.33}Si_{3.67}O_{10}(OH)_2$
Na-Beidellite	$Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$

Table 4-8. Clay Minerals for Which Molar Volumes Will Be Evaluated in This Report (Continued)

Phase	Formula
Na-Montmorillonite	$Na_{0.33}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2$
Na-Nontronite	$Na_{0.33}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$
Na-Saponite	$Na_{0.33}Mg_3Al_{0.33}Si_{3.67}O_{10}(OH)_2$
Reykjanes Smectite	$Na_{0.33}K_{0.03}Ca_{0.66}(Mg_{1.29}Fe^{+++}_{0.35}Fe^{++}_{0.33}Mn_{0.01}Al_{0.28})(Al_{0.83}Si_{3.17})O_{10}(OH)_2$

Source: 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 ($\Delta G_f°$, $\Delta H_f°$, $S°$, $V°$, 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 $\Delta G_f°$, $\Delta H_f°$, $S°$, $V°$, 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 1,000. 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 to 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 $CaCrO_4(aq) = Ca^{2+} + CrO_4^{2-}$ 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 [DIRS 116981]). In addition, data from Perkins and Palmer (2000 [DIRS 153349]) for Cr-ettringite were added to the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) (this mineral was not included in data0.ymp.R0; DTN: MO0009THRMODYN.001 [DIRS 152576]). These data are listed in Table 4-11. Other sources such as studies by 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

Mineral	Formula	Reaction	Source
Analcime	$Na_{0.96}Al_{0.96}Si_{2.04}O_6:H_2O$	Analcime + $3.84H^+ = 0.96\ Al^{3+} + 0.96\ Na^+ + 2.04SiO_2 + 2.92H_2O$	1
Analcime-dehy	$Na_{0.96}Al_{0.96}Si_{2.04}O_6$	Analcime-dehy + $3.84H^+ = 0.96\ Al^{3+} + 0.96\ Na^+ + 2.04SiO_2 + 1.92H_2O$	1
Clinoptilolite	$Na_{0.954}K_{0.543}Ca_{0.761}Mg_{0.124}Sr_{0.036}Ba_{0.062}$ $Mn_{0.002}Al_{3.45}Fe_{0.017}Si_{14.533}O_{46.922}H_{21.844}$	Clinoptilolite + $13.868\ H^+ = 0.002Mn^{2+} + 0.017Fe^{3+} + 0.036Sr^{2+} + 0.062Ba^{2+} + 0.124Mg^{2+} + 0.543K^+ + 0.761Ca^{2+} + 0.954Na^+ + 3.45Al^{3+} + 14.533SiO_2(aq) + 17.856H_2O$	1
Clinoptilolite-dehy	$Na_{0.954}K_{0.543}Ca_{0.761}Mg_{0.124}Sr_{0.036}Ba_{0.062}$ $Mn_{0.002}Al_{3.45}Fe_{0.017}Si_{14.533}O_{36}$	Clinoptilolite + $13.868\ H^+ = 0.002Mn^{2+} + 0.017Fe^{3+} + 0.036Sr^{2+} + 0.062Ba^{2+} + 0.124Mg^{2+} + 0.543K^+ + 0.761Ca^{2+} + 0.954Na^+ + 3.45Al^{3+} + 14.533SiO_2(aq) + 6.934H_2O$	1
Clinoptilolite-Ca	$Ca_{1.7335}Al_{3.45}Fe_{0.017}Si_{14.533}O_{36}:$ $10.922H_2O$	Clinoptilolite-Ca + $13.868H^+ = 0.017Fe^{3+} + 1.7335Ca^{2+} + 3.45Al^{3+} + 14.533SiO_2(aq) + 17.856H_2O$	1
Clinoptilolite-Cs	$Cs_{3.467}Al_{3.45}Fe_{0.017}Si_{14.533}O_{36}:10.922H_2O$	Clinoptilolite-Cs + $13.868H^+ = 0.017Fe^{3+} + 3.467Cs^+ + 3.45Al^{3+} + 14.533SiO_2(aq) + 17.856H_2O$	1
Clinoptilolite-K	$K_{3.467}Al_{3.45}Fe_{0.017}Si_{14.533}O_{36}:10.922H_2O$	Clinoptilolite-K + $13.868H^+ = 0.017Fe^{3+} + 3.467K^+ + 3.45Al^{3+} + 14.533SiO_2(aq) + 17.856H_2O$	1
Clinoptilolite-NH_4	$(NH_4)_{3.467}Al_{3.45}Fe_{0.017}Si_{14.533}O_{36}:$ $10.922H_2O$	Clinoptilolite-NH_4 + $10.401H^+ = 0.017Fe^{3+} + 3.45Al^{3+} + 3.467NH_3(aq) + 14.533SiO_2(aq) + 17.856H_2O$	1
Clinoptilolite-Na	$Na_{3.467}Al_{3.45}Fe_{0.017}Si_{14.533}O_{36}:10.922H_2O$	Clinoptilolite-Na + $13.868H^+ = 0.017Fe^{3+} + 3.467Na^+ + 3.45Al^{3+} + 14.533SiO_2(aq) + 17.856H_2O$	1
Clinoptilolite-Sr	$Sr_{1.7335}Al_{3.45}Fe_{0.017}Si_{14.533}O_{36}:$ $10.922H_2O$	Clinoptilolite-Sr + $13.868H^+ = 0.017Fe^{3+} + 1.7335Sr^{2+} + 3.45Al^{3+} + 14.533SiO_2(aq) + 17.856H_2O$	1
Heulandite	$Ba_{0.065}Sr_{0.175}Ca_{0.585}K_{0.132}Na_{0.383}Al_{2.165}$ $Si_{6.835}O_{18}:6H_2O$	Heulandite + $8.66H^+ = 0.065Ba^{2+} + 0.132K^+ + 0.175Sr^{2+} + 0.383Na^+ + 0.585Ca^{2+} + 2.165Al^{3+} + 6.835SiO_2(aq) + 10.33H_2O$	1
Mesolite	$Na_{0.676}Ca_{0.657}Al_{1.99}Si_{3.01}O_{10}:2.647H_2O$	Mesolite + $7.96H^+ = 0.657Ca^{2+} + 0.676Na^+ + 1.99Al^{3+} + 3.01SiO_2(aq) + 6.627H_2O$	1
Mordenite	$Ca_{0.2895}Na_{0.361}Al_{0.94}Si_{5.06}O_{12}:3.468H_2O$	Mordenite + $3.76H^+ = 0.2895Ca^{2+} + 0.361Na^+ + 0.94Al^{3+} + 5.06SiO_2(aq) + 5.348H_2O$	1
Natrolite	$Na_2Al_2Si_3O_{10}:2H_2O$	Natrolite + $8H^+ = 2Al^{3+} + 2Na^+ + 3SiO_2(aq) + 6H_2O$	1
Scolecite	$CaAl_2Si_3O_{10}:3H_2O$	Scolecite + $8H^+ = Ca^{2+} + 2Al^{3+} + 3SiO_2(aq) + 7H_2O$	1
Stilbite	$Ca_{1.019}Na_{0.136}K_{0.006}Al_{2.18}Si_{6.82}O_{18}:$ $7.33H_2O$	Stilbite + $8.72H^+ = 0.006K^+ + 0.136Na^+ + 1.019Ca^{2+} + 2.18Al^{3+} + 6.82SiO_2(aq) + 11.69H_2O$	1
Chabazite	$K_{0.6}Na_{0.2}Ca_{1.5}Al_{3.8}Si_{8.2}O_{24}:10H_20$	Chabazite + $15.2H^+ = 0.6K^+ + 0.2Na^+ + 1.5Ca^{2+} +3.8Al^{3+} + 8.2SiO_2(aq) + 17.6H_2O$	2
Erionite	$K_{1.5}Na_{0.9}Ca_{0.9}Al_{4.2}Si_{13.8}O_{36}:13.0H_2O$	Erionite + $16.8H^+ = 1.5K^+ + 0.9Na^+ + 0.9Ca^{2+} + 4.2Al^{3+} + 13.8SiO_2 + 21.4H_2O$	2
Laumontite	$K_{0.2}Na_{0.2}Ca_{1.8}Al_4Si_8O_{24}:8H_2O$	Laumontite + $16H^+ = 0.2K^+ + 0.2Na^+ + 1.8Ca^{2+} + 4Al^{3+} + 8SiO_2 + 16H_2O$	2
Phillipsite	$K_{0.7}Na_{0.7}Ca_{1.1}Al_{3.6}Si_{12.4}O_{32}:12.6H_2O$	Phillipsite + $14.4H^+ = 0.7K^+ + 0.7Na^+ + 1.1Ca^{2+} + 3.6Al^{3+} + 12.4SiO_2 + 19.8H_2O$	2
Stellerite	$Ca_{2.0}Al_{4.0}Si_{14}O_{36}:14H_2O$	Stellerite + $16H^+ = 2.0Ca^{2+} + 4.0Al^{3+} + 14SiO_2 + 22H_2O$	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 Capacity Equation[a]							
Phase	**$\Delta G_f°$ (J/mol)**	**$\Delta H_f°$ (J/mol)**	**S° (J/mol-K)**	**V° (cm^3/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	—	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	—	—	—	—	1
Clinoptilolite-dehy[b]	−16,227,300	−17,210,200	893.31	—	−4.781E+02	6.910E+00	−9.031E-03	3.902E-06	—	—	—	1
Clinoptilolite-Ca[b]	−19,027,912	—	1,462.73	632.050	2.990E+01	6.348E+00	4.616E-03	—	1.696E+05	—	—	1
Clinoptilolite-Cs[b]	−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	—	1,509.29	632.050	7.951E+01	6.403E+00	4.616E-03	—	6.628E+05	—	—	1
Clinoptilolite-NH_4[b]	−18,364,701	—	—	—	—	—	—	—	—	—	—	1
Clinoptilolite-Na[b]	−18,978,314	—	1,507.16	632.050	7.762E+01	6.365E+00	4.616E-03	—	—	—	—	1
Clinoptilolite-Sr[b]	−19,047,857	—	1,480.22	632.050	3.476E+01	6.348E+00	4.616E-03	—	−1.173E+04	—	—	1
Heulandite	−9,779,100	−10,594,600	767.18	—	7.456E+02	6.513E-01	—	—	−1.411E+07	—	—	1
Mesolite	−5,513,200	−5,947,154	363.00	—	1.908E+02	6.793E-01	—	—	−1.633E+06	—	—	1
Mordenite	−6,228,100	−6,736,700	486.54	—	5.281E+02	1.625E-01	—	—	−8.197E+06	—	—	1
Natrolite	−5,316,600	−5,718,600	359.73	—	3.020E+02	3.769E-01	—	—	−4.898E+06	—	—	1
Scolecite	−5,597,900	−6,049,000	367.42	—	1.352E+02	8.305E-01	—	—	—	—	—	1
Stilbite	−10,114,100	−11,005,700	805.54	—	4.430E+02	6.173E-01	3.609E-03	-5.247E-06	—	—	—	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	—	—	—	−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.
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 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 ($3CaO\cdot Al_2O_3\cdot CaCO_3\cdot 10H_2O$) and hemicarboaluminate ($3CaO\cdot Al_2O_3\cdot 0.5CaCO_3\cdot 0.5Ca(OH)_2 \cdot 10.5H_2O$) 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 25°C 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 Capacity Coefficients[a]		
Solid Phase	**Formula**	**ΔG°_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_3S)[b]	$3CaO\cdot SiO_2$	-665470	-700430	40.3	49.85	8.62	-10.15
($C_{12}A_7$)[b]	$12CaO\cdot 7Al_2O_3$	-4410000	-4640160	249.7	301.96	65.5	-55.3
(C_2AH_8)[b]	$2CaO\cdot Al_2O_3\cdot 8H_2O$	-1151540	-1299200	106.4	68.38	153.45	-
(C_3A)[b]	$3CaO\cdot Al_2O_3$	-808400	-851000	49.1	62.28	4.58	-12.1
(C_4AF)[b]	$4CaO\cdot Al_2O_3\cdot Fe_2O_3$	-1144000	-1214200	78	89.49	17.4	-
(C_4AH_{13})[b]	$4CaO\cdot Al_2O_3\cdot 13H_2O$	-1756170	-1988000	171.6	109.6	242.19	-
(C_4AH_{19})[b]	$4CaO\cdot Al_2O3\cdot 19H_2O$	-2096330	-2411000	228	122.36	394	-
(CA)[b]	$CaO\cdot Al_2O_3$	-527700	-556180	27.3	36.01	9.98	-7.96
(CA_2)[b]	$CaO\cdot 2Al_2O_3$	-907100	-957060	42.5	66.09	5.48	-17.8
(CAH_{10})[b]	$CaO\cdot Al_2O_3\cdot 10H_2O$	-1103700	-1271400	116.1	67.85	182.46	-
Afwillite	$Ca_3Si_2O_4(OH)_6$	-1052950	-1143200	74.6	81.54	45.1	-14.7
Bellite (C_2S)[b]	$2CaO\cdot \beta SiO_2$	-524190	-551740	30.5	36.25	8.83	-7.24

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

					Heat Capacity Coefficients[a]		
Solid Phase	**Formula**	**ΔG°_f (cal/mol)**	**ΔH°_f (cal/mol)**	**S°_{298} (cal/mol)**	**a (cal/mol-K)**	**$b \times 10^3$ (cal/mol-K^2)**	**$c \times 10^{-5}$ (cal-K/mol)**
Ettringite	$3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$	-3634260	-4201320	417.6	208	740.93	-
Cr-ettringite	$Ca_6Al_2\,(CrO_4)_3(OH)_{12}{\cdot}26H_2O$	-3616395.8	-4141969.4	-	-	-	-
Foshagite	$Ca_4Si_3O_9(OH)_2{\cdot}0.5H_2O$	-1347900	-1439900	78.95	87.95	3.95	-13.5
Friedl Salt	$CaCl_2{\cdot}3CaO{\cdot}16H_2O$	-	-1833000	-	-	-	-
Gyrolite	$Ca_2Si_3O_7(OH)_2{\cdot}1.5H_2O$	-1085650	-1175850	64	79.47	36.3	-17.6
Hillebrandite	$Ca_2SiO_3(OH)_2{\cdot}0.17H_2O$	-592900	-637150	38.4	41.4	22.4	-7.4
Hydrogarnet	$3CaO{\cdot}Al_2O_3{\cdot}6H_2O$	-1198400	-1326000	96.7	68.91	127.17	-
Monosulphate	$3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O$	-1859140	-2096440	178.6	113.71	246.84	-
Okenite	$CaSi_2O_4(OH)_2{\cdot}H_2O$	-686400	-750300	40.9	44.81	18.7	-10.4
Plombierite	$5CaO{\cdot}6SiO_2{\cdot}10.5H_2O$	-2647300	-2911250	193.15	132.2	270	-
Riversideite	$Ca_5H_2(SiO_3)_6{\cdot}2H_2O$	-2215000	-2375000	122.65	143.55	74.7	-20.8
Tobermorite	$5CaO{\cdot}6SiO_2{\cdot}5.5H_2O$	-2361450	-2556300	146.15	110.6	189	-
Xonotlite	$Ca_6[Si_6O_{17}](OH)_2$	-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].

[a] Heat capacity coefficients refer to those in Equation 4-1.

[b] For the cement phases in parentheses, the letter “A” stands for Al_2O_3, “C” for CaO, “S” for SiO_2, and “H” for H_2O components in the cement. This is customary notation for cement phase composition.

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

ΔH°_f	ΔG°_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 H_2O

Phase	**a (cal/mol-K)**[a]	**$b \times 10^3$ (cal/mol-K^2)**[a]	**$c \times 10^{-5}$ (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_2O(s)	7.11	8.24E+00	0	(2)
H_2O(zw)[b]	11.4	0	0	(2)

Sources: (1) Binnewies and Milke 1999 [DIRS 158955].
(2) Helgeson et al. 1978 [DIRS 101596], Table 2, p. 48.

[a] Heat capacity coefficients refer to those in Equation 4-1.

[b] H_2O(zw) refers to “zeolitic water” after Helgeson et al. (1978 [DIRS 101596], Table 2, p. 48).

Table 4-14. Heat Capacity Data for $CaCl_2$(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 Energy of Formation for Na- and Ca-Gismondine Minerals

Mineral	Formula	$\Delta G°_f$ kcal/mol	Source
Gismondine-Na	$Na_2Al_2Si_2O_8{\cdot}4H_2O$	−1179.16	Atkins et al. 1993 [DIRS 131758]
Gismondine-Ca	$CaAl_2Si_2O_8{\cdot}4H_2O$	−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 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 analogue 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-UO_3 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 the work by 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 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-UO_3 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]), and works by 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 qualification of data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), 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 the study by Lemire (2001 [DIRS 159027]) were not scaled for the factor of 1,000 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 for use in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) using thermodynamic data from these two tables in the study by 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.

Table 4-17. Thermodynamic Data Used as Inputs to Calculate log K Grids for Various Solids for data0.ymp.R2

					Heat Capacity Coefficients[a]			
Phase	**ΔG°_f (J/mol)**	**ΔH°_f (J/mol)**	**S° (J/mol-K)**	**V° (cm^3/mol)**	**a (J/mol-K)**	**b × 10^3 (J/mol-K^2)**	**c × 10^{-5} (J-K/mol)**[b]	**Source**
$(NH_4)_4NpO_2(CO_3)_3$	-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 $Ca_2Fe_2O_5$	-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 ($CaSO_4 \cdot 2H_2O$)	-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
$Ca_3Al_2O_6$	-3,411,786	-3,587,800	205.90	88.94	260.580	19.1600	-5.030	2, 3
$CaAl_2O_4$	-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_3O_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
$CoCr_2O_4$	-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
$CoFe_2O_4$	-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 Various Solids for data0.ymp.R2 (Continued)

					Heat Capacity Coefficients[a]			
Phase	**$\Delta G°_f$ (J/mol)**	**$\Delta H°_f$ (J/mol)**	**S° (J/mol-K)**	**V° (cm^3/mol)**	**a (J/mol-K)**	**b × 10^3 (J/mol-K^2)**	**c × 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_2O_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
CrI_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
$Cs_2NaPuCl_6$	-2,143,496	-2,294,200	440.00	-	-	-	-	1
Cs_2NpBr_6	-1,620,121,	-1,682,300	469.00	-	-	-	-	1
Cs_2NpCl_6	-1,833,039	-1,976,200	410.00	-	-	-	-	1
Cs_2PuBr_6	-1,634,326	-1,697,400	470.00	-	-	-	-	1
Cs_2PuCl_6	-1,838,243	-1,982,000	412.00	-	-	-	-	1
Cs_3PuCl_6	-2,208,045	-2,364,415	454.92	-	256.600	34.60	-7.40	1
$CsPu_2Cl_7$	-2,235,119	-2,399,380	424.00	-	237.800	51.50	1.55	1
Ferrite-Cu $CuFe_2O_4$	-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 $FeAl_2O_4$	-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 $FeCr_2O_4$	-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

Table 4-17. Thermodynamic Data Used as Inputs to Calculate log K Grids for Various Solids for data0.ymp.R2 (Continued)

					Heat Capacity Coefficients[a]			
Phase	**$\Delta G°_f$ (J/mol)**	**$\Delta H°_f$ (J/mol)**	**S° (J/mol-K)**	**V° (cm^3/mol)**	**a (J/mol-K)**	**b × 10^3 (J/mol-K^2)**	**c × 10^{-5} (J-K/mol)[b]**	**Source**
Ferrite-Ni	-972,893	-1,084,500	125.90	-	152.670	77.8200	-1.490	2, 3
$FeSO_4$	-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_2O_3	-881,114	-959,000	110.50	-	102.800	35.6700	-1.280	2, 3
Tephroite Mn_2SiO_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_2Cl_2	-623,302	-725,800	120.50	-	127.400	7.0300	-1.940	2, 3
Na_2CO_3	-1,048,005	-1,130,800	138.80	41.86	11.000	244.0500	2.450	2, 3
Na_2CrO_4	-1,234,795	-1,334,300	176.60	59.48	101.040	140.0000	0.000	2, 3
Na_3NpF_8	-3,521,239	-3,714,000	369.00	-	270.000	56.60	-13.00	1
$Na_3NpO_2(CO_3)_2$	-2,833,333	-	-	-	-	-	-	1
Nahcolite $NaHCO_3$	-852,851	-936,300	101.20	38.62	45.310	143.1000	0.000	2, 3
$NaNpO_2CO_3$	-1,764,157	-	-	-	-	-	-	1
$NaNpO_2CO_3 \cdot 3.5H_2O$	-2,591,287	-	-	-	-	-	-	1
Heazlewoodite Ni_3S_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
$NiCr_2O_4$	-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 $NiFe_2O_4$	-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 Various Solids for data0.ymp.R2 (Continued)

					Heat Capacity Coefficients[a]			
Phase	ΔG°_f (J/mol)	ΔH°_f (J/mol)	S° (J/mol-K)	V° (cm^3/mol)	a (J/mol-K)	b × 10^3 (J/mol-K^2)	c × 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
NpI_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(am, hyd)	-957,321	-	-	-	-	-	-	1
$NpO_2(NO_3)_2{\cdot}6H_2O$	-2,428,069	-3,008,241	516.31	-	-	-	-	1
NpO_2CO_3	-1,407	-	-	-	-	-	-	1
NpO_2OH(am)	-1,118,078	-1,222,900	71.95	-	-	-	-	1
NpO_2OH(am, aged)	-1,114,652	-1,222,900	60.46	-	-	-	-	1
$NpO_3{\cdot}H_2O$	-1,238,997	-	-	-	-	-	-	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_2C_3	-156,614	-149,400	150.00	-	-[c]	-	-	1
Pu_2O_3	-1,580,375	-1,656,000	163.00	-	169.446	-79.98	-25.459	1
Pu_3C_2	-123,477	-113,000	210.00	-	120.670	46.86	1.9456	1
PuAs	-241,413	-240,000	94.30	-	-	-	-	1

Table 4-17. Thermodynamic Data Used as Inputs to Calculate log K Grids for Various Solids for data0.ymp.R2 (Continued)

					Heat Capacity Coefficients[a]			
Phase	**ΔG°_f (J/mol)**	**ΔH°_f (J/mol)**	**S° (J/mol-K)**	**V° (cm^3/mol)**	**a (J/mol-K)**	**b × 10^3 (J/mol-K^2)**	**c × 10^{-5} (J-K/mol)[b]**	**Source**
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
$PuCl_3 \cdot 6H_2O$	-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
PuI_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
$PuO_2(OH)_2 \cdot 2H_2O$[d]	-	-	-	-	-	-	-	[d]
$PuO_2(OH)_2 \cdot H_2O$	-1,442,379	-1,632,808	190.00	-	-	-	-	1
PuO_2CO_3	-1,371,307	-	-	-	-	-	-	1
PuO_2OH(am)	-1,061,246	-1,159,793	97.00	-	-	-	-	1
PuOBr	-838,354	-870,000	127.00	-	73.700	17.00	-5.15	1
PuOCl	-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_2O_3	-1,433,824	-1,520,900	77.30	-	53.070	163.4400	-	2, 3
Ti_3O_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

Table 4-17. Thermodynamic Data Used as Inputs to Calculate log K Grids for Various Solids for data0.ymp.R2 (Continued)

					Heat Capacity Coefficients[a]			
Phase	**ΔG°_f (J/mol)**	**ΔH°_f (J/mol)**	**S° (J/mol-K)**	**V° (cm^3/mol)**	**a (J/mol-K)**	**b × 10^3 (J/mol-K^2)**	**c × 10^{-5} (J-K/mol)[b]**	**Source**
$TiBr_3$	-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
TiI_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
UCl_3	-794,530	861,900	159.00	-	87.780	31.1300	0.490	2, 3
UCl_4	-929,927	-1,018,800	197.20	-	113.810	35.8600	-0.0330	2, 3
UCl_5	-950,061	-1,041,500	246.90	-	140.040	35.4400	-0.540	2, 3
UCl_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_2Br_2	-1,066,612	-1,137,600	169.50	-	117.950	17.5300	-1.070	2, 3
UO_2Cl_2	-1,146,105	-1,243,500	150.60	-	115.230	18.2000	-1.140	2, 3
UO_2F_2	-1,551,873	-1,651,400	135.60	-	122.880	8.6200	-1.990	2, 3
UO_2SO_4	-1,683,212	-1,845,100	154.80	-	112.470	108.7800	-	2, 3
UO_3(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

Table 4-17. Thermodynamic Data Used as Inputs to Calculate log K Grids for Various Solids for data0.ymp.R2 (Continued)

					Heat Capacity Coefficients[a]			
Phase	**$\Delta G°_f$ (J/mol)**	**$\Delta H°_f$ (J/mol)**	**S° (J/mol-K)**	**V° (cm^3/mol)**	**a (J/mol-K)**	**b × 10^3 (J/mol-K^2)**	**c × 10^{-5} (J-K/mol)[b]**	**Source**
$UOBr_3$	-901,429	-954,000	205.00	-	130.540	20.5000	-1.380	2, 3
UOCl	-899,108	-833,900	102.50	-	75.810	14.3500	-0.830	2, 3
$UOCl_2$	-996,062	-1,067,500	138.30	-	98.950	14.6400	-0.740	2, 3
$UOCl_3$	-1,068,773	-1,151,600	170.70	-	122.590	20.9200	-1.190	2, 3
WCl_2(s)	-219,977	-260,300	130.50	-	71.280	21.9000	-	2, 3
WCl_4(s)	-359,433	-443,100	198.30	-	113.450	54.6000	-	2, 3
WCl_5(s)	-401,783	-513,000	217.60	-	124.450	109.9200	-0.140	2, 3
WCl_6(s)	-455,511	-593,700	238.50	-	125.560	167.2300	-	2, 3
WO_2Cl_2(s)	-702,770	-780,300	200.80	-	79.510	94.1100	-0.290	2, 3
$WOCl_4$(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. *sprons98.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886]).
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 Equation 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) does not give Maier-Kelley parameters for this species.

[d] Phase $PuO_2(OH)_2{\cdot}2H_2O$ was an incorrect representation of $PuO_2(OH)_2{\cdot}H_2O$ in data0.ymp.R2. The data reported in data0.ymp.R2 are shown in this table for the correct phase $PuO_2(OH)_2{\cdot}H_2O$, consistent with Lemire (2001 [DIRS 159027]).

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 this thermochemical database 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 discussed in Section 6.1.2 of this report.

Data for the dissociation of HF(aq) (Equation 4-2) to 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 (250ºC to 300ºC) (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 15ºC to 200ºC were also used to complement the data from Ellis and Mahon (1977 [DIRS 159230]).

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

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 HF_2^{-} association reaction were taken from data in Clark (1966 [DIRS 153163], Table 18-4, p. 407) (Table 4-19).

$$HF(aq) + F^{-} = HF_2^{-} \qquad \text{(Eq. 4-3)}$$

Table 4-19. Log K Data for the HF_2^{-} Association Reaction Delineated by Equation 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 Equation 4-3 and not the reaction listed in the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), which is $HF_2^{-} = H^{+} + 2\ F^{-}$. 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.

Table 4-20. Thermodynamic Data Input for Gas Phases Updated or Added to data0.ymp.R2

				Heat Capacity Coefficients[a]			
Gas Species	**ΔG_f° (J/mol)**	**ΔH_f° (J/mol)**	**S° (J/mol-K)**	**a (J/mol-K)**	**$b \times 10^3$ (J/mol-K^2)**	**$c \times 10^{-5}$ (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
H_2O(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
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
$TiCl_3$(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

Table 4-20. Thermodynamic Data Input for Gas Phases Updated or Added to data0.ymp.R2 (Continued)

				Heat Capacity Coefficients[a]			
Gas Species	$\Delta G_f°$ (J/mol)	$\Delta H_f°$ (J/mol)	$S°$ (J/mol-K)	a (J/mol-K)	b × 10^3 (J/mol-K^2)	c × 10^{-5} (J-K/mol)[b]	Source
$WOCl_4$(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].
2. Binnewies and Milke 1999 [DIRS 158955].

[a] Heat capacity coefficients a, b, and c defined in Equation 4-1.

[b] 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.

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 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. Some Molar Volumes of Mineral/Solid Phases from data0.ymp.R2

Reference Mineral	Chemical Formula	V° (cm^3/mol)
7A-Amesite	$Mg_2Al_2SiO_5(OH)_4$	103
$CaUO_4$	$CaUO_4$	45.926
Chabazite	$K_{0.6}Na_{0.2}Ca_{1.55}Al_{3.8}Si_{8.2}O_{24}\cdot 10H_2O$	499.4
Cr-ferrihydrite	$Fe_4(CrO_4)(OH)_{10}$	129
7A-Cronstedtite	$Fe_2Fe_2SiO_5(OH)_4$	110.9
Erionite	$K_{1.5}Na_{0.9}Ca_{0.9}Al_{4.2}Si_{13.8}O_{36}\cdot 13H_2O$	672
$Fe_2(MoO_4)_3$	$Fe_2(MoO_4)_3$	131.85
Laumontite	$K_{0.2}Na_{0.2}Ca_{1.8}Al_4Si_{8.0}O_{24}\cdot 8H_2O$	406.40
$Ni_3(PO_4)_2$	$Ni_3(PO_4)_2$	83.36
$Na_4UO_2(CO_3)_3$	$Na_4UO_2(CO_3)_3$	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	$Ca_{2.0}Al_{4.0}Si_{14.0}O_{36}\cdot 14H_2O$	665.50
Uranophane (alpha)	$Ca(UO_2SiO_3OH)_2\cdot 5H_2O$	251.336
Weeksite-Na	$Na_2(UO_2)_2Si_5O_{13}\cdot 3H_2O$	246.04

Source: As listed in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]).
True original sources are not given here. Included in Output DTN: SN0410T0510404.001 (spreadsheet: *Volume_Q_DS_11-01-04.xls*).

4.1.10 Update of Data for CrO_3Cl^-, Eskolaite (Cr_2O_3), and CrO_2 in data0.ymp.R5

The data0 reactions for the aqueous species CrO_3Cl^- and the solids Cr_2O_3 (eskolaite) and CrO_2 are changed for data0.ymp.R5 (Output DTN: SN0612T0502404.014). This is being done mainly to preserve (insofar as this is possible) the oxidation state of the Cr in the reaction.

In data0.ymp.R4 (Output DTN: SN0410T0510404.002), the associated reaction for CrO_3Cl^- is:

CrO3Cl- + 3 H+ = Cr+++ + 0.72 O2(g) + Cl- + 1.5 H2O

(Note: EQ3/6 species names are used here). This is changed to:

CrO3Cl- + H2O = CrO4- + 2 H+ + Cl- (Eq. 4-4)

This preserves Cr(VI) on both sides of the reaction (Cr+++ is Cr(III)). The input data are those used for the original reaction and processed in DTN: MO0302SPATHDYN.001 [DIRS 161886] (folder: *\CD\Spreadsheets\Aqueous*, spreadsheet: *AqueousSpecies_j_sea.xls*). The requisite data were originally included in data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]) and are thus qualified. They will not be repeated here, as they have been used previously in the construction of data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]) and data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]).

In data0.ymp.R4 (Output DTN: SN0410T0510404.002), the reaction for Cr_2O_3 (eskolaite) is:

Eskolaite + 1.5 O2(g) + 2 H2O = 2 CrO4-- + 4 H+ (Eq. 4-5)

This is changed to:

Eskolaite + 6 H+ = 2 Cr+++ + 3 H20 (Eq. 4-6)

This preserves Cr(III) on both sides of the reaction. The input data used are changed from a combination of data from Barin and Platzki (1995 [DIRS 157865]) and Binnewies and Milke (1999 [DIRS 158955]) to just data from Barin and Platzki (1995 [DIRS 157865]). These data are Established Fact. The changes concern the input for heat capacity coefficients. For data0.ymp.R5 (Output DTN: SN0612T0502404.014), the tabulated heat capacities over the 298.15 to 600 K range from Barin and Platzki (1995 [DIRS 157865], p. 573) are used in Section 6.7.1 to obtain a log K for the new reaction (Equation 4-6) on the EQ3/6 temperature grid (0-25-60-100-150-200-250-300°C). These data are given in Table 4-22.

Table 4-22. Heat Capacity (Cp) Data for Cr_2O_3 (Eskolaite)

Temp K	***Cp*** **(Joule/mol-K)**
298.15	120.361
300	121.922
400	112.675
500	117.701
600	120.580

Source: Barin and Platzki 1995 [DIRS 157865], p. 573 (Established Fact)

In data0.ymp.R4 (Output DTN: SN0410T0510404.002), the reaction for *CrO2* is:

$$CrO2 = Cr{+}{+} + HCrO4- \qquad \text{(Eq. 4-7)}$$

Here Cr(IV) on the left is converted to a combination of Cr(II) and Cr(VI). This is changed to:

$$CrO2 + 3H+ = Cr{+}{+}{+} + 1.5\ H2O + 0.25\ O2(g) \qquad \text{(Eq. 4-8)}$$

Here Cr(IV) is converted to Cr(III). There is no aqueous basis species for Cr(IV) in any of the data files in the data0.ymp.R* series, nor one for Cr(V), so this is as close as possible. The input data used are changed from those of Dellien et al. (1976 [DIRS 151392]) to those of Barin and Platzki (1995 [DIRS 157865]), which are Established Fact. The former set of data only permitted a log K to be obtained for 25°C; the latter permits such data to be obtained up to 300°C. For data0.ymp.R5 (Output DTN: SN0612T0502404.014), the new inputs from Barin and Platzki (1995 [DIRS 157865], p. 570) are given in Tables 4-23 and 4-24. These are used in Section 6.7.1 to develop the log K data for the CrO_2 dissolution reaction (Equation 4-8) on the EQ3/6 temperature grid.

Table 4-23. Standard Thermodynamic Data (298.15 K) for CrO_2

ΔG_f^o **(Joule/mol)**	ΔH_f^o **(Joule/mol)**	S^o **(Joule/mol-K)**
-544900.0	-597894.0	51.045

Source: Barin and Platzki 1995 [DIRS 157865], p. 570 (Established Fact).

Table 4-24. Heat Capacity (Cp) Data for CrO_2

Temp K	***Cp*** **(Joule/mol-K)**
298.15	99.673
300	99.705
400	101.420
500	103.136
600	104.851

Source: Barin and Platzki 1995 [DIRS 157865], p. 573 (Established Fact).

4.1.11 Addition of $CaSeO_4{:}2H_2O$ and $CaSeO_4(aq)$ to data0.ymp.R5

Two new Se(VI) or selenate species to be added to data0.ymp.R5 (Output DTN: SN0612T0502404.014) are the solid $CaSeO_4{:}2H_2O$ and the aqueous complex $CaSeO_4(aq)$. The requisite input data (Table 4-25) are taken from the recent OECD/NEA volume on selenium (Olin et al. 2005 [DIRS 177640]). These data are Established Fact. The log K value for the $CaSeO_4(aq)$ dissociation reaction is for 25°C only and will be used directly. The input data for the $CaSeO_4{:}2H_2O$ solid is the reported solubility. The log K at 25°C only for the associated dissolution reaction is computed in Section 6.7.2 using EQ3/6 to iteratively fit the solubility value, under the condition of satisfying the input data for $CaSeO_4(aq)$. The thermochemical database data0.ymp.R4 (Output DTN: SN0410T0510404.002) contains a solid named *CaSeO4*. These data are only for 25°C. This species was removed, as the data it is based on almost certainly represent a mischaracterization of the solid, which is probably $CaSeO_4{:}2H_2O$. In reality, both $CaSeO_4$ and $CaSeO_4{:}2H_2O$ probably exist. By analogy with the corresponding S(VI) solids, anhydrite ($CaSO_4$) and gypsum ($CaSO_4{\cdot}2H_2O$), one would expect $CaSeO_4{:}2H_2O$ to be the stable form at 25°C. At higher temperature, $CaSeO_4$ should eventually become the stable form. However, there appear to be no unambiguous data for this solid.

Table 4-25. Thermodynamic Data for the Added Sn(IV) Solid and Aqueous Species in data0.ymp.R5

Phase	Reaction	log K	Solubility (molality)	Source
$CaSeO_4{:}2H_2O$	$CaSeO_4{:}2H_2O = Ca^{2+} + SeO_4^{2-} + 2H_2O$	-	0.3557	Olin et al. 2005 [DIRS 177640], Table A-16, p. 454
$CaSeO_4(aq)$	$CaSeO_4(aq) = Ca^{2+} + SeO_4^{2-}$	2.0	-	Olin et al. 2005, [DIRS 177640], Table III-2, p. 60

Source: Olin et al. 2005 [DIRS 177640] (Established Fact).

4.1.12 Addition of Kogarkoite (Na_3SO_4F) to data0.ymp.R5

The phase kogarkoite (Na_3SO_4F) is a potential product of evaporation of seepage waters and will be added to data0.ymp.R5 (Output DTN: SN0612T0502404.014). Thermodynamic properties for this phase have been determined by Gurevich et al. (1999 [DIRS 176845]). This source provides standard entropy (Table 4-26) and tabulated heat capacity data (Table 4-27). These data are justified for the intended use in this report because they are published in an international peer-reviewed journal (*Geochemistry International*) and were obtained by a standard accepted methodology, calorimetry. The Gibbs energy of formation is also needed. Felmy and MacLean (2001 [DIRS 177660]) conducted a solubility evaluation of this solid. These authors provide coefficients for computing the dimensionless standard chemical potential (μ^o/RT, where μ^o is the chemical potential, R is the gas constant, and T is the absolute temperature). These data are given in Table 4-28 and are justified for the intended use in this analysis report because (1) the first author has an international reputation for quality development of thermodynamic data, (2) the report the data are taken from addresses the development of a similar type of thermodynamic database for applications modeling (in this case, addressing other kinds of radioactive waste), and (3) the report bases the thermodynamic data on solubility data, using an accepted approach (Pitzer's equations) for modeling concentrated solutions. The chemical potential is converted to the Gibbs energy of formation of the solid (see Section 6.7.3). The data in Tables 4-26, 4-27, and 4-28 are used in Section 6.7.3 to calculate the log K grid for kogarkoite dissolution ($Na_3SO_4F = 3\ Na^+ + SO_4^{2-} + F^-$).

Table 4-26. Standard Thermodynamic Data (298.15 K) for Kogarkoite

ΔG_f^o (Joule/mol)	**ΔH_f^o (Joule/mol)**	**S^o (Joule/mol-K)**
-	-	205.9

Source: Gurevich et al. 1999 [DIRS 176845].

Table 4-27. Heat Capacity (Cp) Data for Kogarkoite

Temp K	***Cp* (Joule/mol-K)**
198.70	146.75
203.07	148.82
207.38	150.62
211.75	151.70
213.25	152.63
217.03	154.31
217.72	154.50
220.55	154.69
224.97	156.19
229.40	157.53
233.96	159.89
238.51	161.39
243.05	162.66
247.58	163.81
252.10	165.09
256.66	166.75
261.22	168.25
263.45	169.05
265.80	169.35
267.79	170.37
267.88	169.85
267.98	171.00
269.57	170.71
270.36	171.01
272.54	171.77
274.21	173.06
277.10	173.54
278.89	173.74
279.53	173.29
281.68	174.94
283.54	175.22
284.11	175.13

Table 4-27. Heat capacity (Cp) data for Kogarkoite (Continued)

Temp K	*Cp* (Joule/mol-K)
284.19	176.56
286.24	175.59
288.67	176.96
290.86	177.30
293.28	178.62
295.52	178.79
297.92	179.75
300.16	179.97
302.58	181.71

Source: Gurevich et al. 1999 [DIRS 176845].

Table 4-28. Coefficients for Computing μ^o/RT for Kogarkoite

a_1 (dimensionless)	a_2 (dimensionless)
-735.77286	0.0044
μ^o/RT (T) = $a_1 + a_2T$, where T is the absolute temperature.	

Source: Felmy and MacLean 2001 [DIRS 177660], Table 3.

4.1.13 Addition of SnO_2(am) and Some Sn(IV) Aqueous Species to data0.ymp.R5

The solid SnO_2(am) along with two new Sn(IV) aqueous complexes is added to data0.ymp.R5 (Output DTN: SN0612T0502404.014). Most of thermodynamic data for solids and aqueous tin species in the previous databases in the data0.ymp.R* series going back to data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]) are from the comprehensive work of Jackson and Helgeson (1985 [DIRS 151264]). This work encompassed the comprehensive retrieval of thermodynamic data for a large suite of Sn(IV) aqueous species as well as the Sn(IV) solid cassiterite. Amaya et al. (1997 [DIRS 176843]) present a more recent study on the thermodynamic and solubility properties of Sn(IV) species. The selected thermodynamic data for Sn(IV) solids and aqueous species selected to represent SnO_2(am) solubility in data0.ymp.R5 (Output DTN: SN0612T0502404.014) are in part from Jackson and Helgeson (1985 [DIRS 151264]), with additional data taken from Amaya et al. (1997 [DIRS 176843]), and one new datum determined in this report (Section 6.7.4) based on the solubility data of Amaya et al. (1997 [DIRS 176843]). All of the new data here are restricted to 25°C. For the present usage, the data from Jackson and Helgeson (1985 [DIRS 151264]) are deemed to have been taken from data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]) and are thus qualified data. The data from Amaya et al. (1997 [DIRS 176843]) are justified for the intended use in this report on the grounds that (1) they were published in a peer-reviewed internationally recognized symposium volume (*Basis for Nuclear Waste Management XX)* and (2) the data are based on a standard, accepted approach (e.g., Baes and Mesmer 1986 [DIRS 100702]) for obtaining thermodynamic data from solubility measurements.

Amaya et al. (1997 [DIRS 176843]) studied the solubility of crystalline and amorphous SnO_2 in 0.1 molal $NaClO_4$ at 25°C. In order to model the solubility behavior of Sn(IV) at pH > 8, two aqueous species need to be added to the database: $Sn(OH)_5^-$ and $Sn(OH)_6^{2-}$. Table V of the study by Amaya et al. (1997 [DIRS 176843]) provides solubility constants (log K values, for 25°C only) for the following reactions:

$$SnO_2(am) + 2\ H_2O = Sn(OH)_4(aq) \qquad \text{(Eq. 4-9)}$$

$$Sn(OH)_4(aq) + H_2O = Sn(OH)_5^- + H^+ \qquad \text{(Eq. 4-10)}$$

$$Sn(OH)_4(aq) + 2H_2O = Sn(OH)_6^{2-} + 2\ H^+ \qquad \text{(Eq. 4-11)}$$

The log K values at 25°C for the above reactions given by Amaya et al. (1997 [DIRS 176843]) are listed in Table 4-29. The log K value of -17.31 for the reaction involving $Sn(OH)_6^{2-}$ is inconsistent with solubility data for SnO_2(am) also given by Amaya et al. (1997 [DIRS 176843]). These data are summarized below in Table 4-30 and are used in Section 6.7.4 to support the argument that the value of -17.31 probably represents a typographical error and that the correct value should be -18.31.

Table 4-29. Thermodynamic Data for the Added Sn(IV) Solid and Aqueous Species in data0.ymp.R5

Species	Reaction	log K
SnO_2(am)	$SnO_2(am) + 2H_2O = Sn(OH)_4(aq)$	-7.46
$Sn(OH)_5^-$	$Sn(OH)_4(aq) + H_2O = Sn(OH)_5^- + H^+$	-7.65
$Sn(OH)_6^{2-}$	$Sn(OH)_4(aq) + 2H_2O = Sn(OH)_6^{2-} + 2H^+$	-17.31[a]

Source: Amaya et al. 1997 [DIRS 176843], Table V, p. 757.

[a] This appears to be a typographical error; the correct value is likely to be -18.31 (see text).

Table 4-30. Solubility Data from Amaya et al. (1997 [DIRS 176843]) for SnO_2(am) (Oversaturation)

pH	Sn (Molar)
2.1	1.8E-08
2.1	1.5E-08
3.0	7.9E-08
3.0	8.4E-08
3.8	6.2E-08
3.8	2.9E-08
5.7	5.6E-08
6.2	5.9E-08
7.8	9.1E-08
7.7	4.7E-07
10.0	4.1E-06
10.1	6.1E-06
5.8	4.7E-08
6.0	4.1E-08
8.1	1.50E-07
8.1	1.36E-07
10.4	6.90E-05

Table 4-30. Solubility Data from Amaya et al. (1997 [DIRS 176843]) for SnO_2(am) (Oversaturation) (Continued)

pH	Sn (Molar)
10.3	3.60E-05
10.2	2.35E-05
10.2	2.52E-05
10.3	5.10E-05
10.3	3.18E-05
11.3	3.71E-03
11.3	1.94E-03
11.5	1.02E-02
11.7	9.1E-03
11.8	1.02E-02
11.9	1.1E-02

Source: Amaya et al. 1997 [DIRS 176843], Table III, p. 755.

As noted above, the data from Jackson and Helgeson (1985 [DIRS 151264]) for various Sn chemical species are adopted in data0.ymp.R4 (Output DTN: SN0410T0510404.002). A minor transcription error in the standard Gibbs energy of formation of $Sn(OH)_4$(aq) was noted in the spreadsheet calculation of the corresponding log K grid for this species (Output DTN: SN0410T0510404.001, folder: *\CD\Spreadsheets\Aqueous*, spreadsheet: *AqueousSpecies_j_SRA_1.xls*); here the value -227310 cal/mol should have been -227360 cal/mol). This error is corrected in Section 6.7.4. The corrected data for $Sn(OH)_4$(aq) is used to transform the data in Table 4-29 to correspond to reactions that are written in terms of Sn^{4+}, not $Sn(OH)_4$(aq). This is necessary because Sn^{4+} is used as the basis species for Sn(IV) in the data0.ymp.R* databases.

4.1.14 Addition of $NiMoO_4$ to data0.ymp.R5

The solid $NiMoO_4$ is a potential product of the long-term corrosion of stainless steels containing nickel and molybdenum; it is added to data0.ymp.R5 (Output DTN: SN0612T0502404.014). Thermodynamic properties for this phase have been determined by Morishita and Navrotsky (2003 [DIRS 176846]). This source provides standard Gibbs energy of formation, enthalpy of formation, and entropy (Table 4-31) and heat capacity coefficients (Table 4-32) for this phase. These data are justified for the intended use in this report on the grounds that (1) the data are published in an internationally recognized peer-reviewed journal (*Journal of the American Ceramic Society*), (2) the second author is one of the world's leading calorimetrists, and (3) the data are based on a standard, generally accepted method, calorimetry. No other source of data is known for this phase in the temperature range of interest (25°C to 300°C). The data in Tables 4-31 and 4-32 is used in Section 6.7.5 to calculate the log K for $NiMoO_4$ dissolution ($NiMoO_4 = Ni^{2+} + MoO_4^{2-}$) on the EQ3/6 temperature grid.

Table 4-31. Standard Thermodynamic Data (298.15 K) for $NiMoO_4$

ΔG_f^o (kJ/mol)	ΔH_f^o (kJ/mol)	S^o (Joule/mol-K)
-921.2	-1026.0	118.0

Source: Morishita and Navrotsky 2003 [DIRS 176846], Tables VI and VII.

Table 4-32. Heat Capacity (Cp) Coefficient Data for $NiMoO_4$

Cp **Coefficient**	**Value**
a	-681.58
b	5.866×10^{-1}
c	-16.838×10^{-5}
d	13.991×10^{3}
e	-15.788×10^{6}
$\mathbf{Cp = a + bT + cT^2 + dT^{-0.5} + eT^{-2}}$	

Source: Morishita and Navrotsky 2003 [DIRS 176846], Table V.

NOTE: Units are consistent with Cp in Joule/mol-K

4.1.15 Additions and Changes for Thorium Species in data0.ymp.R5

Altmaier et al. (2005 [DIRS 173048]) determined the solubility of amorphous Th(IV) hydrated thorium oxide in carbonate solutions using phase separation to remove colloidal particles. From their own data for -log [H+] > ~ 4 and from other data reported by Östhols et al. (1994 [DIRS 150834]) and Neck et al. (2002 [DIRS 168259]) for -log [H+] < ~ 4, Altmaier et al. (2005 [DIRS 173048]) were able to determine the identities of species that contribute significantly to Th(IV) solubility and the values of the equilibrium constants for the formation reactions of those species. The essential data for their model are summarized in Table 4-33; these data are restricted to 25°C. These data are justified for the intended use in this report on the grounds that (1) they were published in a peer-reviewed internationally recognized symposium volume (*Radiochimica Acta)* and (2) the data were based on a standard, accepted approach (e.g., Baes and Mesmer (1986 [DIRS 100702]) for obtaining thermodynamic data from solubility measurements. These data will be used to make changes in data0.ymp.R5 (Output DTN: SN0612T0502404.014). Some species will be added, data for a few will be updated, and some species will be deleted. The reactions in Table 4-33 will be converted to hydrolysis reactions (written in terms of H^+ and H_2O, instead of OH^-) in Section 6.7.6.

Table 4-33. Equilibrium Constants (298.15 K) for Some Thorium Species

Species	**Chemical Reaction**	**log K**
$Th(OH)^{3+}$	$Th^{4+} + OH^- = Th(OH)^{3+}$	11.8 ± 0.2
$Th(OH)_2^{2+}$	$Th^{4+} + 2\ OH^- = Th(OH)_2^{2+}$	21.4 ± 0.2
$Th(OH)_3^{+}$	$Th^{4+} + 3\ OH^- = Th(OH)_3^{+}$	30.6 ± 1.0
$Th(OH)_4(aq)$	$Th^{4+} + 4\ OH^- = Th(OH)_4(aq)$	39.0 ± 0.5
$Th(OH)(CO_3)_4^{(5-)}$	$Th^{4+} + OH^- + 4\ CO_3^{2-} = Th(OH)(CO_3)_4^{(5-)}$	35.8 ± 0.3
$Th(OH)_2CO_3(aq)$	$Th^{4+} + 2\ OH^- + CO_3^{2-} = Th(OH)_2CO_3(aq)$	30.7 ± 0.4
$Th(OH)_2(CO_3)_2^{2-}$	$Th^{4+} + 2\ OH^- + 2\ CO_3^{2-} = Th(OH)_2(CO_3)_2^{2-}$	37.0 ± 0.4
$Th(OH)_3CO_3^-$	$Th^{4+} + 3\ OH^- + CO_3^{2-} = Th(OH)_3CO_3^-$	38.5 ± 0.6
$Th(OH)_4CO_3^{2-}$	$Th^{4+} + 4\ OH^- + CO_3^{2-} = Th(OH)_4CO_3^{2-}$	40.6 ± 0.5
$ThO_2.2H_2O(am)$	$ThO_2{\cdot}2H_2O(am) = Th^{4+} + 4OH^-$	-47.8 ± 0.3

Source: Altmaier et al. 2005 [DIRS 173048]. Aqueous species data are from Table 1, p. 87. The data are labeled in that table as "log β^{o}_{1yz}". The data for the solid are from section 3.3.1, p. 87. The source also refers to the solid as $Th(OH)_4(am)$.

Consistent with the inputs in Table 4-33, the species *ThO2(am)* and *Th(CO3)5(6-)* that appear in data0.ymp.R4 (Output DTN: SN0410T0510404.002) are deleted in data0.ymp.R5 (Output DTN: SN0612T0502404.014). *ThO2(am)* is an anhydrous representation of the "new" solid *ThO2.2H2O(am)*. The formula of the new representation is merely more explicit regarding water content. The species *Th(CO3)5(6-)* is not consistent with the newly added thorium hydroxy-carbonate species (see Altmaier et al. 2005 [DIRS 173048], Section 3.3.3, pp. 88 and 89).

The species *Th(OH)3+*, *Th(OH)4(aq)*, and *Th(OH)3(CO3)-* already appear in data0.ymp.R4 (Output DTN: SN0410T0510404.002). The data for these species are changed by the inputs given in Table 4-33, as converted to hydrolysis reaction format in Section 6.7.6.

4.1.16 Update of Data for $NiCO_3$ Aqueous and Solid Species in data0.ymp.R5

The thermochemical data for $NiCO_3$ (nickel carbonate) are corrected in data0.ymp.R5 (Output DTN: SN0612T0502404.014). Data are added for two new species, $NiCO_3(aq)$ and $NiCO_3{:}5.5H_2O$. The need to correct the data for the solid $NiCO_3$ (nickel carbonate) was identified in CR 7542 (Section 1.2). The data0.ymp.R4 (Output DTN: SN0410T0510404.002) data (for 25°C only) leads to a very high nickel solubility that is realized in the in-package chemistry calculations (BSC 2005 [DIRS 174583]). A recent NAGRA/PSI 2002 report (Hummel et al 2002 [DIRS 161904]) states how previous databases commonly contained this incorrect solubility product. The species $NiCO_3(aq)$ and $NiCO_3{:}5.5H_2O$ are not included in data0.ymp.R4 (Output DTN: SN0410T0510404.002). The data for $NiCO_3(aq)$ are also taken from Hummel et al (2002 [DIRS 161904]). The data for $NiCO_3{:}5.5H_2O$ are taken from the OECD/NEA volume *Chemical Thermodynamics of Nickel* (Gamsjäger et al. 2005 [DIRS 178266]).

The inputs for these changes are given in Table 4-34. The data from Hummel et al (2002 [DIRS 161904]) are justified for the intended use in this analysis report on the grounds that they are taken from a careful review that was conducted to create a thermodynamic database (*Nagra/PSI Chemical Thermodynamic Data Base*) to support applications for the Swiss nuclear waste disposal program. This database is similar in function and scope to those in the data0.ymp.R* series. The data from Gamsjäger et al. (2005 [DIRS 178266]) are Established Fact. In Section 6.7.7, the reactions are written in terms of HCO_3^- (the usual EQ3/6 basis species) instead of CO_3^{2-} or $CO_2(g)$. Also, the results for the anhydrous $NiCO_3$ solid are compared with the recent recommendations of Gamsjäger et al. (2005 [DIRS 178266]).

Table 4-34. Thermodynamic Data (25°C) for $NiCO_3$ Aqueous and Solid Species in data0.ymp.R5

Species	Reaction	log K	Source
$NiCO_3$	$NiCO_3 = Ni^{2+} + CO_3^{2-}$	-11.2	Hummel et al 2002 [DIRS 161904], p. 230
$NiCO_3(aq)$	$NiCO_3(aq) = Ni^{2+} + CO_3^{2-}$	-4.0	Hummel et al 2002 [DIRS 161904], Table B1
$NiCO_3{:}5.5H_2O$	$NiCO_3{:}5.5H_2O + 2H^+ = Ni^{2+} + CO_2(g) + 6.5H_2O$	10.63	Gamsjäger et al. 2005 [DIRS 178266], Table III-2, p. 50. Established Fact.

Sources: as noted above.

4.1.17 Phosphate Corrections for data0.ymp.R5

Thermochemical databases are highly dependent upon so-called key thermodynamic data. These are data for key species, which include both solid and aqueous species, generally of fairly simple composition (e.g., pure metals, elemental gases, oxides, and simple aqueous species). Two major sources of such key data are *CODATA Key Values for Thermodynamics* (Cox et al. 1989 [DIRS 150874]) and *The NBS Tables of Chemical Thermodynamic Properties, Selected Values for Inorganic and C_1 and C_2 Organic Substances in SI Units* (Wagman et al. 1982 [DIRS 159216]; Wagman et al. 1989 [DIRS 179315]). Both sources are considered Established Fact.

As was noted in Section 1.1 of this analysis report, the thermochemical databases in the data0.ymp.R* series are founded on a core of data from two sources. One is the *SUPCRT92* database based on the work of H.C. Helgeson and various students and coworkers (e.g., Helgeson et al. 1978 [DIRS 101596]; Shock and Helgeson 1988 [DIRS 144817]; Shock et al. 1997 [DIRS 150770]). This database is represented in the SUPCRT92 data file *sprons98.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886]). The other source is the *Chemical Thermodynamics* series sponsored by OECD/NEA (e.g., Grenthe et al. 1992 [DIRS 101671]; Silva et al. 1995 [DIRS 102087]). The OECD/NEA sponsored data (themselves considered Established Fact) are based on explicit acceptance of the *CODATA* key values (Cox et al. 1989 [DIRS 150874]). The *SUPCRT92* data (based on an internal reference in *sprons98.dat* to Wagman et al. 1982 [DIRS 159216]) appear to be tied to the *NBS Tables* (Wagman et al. 1982 [DIRS 159216]; Wagman et al. 1989 [DIRS 179315]).

It might be assumed that "standard thermodynamic values" are well-known constants that are effectively the same regardless of source, as long as the source is reputable. Appendix A of this analysis report compares the *CODATA* (Cox et al. 1989 [DIRS 150874]) key values for aqueous ions with the corresponding values from both the *NBS Tables* (Wagman et al. 1982 [DIRS 159216]; Wagman et al. 1989 [DIRS 179315]) and the *SUPCRT92* database as represented by *sprons.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886]) or *speq02.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886]). While numerous differences were found (see Appendix A), substantial discrepancies were found in the case of the two key phosphate ions HPO_4^{2-} and $H_2PO_4^-$. These results are summarized in Table 4-35.

Table 4-35. Standard Thermodyanmic Functions (298.15 K) for HPO_4^{2-} and $H_2PO_4^-$: *CODATA* vs. *NBS Tables* vs. *SUPCRT92*

CODATA[a]			
Species	**ΔG_f^o J/mol**	**ΔH_f^o J/mol**	**S^o J/mol-K**
HPO_4^{2-}	-1095985.0[b]	-1299000.0	-33.500
$H_2PO_4^-$	-1137152.0[b]	-1302600.0	92.500
NBS Tables[c]			
Species	**ΔG_f^o J/mol**	**ΔH_f^o J/mol**	**S^o J/mol-K**
HPO_4^{2-}	-1089150.0	-1292140.0	-33.500
$H_2PO_4^-$	-1130280.0	-1296290.0	90.400

Table 4-35. Standard Thermodyanmic Functions (298.15 K) for HPO_4^{2-} and $H_2PO_4^-$: *CODATA* vs. *NBS Tables* vs. *SUPCRT92* (Continued)

SUPCRT92 [d]			
Species	**ΔG_f^o J/mol**	**ΔH_f^o J/mol**	**S^o J/mol-K**
HPO_4^{2-}	-1089137.0	-1292082.0	-33.5
$H_2PO_4^-$	-1130265.8	-1296286.9	90.4

[a] Cox et al. 1989 [DIRS 150874] (Established Fact).

[b] *CODATA* does not give values of Gibbs energies. The values shown are those given by Grenthe et al. (1992 [DIRS 101671], p. 70) To the nearest J/mol, these values are consistent with those from Table A-1 of Appendix A, which are calculated from the CODATA enthalpies and entropies of formation, along with the CODATA values for the entropies of the elements in their reference states.

[c] Wagman et al. 1982 [DIRS 159216]; Wagman et al. 1989 [DIRS 179315] (Established Fact).

[d] As represented by sprons.dat (DTN: MO0302SPATHDYN.001 [DIRS 161886]) or speq02.dat *cd\SUPCRT_runs_TJW\SUPCRT_datafiles* of DTN: MO0302SPATHDYN.001 [DIRS 161886]]. Values from those files are in calorie units. Values shown here in Joule units are from Table A-4 of Appendix A.

NOTE: This is a table of direct inputs. The data that will be rejected by this analysis report will be necessary in generating corrections to data for other phosphate species.

The values from *SUPCRT92* and the *NBS Tables* are quite close. In Section 6.7.8 it will be shown that such differences are likely due to unit conversion and (in instances excessive) rounding. However, the *CODATA* numbers for Gibbs energies of formation differ from the *SUPCRT92* and *NBS Tables* numbers by ~ 6800-6900 J/mol for both HPO_4^{2-} and $H_2PO_4^-$. The entropy values are very nearly the same for all three sources. The discrepancy in the Gibbs energies is essentially associated with a discrepancy in the enthalpies of formation. The differences in the corresponding thermodynamic properties of the species HPO_4^{2-} and $H_2PO_4^-$ are essentially negligible. Thus, any of the above source sets would produce very nearly the same results for the reaction $H_2PO_4^- = H^+ + HPO_4^{2-}$.

The discrepancy noted above was documented in CR 6731. As noted in Appendix A, a substantial error in calculated thermodynamic properties can result if data consistent with the *CODATA* key values are combined with data consistent with the *NBS Tables* or *SUPCRT92*. The error in an equilibrium constant (log K) calculated in such a manner is about 1.2 units (per phosphate appearing in a reaction). The thermochemical databases in the data0.ymp.R* series from R0 (Steinborn et al. 2003 [DIRS 161956]) through R4 adopted data for solids and aqueous complexes of many radionuclide elements from the then-available OECD/NEA recommendations (e.g., Grenthe et al. 1992 [DIRS 101671]). A number of those solids and aqueous complexes involve phosphate (e.g., for uranium, from Grenthe et al. 1992 [DIRS 101671], p. 44-45: $(UO_2)_3(PO_4)_2$(cr), $UO_2HPO_4.4H_2O$(cr), $U(HPO_4)_2.4H_2O$(cr), UO_2HPO_4(aq), $UO_2H_2PO_4^+$, and $UO_2(HPO_4)_2$(aq)). Because those data0.ymp.R* databases used the *SUPCRT92* data for the species HPO_4^{2-} (the P[V] basis species for those databases), there appears to be a thermodynamic inconsistency in the way the data were treated.

Before the issue of inconsistencies can be addressed, it must be determined which set of values (*CODATA* or *NBS Tables*/*SUPCRT92*) should be used for the thermochemical properties of HPO_4^{2-} (and $H_2PO_4^-$). Appendix B presents an evaluation that favors the *CODATA* values. The *SUPCRT92* values trace to the *NBS Tables* (Wagman et al. 1982 [DIRS 159216]; Wagman et al. 1989 [DIRS 179315]). The *NBS Tables* give only recommended values; they include no information as to sources or alternative values considered. Nevertheless, it appears (see Appendix B) that the *NBS Tables* values are based on a now-discredited study (Holmes (1962 [DIRS 178649]) of the enthalpy of formation of the solid P_4O_{10}(cr) (this solid is the acid anhydride of phosphoric acid). Therefore, the *CODATA* values (Cox et al. 1989 [DIRS 150874]) adopted by OECD/NEA (e.g., Grenthe et al. 1992 [DIRS 101671]) are used in making corrections that are incorporated into data0.ymp.R5 (Output DTN: SN0612T0502404.014).

In making these corrections, the original input data for most of the phosphate solids and aqueous species in data0.ymp.R4 (Output DTN: SN0410T0510404.002) remain the same. Depending on the nature of these inputs (See Section 4.7.8), the resulting log K data put in data0.ymp.R5 (Output DTN: SN0612T0502404.014) may be changed or remain unchanged by the shift to the *CODATA* key values (Cox et al. 1989 [DIRS 150874]). The outcome depends on whether or not they are already consistent with those key values. While most of the original inputs for phosphate species are unchanged, the inputs are changed for some solids and aqueous species in order (a) to make use of improved data and/or (b) to use data whose origin (and consistency with the *CODATA* key values or the lack thereof) is better documented.

In addition to HPO_4^{2-} and $H_2PO_4^-$, there are other simple phosphate species (PO_4^{3-} and H_3PO_4(aq)). There are also the closely related diphosphate (or pyrophosphate) species that form in equilibrium with the simple phosphate species. Table 4-36 contains the recommendations of OCED/NEA (e.g., Grenthe et al. 1992 [DIRS 101671]) for both simple phosphate and diphosphate species. These data are Established Fact. They are used as direct inputs to data0.ymp.R5 (Output DTN: SN0612T0502404.014).

Table 4-36. Standard Thermodyanmic Functions (298.15 K) for Phosphate and Diphosphate Species (OECD/NEA Recommendations)

Species	ΔG_f^o kJ/mol	ΔH_f^o kJ/mol	S^o J/mol-K
PO_4^{3-}	-1025.491	-1284.400	-220.970
$P_2O_7^{4-}$	-1935.503	-	-
HPO_4^{2-}	-1095.985	-1299.000	-33.500
$H_2PO_4^-$	-1137.152	-1302.600	92.500
H_3PO_4(aq)	-1149.367	-1294.120	161.912
$HP_2O_7^{3-}$	-1989.158	-	-
$H_2P_2O_7^{2-}$	-2027.117	-	-
$H_3P_2O_7^-$	-2039.960	-	-
$H_4P_2O_7$(aq)	-2045.668	-2280.210	274.919

Source: Grenthe et al. 1992 [DIRS 101671]. Established Fact.

Note that enthalpy of formation and entropy data are not included for four of the five diphosphate species. To fill in the missing data, entropy data from the *NBS Tables* (Wagman et al. 1982 [DIRS 159216]) are used. These data are summarized in Table 4-37. They are Established Fact. It is noted that the value for $H_4P_2O_7$(aq)in Table 4-37 is close to but distinct from that in Table 4-36. In Section 6.7.8, the values for the diphosphate species in Table 4-37 other than $H_4P_2O_7$(aq) are corrected for consistency with the data in Table 4-36 by assuming that the NBS data yield the correct entropies of reaction for reactions linking the other species with $H_4P_2O_7$(aq) (e.g., $P_2O_7^{4-} + 4\ H^+ = H_4P_2O_7$(aq); $HP_2O_7^{3-} + 3\ H^+ = H_4P_2O_7$(aq)). This correction is possible because $H_4P_2O_7$(aq) appears in both datasets. The assumption regarding the entropies of reaction should be safe as entropies of reaction were almost certainly used to derive the entropies for all but one of the diphosphate species appearing in Table 4.37. Consequently, the data listed in Table 4-37 from this handbook source are appropriate to use in this analysis report in conjunction with the stated correction. Corresponding enthalpies of formation data are then calculated from the Gibbs energies of formation and the entropies. For that purpose, data for the entropies of the relevant chemical elements in their standard reference states (Table 4-38) are employed. These data are Established Fact. In Section 6.7.8, data will be calculated for reactions involving these diphosphate species that use $H_2P_2O_7^{2-}$ as an auxiliary basis species. Only the species $H_2P_2O_7^{2-}$ among these is linked to HPO_4^{2-} (the strict basis species for P[V] in data0.ymp.R5, Output DTN: SN0612T0502404.014).

Table 4-37. Standard Entropies (298.15 K) for Diphosphate Species from the *NBS Tables*

Species	**S° J/mol-K**
$P_2O_7^{4-}$	-117.000
$HP_2O_7^{3-}$	46.000
$H_2P_2O_7^{2-}$	163.000
$H_3P_2O_7^{-}$	213.000
$H_4P_2O_7$(aq)	268.000

Source: Wagman et al. 1982 [DIRS 159216], p. 2-74 to 2-75. Established Fact.

NOTE: These data will be converted in Section 6.7.8 to be consistent with the data in Table 4-36.

Table 4-38. Standard Entropies (298.15 K) of Relevant Chemical Elements in Their Standard Reference States (*CODATA* Recommendations)

Species	**S° J/mol-K**
H_2	130.680
P(cr, white)	41.090
O_2	205.152

Source: Cox et al. 1989 [DIRS 150874], Table 5. Established Fact.

Other related sets of species of geochemical significance are the mono- and difluorophosphate species. The thermochemical properties of these have been studied by Larson and Su (1994 [DIRS 179362]) and Larson and Su (1994 [DIRS 179363]). Table 39 gives the input data that are used. These data are justified for the intended use in this analysis report because (1) they were published in an internationally-recognized peer-reviewed journal (*Journal of Chemical and Engineering Data*) and (2) they were obtained using a very sensitive method (phosphorus-31 nuclear magnetic resonance) to study the equilibria of relevant reactions (including equilibrium with simple phosphate). The data were processed by assuming key data for simple phosphate taken from the *NBS Tables* (Wagman et al. 1982 [DIRS 159216]). In Section 6.7.8, these data are converted to consistency with the CODATA recommendations (Cox et al. 1989 [DIRS 150874]) for key phosphate data.

Table 4-39. Standard Thermodyanmic Functions (298.15 K) for Mono- and Di-fluorophosphate Species

Species	ΔG_f^o kJ/mol	ΔH_f^o kJ/mol	S^o J/mol-K
$H_2PO_3F(aq)$	-1186.7	-1307.3	176
HPO_3F^-	-1183.6	-1324.2	109
PO_3F^{2-}	-1156.2	-1332.1	-9
$HPO_2F_2(aq)$	-1224.2	-1327.6	168
$PO_2F_2^-$	-1222.5	-1335.4	136

Source: Larson and Su 1994 [DIRS 179363], Table 4, p. 38.

NOTE: These data are consistent with the NBS Tables and will be converted in Section 6.7.8 to be consistent with the data in Table 4-36.

Better data are available for the species $KP_2O_7^{3-}$, $MgP_2O_7^{2-}$, and $NiP_2O_7^{2-}$. These newer data permit temperature extrapolation (the previous data were restricted to 25°C). Data for the first two complexes are taken from Smith and Martell (1976 [DIRS 127382]) and are given in Table 4-40. This source is a handbook and the data are Established Fact. Additional data (from the same source) for reactions involving the first two protonations of $P_2O_7^{4-}$ are included and are used in Section 6.7.8 to rewrite the reactions involving these complexes to be in terms of $H_2P_2O_7^{2-}$. That species is used in data0.ymp.R5 (Output DTN: SN0612T0502404.014) as an auxiliary basis species.

Table 4-40. Equilibrium Constants and Entropies of Reaction (298.15 K) for Some Diphosphate Complexes

Species	Chemical Reaction	log K	ΔS_r^o (Joule/mol-K)
$KP_2O_7^{3-}$	$K^+ + P_2O_7^{4-} = KP_2O_7^{3-}$	2.10	15
$MgP_2O_7^{2-}$	$Mg^{2+} + P_2O_7^{4-} = MgP_2O_7^{2-}$	7.20	43
$HP_2O_7^{3-}$	$H^+ + P_2O_7^{4-} = HP_2O_7^{3-}$	9.40	42
$H_2P_2O_7^{2-}$	$H^+ + HP_2O_7^{3-} = H_2P_2O_7^{2-}$	6.70	30

Source: Smith and Martell 1976 [DIRS 127382], p. 59 (Established Fact).

Table 4-41 gives the data that are used for $NiP_2O_7^{2-}$. These data are also Established Fact. These data are presumed tied to the phosphate key data in the NBS Tables In Section 6.7.8, these data are converted to consistency with the CODATA recommendations (Cox et al. 1989 [DIRS 150874]) for key phosphate data.

Spahiu and Bruno (1995 [DIRS 103804]) are the source of most of the rare earth element (REE) data taken from data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]), which itself is a direct input to the other databases in the data0.ymp.R* series. The data for aqueous REE phosphate complexes are recalculated for inclusion in data0.ymp.R5 (Output DTN: SN0612T0502404.014). For that purpose, data from Spahiu and Bruno (1995 [DIRS 103804]) are used as a direct input. This source remains the best evaluation of data in the subject area. It contains an evaluation that was created for the Swedish high-level nuclear waste disposal program. The authors are also contributors to the development of the OECD/NEA series of volumes on thermodynamic data for radioactive waste disposal.

Table 4-41. Standard Thermodynamic Data (298.15 K) for $NiP_2O_7^{2-}$

ΔG_f^o (kJ/mol)	S^o (Joule/mol-K)
-2004.4	-173.6

Source: Wagman et al. 1982 [DIRS 159216], p. 2-168 (Established Fact).

Improved data were found for the species $UO_2PO_4^-$. Rai et al. (2005 [DIRS 181002]) recently conducted a solubility study of the solid $(UO_2)_3(PO_4)_2$:$4H_2O$. They found that the previously used data (from Grenthe et al. 1992 [DIRS 101671], reiterated by Guillaumont et al. 2003 [DIRS 168382]) lead to significant overpredictions of solubility above about pH 6-7. This is clearly illustrated in their Figures 5 and 6 (Rai et al. 2005 [DIRS 181002]). The authors recommend a bounding value for the dimensionless Gibbs energy given in Table 4-41a. The use of this datum is justified because (a) the study was published in a peer-reviewed journal (*Journal of Solution Chemistry*), (b) the study uses a standard accepted method, solubility determination, (c) the study is very detailed and methodical, and (d), two of the co-authors (Rai and Felmy) have excellent reputations in the technical community for this kind of work.

Table 4-41a. Standard Thermodynamic Data (298.15 K) for $UO_2PO_4^-$

$\Delta G_f^o/RT$ [(a)](dimensionless)
≥ -823.3

Source: Rai et al. 2005 [DIRS 181002], Table II, p. 486

[a] T is the absolute temperature.

The species $PbH_2PO_4^+$ is added to data0.ymp.R5 (Output DTN: SN0612T0502404.014). Nriagu (1972 [DIRS 151244]) measured the solubility of $PbHPO_4$ in dilute phosphoric acid solutions at 25°C. He interpreted the solubility behavior in terms of the formation of two aqueous complexes, $PbH_2PO_4^+$ and $PbHPO_4$(aq). The resulting data are given in Table 4-41b.

Table 4-41b. Equilibrium Constants (298.15 K) for Two Lead Phosphate Complexes

Species	Chemical Reaction	log K
$PbH_2PO_4^+$	$Pb^{2+} + H_2PO_4^- = PbH_2PO_4^+$	1.5
$PbHPO_4$(aq)	$Pb^{2+} + HPO_4^{2-} = PbHPO_4$(aq)	3.1

Source: Nriagu 1972 [DIRS 151244], pp. 2500 to 2501.

The datum for $PbHPO_4$(aq) (with the reaction reversed and the log K changed in sign) was in data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]), was carried forward into subsequent members of the data0.ymp.R* series, and thus is not new. However, the datum for $PbH_2PO_4^+$ was not included. The use of this datum is justified because (a) a standard, accepted method, solubility determination, was used to obtain it, (b) the datum is published in a peer-reviewed journal (*Inorganic Chemistry*), (c) the author is well known for similar studies, and (d) the data for both species taken from this source should be used together, as the data were determined from a single, common analysis.

Data for the mineral berlinite ($AlPO_4$) are taken from two sources. The standard 298.15 K properties (Gibbs energy of formation, enthalpy of formation, and entropy) are taken from the *NBS Tables* (Wagman et al. 1982 [DIRS 159216]). The heat capacity coefficients were taken from Robie et al. (1979 [DIRS 107109]). These are replaced by data taken from a single source (Barin and Platzki 1995 [DIRS 157865]). These data are given in Tables 4-42 and 4-43. They are Established Fact.

Table 4-42. Standard Thermodynamic Data (298.15 K) for Berlinite ($AlPO_4$)

ΔG_f^o (Joule/mol)	**ΔH_f^o (Joule/mol)**	**S^o (Joule/mol-K)**
-1617497.0	-1733431.0	90.793

Source: Barin and Platzki 1995 [DIRS 157865], p. 65 (Established Fact).

Table 4-43. Heat Capacity (Cp) Data for Berlinite ($AlPO_4$)

Temp K	***Cp* (Joule/mol-K)**
298.15	93.004
300	93.261
400	107.194
500	121.127
600	135.060

Source: Barin and Platzki 1995 [DIRS 157865], p. 65 (Established Fact).

Data for the mineral strengite ($FePO_4.2H_2O$) are from the *NBS Tables* (Wagman et al. 1982 [DIRS 159216]), including both the standard 298.15 K properties (Gibbs energy of formation, enthalpy of formation, and entropy) and a single heat capacity value. These data are replaced by data taken from Barin and Platzki (1995 [DIRS 157865]). These data are given in Tables 4-44 and 4-45. They are Established Fact.

Table 4-44. Standard Thermodynamic Data (298.15 K) for Strengite ($FePO_4.2H_2O$)

ΔG_f^o (Joule/mol)	**ΔH_f^o (Joule/mol)**	**S^o (Joule/mol-K)**
-1657462.0	-1888200.0	171.250

Source: Barin and Platzki 1995 [DIRS 157865], p. 711 (Established Fact).

Table 4-45. Heat Capacity (Cp) Data for Strengite ($FePO_4.2H_2O$)

Temp K	*Cp* (Joule/mol-K)
298.15	171.250
300	172.369
400	228.344
500	276.068
600	317.313

Source: Barin and Platzki 1995 [DIRS 157865], p. 711 (Established Fact).

[a] The data shown here are actually the entropy data from the source. See Section 6.8 for a correction.

Data for the mineral whitlockite ($Ca_3(PO_4)_2$) are taken from Robie et al. (1979 [DIRS 107109]), including both the standard 298.15 K properties (Gibbs energy of formation, enthalpy of formation, and entropy) and heat capacity coefficients. These data are replaced by data taken from Barin and Platzki (1995 [DIRS 157865]). These data are given in Tables 4-46 and 4-47. They are Established Fact.

Table 4-46. Standard Thermodynamic Data (298.15 K) for Whitlockite ($Ca_3(PO_4)_2$)

ΔG_f^o (Joule/mol)	ΔH_f^o (Joule/mol)	S^o (Joule/mol-K)
-3884966.0	-4120801.0	235.999

Source: Barin and Platzki 1995 [DIRS 157865], p. 570 (Established Fact).

Table 4-47. Heat Capacity (Cp) Data for Whitlockite ($Ca_3(PO_4)_2$)

Temp K	*Cp* (Joule/mol-K)
298.15	227.799
300	228.073
400	242.879
500	257.684
600	272.490

Source: Barin and Platzki 1995 [DIRS 157865], p. 478 (Established Fact).

Data for the mineral hydroxyapatite ($Ca_5(PO_4)_3OH$) are taken from Robie et al. (1979 [DIRS 107109]), including both the standard 298.15 K properties (Gibbs energy of formation, enthalpy of formation, and entropy) and heat capacity coefficients. These data are replaced by data taken from Robie and Hemingway (1995 [DIRS 153683]). These data are given in Tables 4-48 and 4-49. The source is a handbook and these data are Established Fact.

Table 4-48. Standard Thermodynamic Data (298.15 K) for Hydroxyapatite ($Ca_5(PO_4)_3OH$)

ΔG_f^o (kJ/mol)	ΔH_f^o (kJ/mol)	S^o (Joule/mol-K)
-6337.1	-6738.5	390.4

Source: Robie and Hemingway 1995 [DIRS 153683], p. 30 (Established Fact).

Table 4-49. Heat Capacity (Cp) Coefficients for Hydroxyapatite ($Ca_5(PO_4)_3OH$)

Cp Coefficient	Value
a	3.878×10^{2}
b	1.186×10^{-1}
c	-1.270×10^{7}
d	1.811×10^{3}

Source: Robie and Hemingway 1995 [DIRS 153683], p. 57 (Established Fact).

NOTES: Units are consistent with Cp in Joule/mol-k.

$Cp = a + bT + cT^{-2} + dT^{-0.5}$.

Data for the mineral fluorapatite ($Ca_5(PO_4)_3OH$) are also taken from Robie et al. (1979 [DIRS 107109]), including both the standard 298.15 K properties (Gibbs energy of formation, enthalpy of formation, and entropy) and heat capacity coefficients. These data are replaced by data taken from a combination of sources. The enthalpy of formation is recalculated in Section 6.7.8 from data taken from Westrich and Navrotsky (1981 [DIRS 178567]). A full elucidation of these data here is not feasible; see Section 6.7.8. These data are justified for the intended usage in this analysis report because (1) they were published in an internationally-recognized peer-reviewed journal (*American Journal of Science*), (2) the second author is one of the world's premier calorimetrists, and (3) the data were obtained using a standard, accepted methodology, calorimetry. The entropy (Table 4-50) was taken from Egan et al. (1951 [DIRS 178570]). This datum is justified for the intended use in this analysis report because (1) it was published in an internationally-recognized peer-reviewed journal (*Journal of the American Chemical Society*) and (2) it was obtained using a standard, accepted methodology, calorimetry. The heat capacity coefficients (Table 4-51) are taken from Robie and Hemingway (1995 [DIRS 153683]). They are Established Fact.

Table 4-50. Standard Thermodynamic Data (298.15 K) for Fluorapatite (normally $Ca_5(PO_4)_3F$), for the doubled formula $Ca_{10}(PO_4)_6F_2$

ΔG_f^o (kcal/mol)	ΔH_f^o (kcal/mol)	S^o (cal/mol-K)
-[a]	-[a]	185.5[b]

Source: Egan et al. 1951 [DIRS 178570], Table IV, p. 5582.

[a] Values are determined in Section 6.7.8, based mainly on data from Westrich and Navrotsky (1981 [DIRS 178567]).

[b] Data for the doubled formula must be divided by two to obtain data for the normal formula as defined above.

Table 4-51. Heat Capacity (Cp) Coefficients for Fluorapatite ($Ca_5(PO_4)_3F$)

***Cp* Coefficient**	**Value**
a	7.543×10^{2}
b	-3.026×10^{-2}
c	-9.084×10^{5}

Source: Robie and Hemingway 1995 [DIRS 153683], p. 57 (Established Fact).

NOTES: Units are consistent with Cp in Joule/mol-k.

$Cp = a + bT + cT^{-2}$.

Data for the species $AmPO_4$(am) and $AmH_2PO_4^{2+}$ are taken from the OECD/NEA volume *Chemical Thermodynamics of Americium* (Silva et al. 1995 [DIRS 102087]). These data are Established Fact. Also, data for the species UP_2, UPO_5, $UO_2P_2O_7$, $U(HPO_4)_2{\cdot}4H_2O$, $(UO_2)_3(PO_4)_2$, and $(UO_2)_3(PO_4)_2{\cdot}6H_2O$ are taken from the OECD/NEA volume *Chemical Thermodynamics of Uranium* (Grenthe et al. 1992 [DIRS 101671]). These data are also Established Fact. The data for these species are checked against those in the newer OECD/NEA volume *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium* (Guillaumont et al. 2003 [DIRS 168382]). Data from this source are also Established Fact. The only change of note is that a standard molar entropy is now given for $(UO_2)_3(PO_4)_2{\cdot}6H_2O$: 669.00 J/mol-K (Guillaumont et al. 2003 [DIRS 168382], p. 57; Established Fact); this value is used as a direct input in the development of data0.ymp.R5 (Output DTN: SN0612T0502404.014). A very small difference was found for the leading heat capacity coefficient (*a*) for UPO_5: Grenthe et al. (1992 [DIRS 101671], p. 62) give $a = 1.10427 \times 10^{2}$ J/mol-K, whereas Guillaumont et al. (2003 [DIRS 168382], p. 77) give $a = 1.10430 \times 10^{2}$ J/mol-K. This newer value is used as a direct input to the development of data0.ymp.R5 (Output DTN: SN0612T0502404.014). As the other coefficients for this solid are unaffected, the slight difference appears to be due to some minor data processing inconsistency.

Molar volume data for the phases UP_2O_7, $(UO_2)_3(PO_4)_2$:$4H_2O$, $(UO_2)_3(PO_4)_2$:$6H_2O$, and UO2HPO_4:$4H_2O$ [and an entropy for $(UO_2)_3(PO_4)_2$:$6H_2O$] are estimated on worksheet "Cp of Phosphates" in workbook *Minerals_j_YC_U_phosphates.xls* of DTN: MO0302SPATHDYN.001 [DIRS 161886]. These data were used in developing the log K grids for these four solids used in data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]). As noted above, the single estimated entropy is now replaced by an Established Fact value. These estimated molar volumes are in part based on a molar volume of 34.460 cm^3/mol for $UO_{3(beta)}$, which was taken from data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]). Weast and Astle (1982 [DIRS 100833], p. B-161; Established Fact) give a density of 7.92 g/cc for $UO_{3(beta)}$. Combined with a molecular weight of 286.03 g/mol (same source), this yields a molar volume of 39.236 cm^3/mol. This new value is used in Section 6.7.8 and notably changes the estimated molar volumes of $(UO_2)_3(PO_4)_2$:$4H_2O$, $(UO_2)_3(PO_4)_2$:$6H_2O$, and UO2HPO_4:$4H_2O$. These molar volumes are only used in the estimation of the corresponding log K grids.

A molar volume is estimated for $AmPO_4$(am) on worksheet "CpofSolids" in workbook *Solids_j_YC_Am.xls* of DTN: MO0302SPATHDYN.001 [DIRS 161886]. This was used in developing the log K grid used in data0.ymp.R2 Database (DTN: MO0302SPATHDYN.000

[DIRS 161756]). The molar volume calculation depends on an input for the volume of the phase Am_2O_3. The value used is 11.68 g/cc (Weast and Astle 1982 [DIRS 100833], p. B-74; Established Fact). Unfortunately, this value is for the density of the related solid AmO_2. Lide (2006 [DIRS 178081], p. 4-46) gives a density of 11.77 g/cc for Am_2O_3, and repeats the previously cited value for Am_2O_3. As noted in Section 6.7.8, the use of the incorrect value has negligible effect.

CR 6731 (Section 1.2) in addition to addressing the problem in data for key phosphate species also addresses a problem regarding the compositions of rare earth phosphates. Data (25°C only) were previously taken for a large set of such compounds from the compilation of Spahiu and Bruno (1995 [DIRS 103804]). These data entered the databases in the data0.ymp.R* series through data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]). In this set, a number of the phosphate compounds (whose thermochemical properties were determined by solubility) were indeterminate in regard to water of hydration. Europium phosphate was for example represented in this compilation as "EuPO4.XH_2O", where X was intended to represent an unknown number whose value was probably close to one or two (and probably also varying according to the exact phase). When these data were originally processed, the "X" was misinterpreted as the roman numeral for ten. This causes no significant errors in calculated solubilities as long as solutions remain very dilute and the activity of water is very close to unity. In more concentrated solutions, however, the solubilities could be substantially overpredicted. Structural studies on REE (Rare Earth Element) phosphates (Hezel and Ross 1966 [DIRS 177990]; Hezel and Ross 1967 [DIRS 178227]; Assaaoudi et al. 1997 [DIRS 177936]; Assaaoudi et al. 2000 [DIRS 177992]; Assaaoudi et al. 2001 [DIRS 179602]) are used in Section 6.7.8 to assign values for waters of hydration to REE phosphates for which Spahiu and Bruno (1995 [DIRS 103804]) had indicated "XH2O."

4.1.18 Addition of Some Magnesium Silicates to data0.ymp.R5

The magnesium silicates palygorskite ($Mg_{2.84}Al_{1.8}Si_{7.73}O_{20}(OH)_2(OH_2)_4$), amorphous sepiolite ($Mg_4Si_6O_{15}(OH)_2{:}6H_2O$), and amorphous antigorite ($Mg_3Si_2O_5(OH)_4$) have been added to data0.ymp.R5 (Output DTN: SN0612T0502404.014). These supplement the crystalline sepiolite already in data0.ymp.R4 (Output DTN: SN0410T0510404.002). These changes address CR 6489.

Palygorskite: The standard Gibbs energy of formation for palygorskite is evaluated in Section 6.7.9 using the estimation methodology described by Birsoy (2002 [DIRS 178220]). To use this approach, the thermodynamic functions (here standard Gibbs energies of formation) of various oxide and hydroxide components must be known. The methodology is in part analogous to the methodology applied to some clay minerals in Section 4.1.4. The components here correspond to actual oxide and hydroxide solids. Table 4-52 lists the standard Gibbs energies of formation for the various components used in the estimation of the standard Gibbs energy of formation of palygorskite. The methods obtained from Birsoy (2002 [DIRS 178220] are justified for the intended use in this analysis report on the grounds that (1) they were published in an international peer-reviewed journal, *Clays and Clay Minerals,* which is published by the Clay Minerals Society and (2) the data were based on a standard, accepted approach for obtaining the estimation of thermodynamic data.

Table 4-52. Thermodynamic Data of Components Used in the Estimation of Palygorskite Standard Gibbs Energy of Formation

Component	ΔG_f^o (J/mol)	Source[a]
$Mg(OH)_2$	-835318.9	Spreadsheet: *BasisSpeciesLib_j_TJW_2p0.xls*, worksheet: "Misc. Solids" [b]
$Al(OH)_3$	-1155486.9	data0.ymp.R4 (DTN: SN0410T0510404.002)
SiO_2(quartz)	-856280.7	Spreadsheet: *ReferenceSpecies_j_TJW_2p0.xls*, worksheet: "Misc. Solids" [b]
H_2O	-237181.4	Spreadsheet: *BasisSpeciesLib_j_TJW_2p0.xls*, worksheet: "Basis Species 1" [b]

[a] The immediate sources identified here were actually used in the calculations to be described in Section 6.7.9. These are intermediate products of this analysis report. Sources for all of the above data would have been better referenced to the *speq02.dat* file which is in folder *\CD\SUPCRT_Runs_TJW\SUPCRT_datafiles* of DTN: MO0302SPATHDYN.001 [DIRS 161886]. The data there are in cal/mol.

[b] These library workbooks are in folder *\Library Workbooks* of Output DTN: SN0702T0502404.015.

Amorphous sepiolite: The log K value at 25°C for amorphous sepiolite was obtained from the study by Wollast et al. (1968 [DIRS 162340]. This source provides a log K value of -75.12 for the precipitation reaction, and for a sepiolite composition with twice the number of stoichiometric components as that adopted in the database. For consistency with EQ3/6 database convention, the source log K value is divided by two and the sign is reversed (to correspond to a dissolution reaction) yielding 37.56 (See Section 6.7.9). The data from Wollast et al. (1968 [DIRS 162340] are justified for the intended use in this report on the grounds that (1) they were published in an international peer-reviewed journal, *American Mineralogist,* which has been published by the Mineralogical Society of America since 1916 and (2) the data were based on a standard, accepted approach for obtaining thermodynamic data.

Poorly crystalline antigorite: Data for this phase were obtained from Gunnarsson et al. (2005 [DIRS 176844]). They define the stoichiometry of "poorly crystalline antigorite" as $Mg_3Si_2O_5(OH)_4$, which corresponds to the chemical formula of a serpentine mineral. The reaction defined by the source is:

$$Mg_3Si_2O_5(OH)_4 + 6\ H^+ = Mg^{2+} + 2\ SiO_2(aq) + 5\ H_2O \qquad \text{(Eq. 4-12)}$$

Gunnarsson et al. (2005 [DIRS 176844]) represent the equilibrium constant by the following equation:

$$\log K_{sp} = \frac{9309}{T} + 3.28 \qquad \text{(Eq. 4-13)}$$

where K_{sp} stands for the solubility product and T designates absolute temperature. This equation is used in Section 6.7.9 to obtain log K values on the EQ3/6 temperature grid. The stoichiometry and the equilibrium constant equation for *poorly crystalline (*amorphous) antigorite obtained from Gunnarsson et al. (2005 [DIRS 176844]). These data are justified for the intended use in this analysis report on the grounds that (1) they were published in an international peer-reviewed journal, *Geochimica et Cosmochimica Acta„* which is a journal from The Geochemical Society and The Meteoritical Society and (2) the data were based on a standard, accepted approach for obtaining thermodynamic data.

All three of these data sources, the works by Birsoy (2002 [DIRS 178220]), Wollast et al. (1968 [DIRS 162340]) and Gunnarsson et al. (2005 [DIRS 176844]) discussed in this section, were also used in the project qualified Pitzer database, data0.ypf.R2 (DTN: SN0609T0502404.012 [DIRS 179067]. The use of the data in this report is exactly the same as in the Pitzer database, data0.ypf.R2, which is documented in the report *In-Drift Precipitates/Salts Model* (SNL 2007 [DIRS 177411], Appendix I.4.5.15).

4.1.19 Addition of Some Uranyl Oxy-Hydrates and Silicates to data0.ymp.R5

Uranyl oxy-hydrates and silicates have been reported as alteration products of spent nuclear fuel in oxidizing environments, several of which were observed to form during corrosion tests on both unirradiated UO_2 and spent fuel (Wronkiewicz et al. 1996 [DIRS 102047]; Chen et al. 1999 [DIRS 123270]); however, many of these uranyl compounds were not included in the development of the data0.ymp.R5 (Output DTN: SN0612T0502404.014) thermodynamic database (see CR 7756 description in Section 1.2). Recent studies have focused on directly determining thermodynamic properties for many potentially YMP-relevant uranyl compounds (Perez et al. 2000 [DIRS 157910]; Guillaumont et al. 2003 [DIRS 168382]; McKenzie et al. 2001 [DIRS 172346]; Perez et al. 1997 [DIRS 100812]; Möll et al. 1996 [DIRS 106349]; Sandino and Grambow 1994 [DIRS 113360]; Rai et al. 2002 [DIRS 168155]; Vochten and Van Haverbeke 1990 [DIRS 113433]; Casas et al. 1997 [DIRS 102432]; Kubatko et al. 2003 [DIRS 173070]) and efforts have been made to estimate thermodynamic properties of additional uranyl solids by using high-quality structural data (Finch 1997 [DIRS 106347]; Chen et al. 1999 [DIRS 123270]). Table 4-53 list the recent additions of several uranyl compounds to the data0.ymp.R5 (Output DTN: SN0612T0502404.014) thermodynamic database. The requisite processing of these data to obtain the needed log K data is done in Section 6.7.10. Evaluations of these data are also given in this section.

For the phase uranophane-alpha ($Ca[(UO_2)(SiO_3OH)]_2{:}5H_2O$), the data from Chen et al. (1999 [DIRS 123270]) and Perez et al. (2000 [DIRS 157910]) are justified for the intended use in this analysis report because they are published in an international peer-reviewed journal (*Geochimica Cosmochimica Acta and American Mineralogist*). Also, in the study by Perez et al. (2000 [DIRS 157910]), the data were obtained by a standard accepted methodology (e.g., Baes and Mesmer 1986 [DIRS 100702]) to retrieve thermodynamic data from solubility measurements.

The data from Möll et al. (1996 [DIRS 106349]) for Soddyite $(UO_2)_2(SiO_4){:}2H_2O$ includes solubility data for this phase. This source is justified for intended use in this report because the data are published in an international peer-reviewed journal (*Radiochimica Acta*), and the thermodynamic parameters were obtained by a standard accepted methodology (e.g., Baes and Mesmer 1986 [DIRS 100702]) to retrieve thermodynamic data from solubility measurements.

Data sources for the dehydrated forms of the phase schoepite ($UO_3{:}0.9H_2O$ and_$UO_3{:}H_2O$), becquerelite ($Ca(UO_2)_6O_4(OH)_6{:}8H_2O$), and compreignacite ($K_2[(UO_2)_3O_2(OH)_3]{:}7H_2O$) were obtained from the analysis by Guillaumont et al. (2003 [DIRS 168382]). This source is considered Established Fact. For the phase_compreignacite, the updated number of H_2O reported as a correction in Section 6.7.10 is constrained from the structural study by Burns (1998 [DIRS 127210]). This source is justified for the intended use in this analysis report because (1) the data is published in an international peer-reviewed journal (*The Canadian Mineralogist*), and (2) the authors is a recognized expert on the crystal chemistry of uranium-bearing solids.

The source of thermodynamic parameter data for the phase Weeksite-Na; ($Na_2(UO_2)_2(Si_5O_{13}):3H_2O$), boltwoodite ($K[(UO_2)(SiO_3OH)]:1.5H_2O$), weeksite ($K_2[(UO_2)_2(Si_5O_{13})]:(3-x)H_2O$), and sklodowskite ($Mg[(UO_2)(SiO_3OH)]_2:6H_2O$) are entirely from the analysis of Chen et al. (1999 [DIRS 123270]). This source is justified for the intended use in this analysis report because the data are published in an international peer-reviewed journal (*American Mineralogist*). Also, the methodology used by the authors in the retrieval of thermodynamic data has yielded estimates that are in reasonable agreement within the uncertainty bounds of values determined by other methods. One of the authors is a leading expert in the crystal chemistry of uranium-bearing solids.

The sources of thermodynamic parameter data for sodium boltwoodite ($Na[(UO_2)(SiO_3OH)]:1.5H_2O$) are the works by Guillaumont et al. (2003 [DIRS 168382]) and more recently Ilton et al. (2006 [DIRS 178810]). The source from Guillaumont et al. (2003 [DIRS 168382]) is considered Established Fact. The source from Ilton et al. (2006 [DIRS 178810]) is justified for the intended use in this analysis report because (1) the results are published in an international peer-reviewed journal (*Geochimica Cosmochimica Acta*), and (2)the authors used a standard accepted methodology (e.g., Baes and Mesmer 1986 [DIRS 100702]) to retrieve thermodynamic parameter data from solubility measurements. Furthermore, some of the authors in this study have the reputation of evaluating and producing quality thermodynamic data obtained from solubility experiments.

The source of thermodynamic parameter data for studtite ($UO_2O_2(H_2O)_4$) is the study by Kubatko et al. (2003 [DIRS 173070]). This source is justified for the intended use in this analysis report because (1) the data are published in an internationally-recognized peer-reviewed journal (*Science*), (2) the third author is one of the world's leading experts in the thermochemical analysis of solids, and (3) the data are based on a standard accepted methodology (e.g., Baes and Mesmer 1986 [DIRS 100702]) to retrieve thermodynamic parameter data from solubility measurements.

Table 4-53. Summary of Inputs for Uranyl Oxy-Hydrates and Silicates

Mineral	Action[a]	Data0.ymp.R5 reaction	Input Parameter	Sources
Uranophane-alpha $Ca(UO_2SiO_3OH)2:5H_2O$	NC	Uranophane-alpha + $6H^+$ = Ca^{2+} + $2SiO_2(aq)$ + $2UO_2^{2+}$ + $9H_2O$	ΔG_o = -6192.3 kJ/mol	Perez et al. 2000 [DIRS 157910]; and Chen et al. 1996 [DIRS 123270]
Soddyite $(UO_2)_2SiO_4:2H_2O$	NC	Soddyite + $4H^+$ = $SiO_2(aq)$ +$2UO_2^{2+}$ + $4H_2O$	ΔG_f°-3653.0 kJ/mol	Möll et al. 1996 [DIRS 106349]
Dehydrated schoepite (1) $(UO_2)O_{0.1}(OH)_{1.8}$ or $UO_3:0.9H_2O$ (2) alpha-$UO_3(OH)_2$	NC A	$UO_3:0.9H_2O + 2H^+$ = $UO_2^{2+} + 1.9H_2O$ $UO_3:H_2O + 2H^+$ = $UO_2^{2+} + 2H_2O$	log K = 5.08 log K = 5.8	Guillaumont et al. 2003 [DIRS 168382]

Table 4-53. Summary of Inputs for Uranyl Oxy-Hydrates And Silicates (Continued)

Mineral	Action[a]	Data0.ymp.R5 reaction	Input Parameter	Sources
Becquerelite $Ca(UO_2)_6O_4(OH)_6{:}8H_2O$	A	Becquerelite + $14H^+$ = Ca^{2+} + $6UO_2^{2+}$ + $18H_2O$	log K = 40.5	Guillaumont et al. 2003 [DIRS 168382]
Compreignacite $K_2[(UO_2)_3O_2(OH)_3]2{:}7H_2O$	A	Compreignacite + $14H^+$ = $2K^+$ + $3UO_2^{2+}$ + $17H_2O$	log K = 37.1	Guillaumont et al. 2003 [DIRS 168382]; Burns 1998 [DIRS 127210]
Weeksite-Na $Na_2(UO_2)_2Si_5O_{13}{:}3H_2O$	NC	Weeksite-Na + $6H^+$ = $2Na^+$ + $2UO_2^{2+}$ + $5SiO_2(aq)$ + $6H_2O$	ΔG_f^0 = -7993.9	Chen et al. 1996 [DIRS 123270]
Boltwoodite-Na $NaUO_2SiO_3OH{:}1.5H_2O$	NC	Boltwoodite-Na + $3H^+$ = Na^+ + $SiO_2(aq)$ + UO2^{2+} + 3.5H2O	ΔG_f^0 = -2844.8	Chen et al. 1996 [DIRS 123270]; Ilton et al. 2006 [DIRS 178810]
Studtite $UO_2O_2(H_2O)_4$	NC	Studtite + $2H^+$ = UO_2^{2+} + $5H_2O$ + $0.5O_2(g)$	[b]Average K_{sp} = 1.34 × 10^{-3}	Kubatko et al. 2003 [DIRS 173070]
Boltwoodite $KUO_2SiO_3OH{:}1.5H_2O$	A	Boltwoodite +$3H^+$ = K^+ + $SiO_2(aq)$ + UO_2^{2+} + $3.5H_2O$	[c] See Chen et al. 1999 [DIRS 123270]	Chen et al. 1996 [DIRS 123270]
Weeksite $K_2[(UO_2)_2(Si_5O_{13})]{:}(3-x)H_2O$ $0 \le x \le 2$	A	Weeksite + $6H^+$ = $2K^+$ + $2UO_2^{2+}$ + $5SiO_2(aq)$ + $(6-x)H_2O$	[c] See Chen et al. 1999 [DIRS 123270]	Chen et al. 1996 [DIRS 123270]
Sklodowskite $Mg[(UO_2)(SiO_3)(OH)]_2{:}6H_2O$	A	Sklodowskite + $6H^+$ = Mg^{2+} + $2UO_2^{2+}$ + $2SiO_2(aq)$ + $10H_2O$	[c] See Chen et al. 1999 [DIRS 123270]	Chen et al. 1996 [DIRS 123270]

[a] Note on acronyms: “NC” indicates No Changes were made to the preexisting data block. “‘A“ designates a new data block was added to the database. Log K values in brackets are best estimates for log K values following minor corrections (see text for discussion).

[b] Note: The value of log K for studtite is retained in data0.ymp.R5; however, there remains doubt as to whether the value represents true equilibrium (see discussion on studtite in Section 6.7.10)

[c] Log K calculated using the method from Chen et al. 1999 [DIRS 123270].

4.1.20 Correction of Data for Some Additional Cr Species in data0.ymp.R5

Changes are made for some Cr species to obtain better consistency with the solubility of $Cr(OH)_3(am)$ as a function of pH as reported by Rai et al. (1987 [DIRS 163369]), Ball and Nordstrom (1998 [DIRS 163015]), and Rai et al. (2004 [DIRS 179582]). The species $Cr_2(OH)_2^{4+}$ and $Cr_3(OH)_4^{5+}$ are deleted, and the data for $CrOH^{2+}$, $Cr(OH)_3(aq)$, and $Cr(OH)_3(am)$ are changed. The case for deleting $Cr_3(OH)_4^{5+}$ and $Cr_2(OH)_2^{4+}$ is discussed by Ball and Nordstrom (1998 [DIRS 163015], p. 912). They cite earlier results reported by Rai et al. (1987 [DIRS 163369]) who found no measurable evidence of the formation of such complexes, although they did suggest limiting values for the formation constants. As it likely that such species do not exist, they have been simply deleted. Table 4-54 contains the data recommended by Ball and Nordstrom (1998 [DIRS 163015]) for $CrOH^{2+}$, $Cr(OH)_3(aq)$, and $Cr(OH)_3(am)$. Also included in this table is a datum from a later paper by Rai et al. (2004 [DIRS 179582]) for the reaction $CrOH^{2+} + 2\ H_2O = Cr(OH)_3(aq) + 2\ H^+$.

This reaction from Rai et al. (2004 [DIRS 179582]) is equivalent to a combination of two of the reactions (for $CrOH^{2+}$ and $Cr(OH)_3(aq)$) for which data are given by Ball and Nordstrom (1998 [DIRS 163015]). It is used in Section 6 to derive a log K value for the reaction $CrOH^{2+} + H^+ = Cr^{3+} + H_2O$ that is not consistent with what Ball and Nordstrom (1998 [DIRS 163015]) give for the reverse reaction (shown in Table 4-54). The reasoning is as follows. The solubility of $Cr(OH)_3(am)$ at relatively low pH (less than about 4 or so) is controlled by the reaction $Cr(OH)_3(am) + 2\ H^+ = CrOH^{2+} + 2\ H_2O$. The solubility curve in this region decreases sharply with increasing pH at a slope consistent with this as the controlling reaction (Rai et al. 1987 [DIRS 163369]). The thermodynamic data recommended for $Cr(OH)^{2+}$ by Ball and Nordstrom (1998 [DIRS 163015]) are based on the solubility measurements of Rai et al. (1987 [DIRS 163369]). Rai et al. (2004 [DIRS 179582]) present newer solubility measurements in which the solubility curve in this low pH region is lower but with the same slope (i.e., shifted toward lower pH). One may compare Figure 1 of Rai et al. (2004 [DIRS 179582]) with Figure 2 of the earlier study by Rai et al. (1987 [DIRS 163369]). The low-pH limb in the former figure is shifted substantially to the left, by about 1.7 pH units). Other parts of the solubility curve in this figure are essentially unchanged. Rai et al. (2004 [DIRS 179582]) attribute this result to more closely attaining a state of equilibrium in this pH region than in the earlier study. This implies that the thermodynamic data pertaining to $CrOH^{2+}$ need to be revised from those given by Ball and Nordstrom (1998 [DIRS 163015]). That development is carried out in Section 6.7.11.

The data from Ball and Nordstrom (1998 [DIRS 163015]) are justified for the intended use in this analysis report on the grounds that (1) they were published in an international peer-reviewed journal, *Journal of Chemical & Engineering Data,* which is a journal from American Chemical Society, and published since 1959 and (2) the data were based on a standard, accepted approach for obtaining thermodynamic data and (3) these data are extensively used on the project as a source in seven other controlled and qualified YMP reports.

The data from Rai et al. (2004 [DIRS 179582]) are justified for the intended use in this analysis report on the grounds that (1) they were published in an international peer-reviewed journal, *Journal of Solution Chemistry,* and (2) the data were based on a standard, accepted approach for obtaining thermodynamic data. Furthermore, some of the authors in this study have the reputation of evaluating and producing quality thermodynamic data obtained from chromium solubility experiments.

The data from Rai et al. (1987 [DIRS 163369]) are justified for the intended use in this analysis report on the grounds that (1) they were published in an international peer-reviewed journal, *Inorganic Chemistry,* and (2) the data were based on a standard, accepted approach for obtaining thermodynamic data. Furthermore, some of the authors in this study have the reputation of evaluating and producing quality thermodynamic data obtained from chromium solubility experiments.

Table 4-54. Equilibrium Constants (298.15 K) for Some Additional Chromium-Bearing Species

Species	Chemical Reaction[a]	log K	Source
$Cr_2(OH)_2^{4+}$	species deleted	—	1
$Cr_3(OH)_4^{5+}$	species deleted	---	1
$Cr(OH)_3(am)$	$Cr(OH)_3(am) + 3H^+ = Cr^{3+} + 3H_2O$	9.35[a]	1
$CrOH^{2+}$	$Cr^{3+} + H_2O = CrOH^{2+} + H^+$	-3.57[a]	1
$Cr(OH)_3(aq)$	$Cr^{3+} + 3H_2O = Cr(OH)_3(aq) + 3H^+$	-16.19	1
$CrOH^{2+}$, $Cr(OH)_3(aq)$	$CrOH^{2+} + 2H_2O = Cr(OH)_3(aq) + 2H^+$	-10.93	2

Source: (1) Ball and Nordstrom 1998 [DIRS 163015], Table 8 (p. 910) and Table 10 (p. 911); (2) Rai et al. 2004 [DIRS 179582], p. 1223.

[a] This value is not used in developing the data to be used for the species $CrOH^{2+}$. It is included here for completeness and for purposes of comparison in Section 6.7.11.

4.2 CRITERIA

YMRP acceptance criteria (NRC 2003 [DIRS 163274]) applicable to this report are identified in Section 3.2 of the TWP (BSC 2006 [DIRS 177885]). In particular, the requirements identified in 10 CFR 63.114 (a), (b), (c), and (g). There are no U.S. Department of Energy (DOE) orders applicable to the scope of work identified in this TWP.

4.2.1 Quantity and Chemistry of Water Contacting Waste Packages and Waste Forms (NRC 2003 [DIRS 163274], Section 2.2.1.3.3.3), from 10 CFR 63.114(a)–(c) and (e)–(g)

4.2.1.1 Acceptance Criterion 1—System Description and Model Integration Are Adequate:

(5) Sufficient technical bases and justification are provided for total system performance assessment assumptions and approximations for modeling coupled thermal-hydrologic-mechanical-chemical effects on seepage and flow, the waste package chemical environment, and the chemical environment for radionuclide release. The effects of distribution of flow on the amount of water contacting the engineered barriers and waste forms are consistently addressed, in all relevant abstractions.

(6) The expected ranges of environmental conditions within the waste package emplacement drifts, inside the breached waste packages, and contacting the waste forms and their evolution with time are identified.

(12) Guidance in NUREG–1297 and NUREG-1298 (Altman et al. 1988 [DIRS 103597]; Altman et al. 1988 [DIRS 103750]), or other acceptable approaches, is followed.

4.2.1.2 Acceptance Criterion 2—Data Are Sufficient for Model Justification:

(1) Geological, hydrological, and geochemical values used in the license application are adequately justified. Adequate description of how the data were used, interpreted, and appropriately synthesized into the parameters is provided.

4.2.1.3 Acceptance Criterion 3—Data Uncertainty Is Characterized and Propagated Through the Model Abstraction:

(1) Models use parameter values, assumed ranges, probability distributions, and bounding assumptions that are technically defensible, reasonably account for uncertainties and variabilities, and do not result in an under-representation of the risk estimate.

(2) Parameter values, assumed ranges, probability distributions, and bounding assumptions used in the total system performance assessment calculations of quantity and chemistry of water contacting engineered barriers and waste forms are technically defensible and reasonable, based on data from the Yucca Mountain region (e.g., results from large block and drift-scale heater and niche tests), and a combination of techniques that may include laboratory experiments, field measurements, natural analogue research, and process-level modeling studies.

(3) Input values used in the total system performance assessment calculations of quantity and chemistry of water contacting engineered barriers (e.g., drip shield and waste package) are consistent with the initial and boundary conditions and the assumptions of the conceptual models and design concepts for the Yucca Mountain site. Correlations between input values are appropriately established in the U.S. Department of Energy total system performance assessment. Parameters used to define initial conditions, boundary conditions, and computational domain in sensitivity analyses involving coupled thermal-hydrologic-mechanical-chemical effects on seepage and flow, the waste package chemical environment, and the chemical environment for radionuclide release, are consistent with available data. Reasonable or conservative ranges of parameters or functional relations are established.

(4) Adequate representation of uncertainties in the characteristics of the natural system and engineered materials is provided in parameter development for conceptual models, process-level models, and alternative conceptual models. The U.S. Department of Energy may constrain these uncertainties using sensitivity analyses or conservative limits. For example, the U.S. Department of Energy demonstrates how parameters used to describe flow through the engineered barrier system bound the effects of backfill and excavation-induced changes.

4.2.2 Radionuclide Release Rates and Solubility Limits (NRC 2003 [DIRS 163274], Section 2.2.1.3.4.3), from 10 CFR 63.114(a)–(c) and (e)–(g)

4.2.2.1 Acceptance Criterion 1—System Description and Model Integration Are Adequate

(4) The U.S. Department of Energy reasonably accounts for the range of environmental conditions expected inside breached waste packages and in the engineered barrier environment surrounding the waste package. For example, the U.S. Department of Energy should provide a description and sufficient technical bases for its abstraction of changes in hydrologic properties in the near field, caused by coupled thermal-hydrologic-mechanical-chemical processes;

(8) Guidance in NUREG–1297 and NUREG–1298 (Altman et al. 1988 [DIRS 103597]; Altman et al. 1988 [DIRS 103750]), or other acceptable approaches for peer reviews and data qualification, is followed.

4.2.2.2 Acceptance Criterion 2—Data Are Sufficient for Model Justification

(1) Geological, hydrological, and geochemical values used in the license application are adequately justified. Adequate description of how the data were used, interpreted, and appropriately synthesized into the parameters is provided.

4.2.2.3 Acceptance Criterion 3—Data Uncertainty Is Characterized and Propagated Through the Model Abstraction

(1) Models use parameter values, assumed ranges, probability distributions, and bounding assumptions that are technically defensible, reasonably account for uncertainties and variabilities, and do not result in an under-representation of the risk estimate.

(2) Parameter values, assumed ranges, probability distributions, and bounding assumptions used in the abstractions of radionuclide release rates and solubility limits in the total system performance assessment are technically defensible and reasonable based on data from the Yucca Mountain region, laboratory tests, and natural analogues. For example, parameter values, assumed ranges, probability distributions, and bounding assumptions adequately reflect the range of environmental conditions expected inside breached waste packages.

(3) The U.S. Department of Energy uses reasonable or conservative ranges of parameters or functional relations to determine effects of coupled thermal-hydrologic-chemical processes on radionuclide release. These values are consistent with the initial and boundary conditions and the assumptions for the conceptual models and design concepts for natural and engineered barriers at the Yucca Mountain site. If any correlations between the input values exist, they are adequately established in the total system performance assessment. For example, estimations are based on a thermal loading and ventilation strategy; engineered barrier system design (including drift liner, backfill, and drip-shield); and natural system masses and fluxes that are consistent with those used in other abstractions.

(4) Uncertainty is adequately represented in parameter development for conceptual models, process models, and alternative conceptual models considered in developing the abstraction of radionuclide release rates and solubility limits, either through sensitivity analyses, or use of bounding analyses.

(8) The U.S. Department of Energy adequately considers the uncertainties, in the characteristics of the natural system and engineered materials, such as the type, quantity, and reactivity of material, in establishing initial and boundary conditions for conceptual models and simulations of thermal-hydrologic-chemical coupled processes that affect radionuclide release.

4.3 CODES, STANDARDS, AND REGULATIONS

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

INTENTIONALLY LEFT BLANK

5. ASSUMPTIONS

Assumption 1: The thermodynamic databases in the data0.ymp.R* series are parameterized such that the pressure is a function of temperature: 1.013 bar (101.3 kPa) up to 100°C, and following the steam/liquid saturation pressure for pure water from 100°C to 300°C. For purposes of qualifying the thermochemical databases data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756], data0.ymp.R4 (Output DTN: SN0410T0510404.002), and data0.ymp.R5 (Output DTN: SN0612T0502404.014) a two-part assumption is made. First, it is assumed that small differences between the database pressure and the actual pressure can be neglected. Second, it is assumed that systems modeled with these databases at temperatures above the boiling point of water (not necessarily 100°C, but close to it) will be sufficiently pressurized that aqueous solutions are stable (will not simply vaporize). The minimum pressure for this condition is the steam/liquid saturation pressure for pure water used in this series of databases.

The pressure in the repository is expected to remain close to the ambient range. Average total pressure at the top and bottom of the unsaturated zone is 85.8 to 91.8 kPa, respectively (BSC 2004 [DIRS 169565], Table I-2). Because of the elevation effect on atmospheric pressure, the boiling temperature of pure water in the repository is reduced to 96°C to 97°C (BSC 2004 [DIRS 161237] Section 6.7.2.6). Thermohydrologic modeling (e.g., BSC 2004 [DIRS 169565]) does not anticipate the development of significant overpressure during the thermal pulse period, owing to the permeability of the rock and the relatively slow rate of heating and vaporization of liquid water present. Higher pressure might occur in laboratory experiments used to develop or test thermodynamic or kinetic data under pressure conditions that exceed those anticipated in the actual repository (for an example, see Delany 1985 [DIRS 100134]). It is not anticipated to occur in the actual repository.

A difference between actual pressure and the data file reference pressure (for the temperature of interest) in theory requires correction ("pressure correction") to the thermodynamic data. The theory is discussed in many parts of the chemical thermodynamics literature. Johnson et al. (1992 [DIRS 101632]) provide a discussion in the contents of the SUPCRT92 computer code (SUPCRT92 V1.0; see Section 3.1.2), which is used in this analysis report. In essence, the effect of pressure difference on the equilibrium constant of a reaction is relatively weak, at least for reactions among condensed species. Pressure differences of several tens of bars have little effect. Pressure corrections are commonly neglected in the temperature and pressure ranges found in geothermal systems (e.g., Helgeson 1969 [DIRS 137246]), which bound the ranges pertinent to the repository.

The databases in the data0.ymp.R* series are designed to support the modeling of dilute aqueous solutions (such that the properties of solvent water do not differ appreciably from pure water). They cannot be used to model the deliquescence of highly soluble salts at any temperature, as they are not consistent with the usage of a high-ionic strength activity coefficient model. To model salt deliquescence at temperatures above 100°C, a different kind of database, such as one in the data0.ypf.R* series (e.g., BSC 2005 [DIRS 174223]) is required.

This assumption (both parts) is appropriate for the anticipated repository temperature-pressure conditions. No confirmation or additional investigation of this assumption is needed. This assumption is used throughout Section 6 in the data qualification discussion.

6. SCIENTIFIC ANALYSIS DISCUSSION

The primary source of data making up the data0.ymp.R2 thermochemical database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) is the original database in the series, data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]). In support of the changes made in developing data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), data0.ymp.R4 (Output DTN: SN0410T0510404.002), and data0.ymp.R5 (Output DTN: SN0612T0502404.014), 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. The source inputs are then either directly used or processed into a form appropriate for use.

There are several types of data required to be incorporated into a thermochemical database in the data0.ymp.R* series. The first two are the names (symbols) of the chemical elements represented in the database and their respective atomic weights. The amount of data here is rather limited and readily available. Next are the names of the phases and chemical species. The phases may be solid, liquid, or gas. Some phases, mainly of the solid variety, consistent of a single chemical species, and both may be referred to by the same name (e.g., Quartz, Calcite, Albite). This is also true of a few liquid species (e.g., Mercury, Bromine).

For each chemical species, the chemical composition must be known. Distinctions may be required to account for structural differences (e.g., isomerism, polymorphism). Occasionally isotopic distinctions must also be made. However, for the thermochemical databases in the data0.ymp.R5 series, isotopic distinctions are not made and natural or usual isotopic abundances are assumed. The point is that thermodynamic properties depend on what a phase or a chemical species really is. In some instances, the characterization of a phase or species is not entirely known, or it is known but only for a sample (or a few samples) of material whose nature is significantly variable. This is mainly a problem with certain solids which have varying degrees of crystallinity and/or varying degree of water content. Derived thermodynamic properties may have an effective or empirical nature and should be used with appropriate care.

The actual thermodynamic data required for a chemical species in a thermochemical database in the data0.ymp.R* series is the equilibrium constant (log K) on the EQ3/6 temperature grid (0-25-60-100-150-200-250-300°C). For solids, molar volumes are desirable for making volumetric calculations (these are "thermodynamic" properties, but are not used as such, as would be the case if one were making thermodynamic pressure corrections to the equilibrium constants). The remaining thermodynamic data pertain to thermodynamic activity coefficients for aqueous species. For databases in the present series, these include two Debye-Hückel parameters and the B-dot parameter of Helgeson (1969 [DIRS 137246]). Basically these are constants whose values are needed on the same EQ3/6 temperature grid used for equilibrium constants. The only species-specific data are the "azero" or "ion size" parameters (hard core diameters) for which one constant value is assigned to each solute species.

Thermodynamic data are reduced, tabulated, and reported in different forms. Some reports give equilibrium constants for chemical reactions (e.g., dissolution or dissociation). This is common for low-temperature studies of solubility or aqueous complexation. Where some range of temperature is addressed, equilibrium constants may be tabulated for various temperatures, or represented by some temperature function. The log K for a reaction can be calculated over a range of temperature from the value at some reference temperature (usually 25°C), the entropy of reaction (ΔS_r^o) at the reference temperature, and the heat capacity of reaction ($\Delta C_{p,r}^o$), which in general will have some dependence on temperature. Some sources present data in this format , though it is often limited to the equilibrium constant and entropy of reaction at or near 25°C (e.g., Martell and Smith 1976 [DIRS 127382]). The other common form of reporting thermodynamic data is as the standard Gibbs energy of formation (ΔG_f^o), enthalpy of formation (ΔH_f^o), and entropy (S^o), usually along with some form of heat capacity data (tabulated as a function of temperature, or given as a temperature function). This form is used by such sources as works by Barin and Platzki (1995 DIRS 157865]), Robie and Hemingway (1995 [DIRS 153683]), and Chase (1998 [DIRS 157874]). Equilibrium constants can then be calculated from the Gibbs energies of formation of the chemical species appearing in a reaction using standard thermodynamic relations (which is discussed in Section 6.1).

Constructing a thermochemical database is a significant endeavor. To maximize efficiency and credibility, the thermochemical databases in the data0.ymp.R* (and data0.ypf.R*) series rely heavily on existing compilations and evaluations. A principal source is a geochemical database that is associated with the computer code SUPCRT92 (Johnson et al. 1992 [DIRS 101632]). SUPCRT92 is based on the work of H.C. Helgeson and various students and coworkers (e.g., Helgeson et al. 1978 [DIRS 101596]; Helgeson and Kirkham 1974 [DIRS 157904]; Shock and Helgeson 1988 [DIRS 144817]; Shock et al. 1997 [DIRS 150770]; Shock et al. 1997 [DIRS 127953]). The SUPCRT92 database contains standard Gibbs energies, enthalpies, and entropies of many mineral and aqueous species of geochemical interest. It also contains standard heat capacity coefficients and standard molar volumes for mineral species, and equation of state data for aqueous species, including equivalent data for water (H_2O liquid). The SUPCRT92 code can be used to calculate log K values (and other standard state thermochemical properties, and Debye-Huckel parameters) as functions of temperature. The use of SUPCRT92 is discussed in detail in Section 6.1.2.

The other principal source of data is the OECD/NEA *Chemical Thermodynamics* series sponsored by the Nuclear Energy Agency (NEA) of the Organisation for Economic Co-operation and Development (OECD) (e.g., Grenthe et al. 1992 [DIRS 101671]; Silva et al. 1995 [DIRS 102087]; Rare et al. 1999 [DIRS 157912]; Lemire et al. 2001 [DIRS 159027]; Guillaumont et al. 2003 [DIRS 168382]; Gamsjäger et al. 2005 DIRS [178266]; Olin et al. 2005 DIRS [177640]). These constitute handbook sources. These sources are recent, of exceptional quality and thoroughness, and are generally well-accepted in the scientific community, particularly the international nuclear waste disposal community. They contain the most transparent and traceable review to be found among major compilations of thermodynamic data. The data in this series are consistent with the *CODATA Key Values for Thermodynamics* (Cox et al. 1989 [DIRS 150874]).

Other major compilations are also used. These include works by Barin and Platzki (1995 [DIRS 157865]), Binnewies and Milke (1999 [DIRS 158955]), Babushkin et al. (1985 [DIRS 116981]), Chase (1998 [DIRS 157874]), Smith and Martell (1976 [DIRS 127382]), and Martell and Smith (1982 [DIRS 159196]). The work by 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 by Binnewies and Milke (1999 [DIRS 158955]). The other sources noted above are likewise comprehensive compilations of thermodynamic data that include extensive lists of references. These various handbook sources 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.

Another compilation that is used is *The NBS Tables of Chemical Thermodynamic Properties, Selected Values for Inorganic and C_1 and C_2 Organic Substances in SI Units* (Wagman et al. 1982 [DIRS 159216]; Wagman et al. 1989 [DIRS 179315]). This compilation is less favored, despite the sponsorship of a premier standards organization, because it lacks transparency and traceability. It simply gives recommended values, without including references.

Section 6.1 describes the approach used to convert the data into the forms and parameters used in the thermochemical databases data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), data0.ymp.R4 (Output DTN: SN0410T0510404.002), and data0.ymp.R5 (Output DTN: SN0612T0502404.014). In Sections 6.2 through 6.4, the data, as collected from the sources, are evaluated and qualified for use in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), data0.ymp.R4 (Output DTN: SN0410T0510404.002), and data0.ymp.R5 (Output DTN: SN0612T0502404.014) using the approaches described in Section 6.1. However, data unique to data0.ymp.R5 (Output DTN: SN0612T0502404.014) are not included here. Those data are addressed in Sections 6.7 and 6.8. In this manner, the thermochemical databases data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), data0.ymp.R4 (Output DTN: SN0410T0510404.002), and data0.ymp.R5 (Output DTN: SN0612T0502404.014) are qualified. SUPCRT92 (Johnson et al. 1992 [DIRS 101632]) calculations provide a core of data (see Section 6.1.2). Otherwise, 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 (See Section 6.1.3).

Qualified data from two sources are used: data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]), which is the pre-existing project database used for geochemistry calculations, and *sprons98.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886]), a SUPCRT92 database that supports the data0.ymp.R0 database (DTN: MO0009THRMODYN.001 [DIRS 152576]) and contains organic data.

For the development of data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), the SUPCRT92 database *sprons98.dat* was modified to produce a new one called *speq02.dat*. This newer database uses EQ3/6-style species names. Also, the thermodynamic data for quartz (SiO_2) and SiO2(aq) were modified for consistency with the "Rimstidt" paradigm of silica solubility (see Section 6.1.5). Later, for the development of data0.ymp.R5 (Output DTN: SN0612T0502404.014), a further modification of the SUPCRT92 database called *speq06.dat* was created to incorporate consistency with the CODATA key data (Cox et al. 1989 [DIRS 150874]) for phosphate species (see Section 6.7.7).

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

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 data0.ymp.R4 database (Output DTN: SN0410T0510404.002), and the data0.ymp.R5 database (Output DTN: SN0612T0502404.014). 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 that support data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), data0.ymp.R4 (Output DTN: SN0410T0510404.002), and data0.ymp.R5 (Output DTN: SN0612T0502404.014) are contained in the corresponding supporting calculations data packages (DTN: MO0302SPATHDYN.001 [DIRS 161886], Output DTN: SN0410T0510404.001; and Output DTN: SN0702T0502404.015).

6.1 APPROACH TO DATA REDUCTION

While the basic thermodynamic data used in the development of the data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), data0.ymp.R4 (Output DTN: SN0410T0510404.002), and data0.ymp.R5 (Output DTN: SN0612T0502404.014) databases 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 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 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 Heat Capacity of Solids as a Function of Temperature and Its Relationship to Gibbs 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):

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

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 by Helgeson et al. (1978 [DIRS 101596]). However, Johnson et al. (1992 [DIRS 101632], p. 910) write the equation as:

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

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 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), data0.ymp.R4 (Output DTN: SN0410T0510404.002), and data0.ymp.R5 (Output DTN: SN0612T0502404.014) databases, 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 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. Helgeson et al. (1978 [DIRS 101596], Table 8, pp. 120 to 125) gives a number of examples. Cristobalite, one mineral of interest to the Yucca Mountain Project, undergoes a phase transition at 543 K (270°C), just inside the range of possible interest. Kyanite (Al_2SiO_5) has a transition at 466 K (193°C), but this mineral has little if any relevance to the Yucca Mountain Project.

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 to 73) (in all instances the old sign convention for "c" is employed as in Equation 6-1). 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., *sprons98.dat*; DTN: MO0302SPATHDYN.001 [DIRS 161886]) if values are desired as input for new calculations. These updated data also include a broader range of solids and gases. In both the study by 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 J; Weast and Astle 1979 [DIRS 102865]). Also in both places the tabulated values are actually expressed as a, $b \times 10^3$, and $c \times 10^{-5}$. 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, $b \times 10^3 = 8.20$, and $c \times 10^{-5} = -2.70$, meaning a = 11.22, $b = 8.20 \times 10^{-3}$, and $c = -2.70 \times 10^5$.

Heat capacity temperature functions such as the Maier-Kelley equation are important because they are needed to calculate thermodynamic properties such as the Gibbs energy as functions of temperature. In relation to EQ3/6, their role is to provide the Gibbs energies of solids and gases, thus the Gibbs energy change for reactions involving these species, and finally the corresponding equilibrium constants (log K values) on the EQ3/6 temperature grid. The temperature grid of relevance to the data0.ymp.R* databases consists of values for 0°C, 25°C, 60°C, 100°C, 150°C, 200°C, 250°C, and 300°C; corresponding pressures are usually 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 energies is discussed by both Helgeson et al. (1978 [DIRS 101596], pp. 28 to 30) and Johnson et al. (1992 [DIRS 101632], pp. 909 to 911). The equations as given in Johnson et al. (1992 [DIRS 101632]) are for the special case of Gibbs energy of reactions among minerals. To obtain the equations for the Gibbs energy for a single mineral, one is better served by referring to the work by 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 energy of a solid as a function of temperature T and pressure P is from Helgeson et al. (1978 [DIRS 101596], p. 28):

$$\Delta G^{o(app)}_{f,\,T,\,P} = \Delta G^{o}_{f,\,T_r,\,P_r} - S^{o}_{T_r,\,P_r}(T - T_r) + \int_{T_r}^{T} C^{o}_{P_r}\,dT - T\int_{T_r}^{T} C^{o}_{P_r}\,d\ln T + \int_{P_r}^{P} V^{o}_{T}\,dP \quad \text{(Eq. 6-3)}$$

where T_r is the reference temperature of 298.15 K (25°C), P_r is the reference pressure of 1 bar, $\Delta G^{o}_{f,\,T_r,\,P_r}$ is the actual standard partial molar Gibbs energy of formation from the elements at the reference temperature and pressure, $S^{o}_{T_r,\,P_r}$ is the corresponding standard molar entropy, V^{o}_{T} is the corresponding standard partial molar volume at temperature T (for many solids, this is closely approximated by $V^{o}_{T_r,P_r}$, thus simplifying the final integral in this equation), and $C^{o}_{P_r}$ 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 energy relation is immediately pertinent here and therefore Equation 6-3 was used to retrieve log K data for the data0.ymp.R* databases.

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

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

and

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

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 by Haas and Fisher (1976 [DIRS 158983]):

$$C^o_{P_r} = a + 2bT + \frac{c}{T^2} + fT^2 + \frac{g}{\sqrt{T}} \qquad \text{(Eq. 6-6)}$$

(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 energy as a function of temperature. Alternatively, if one uses the retrieval equations for the Gibbs 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 Equation 6-6 can be used in the Maier-Kelley equation if the coefficient for the terms are zero (i.e., Equation 6-6 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, Equation 8, p. 430):

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

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.

Equation 6-7 may also be written as:

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

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

$$\begin{aligned}\int_{T_r}^{T} C_{P_r}^{o}\, dT &= a(T - T_r) + \frac{b(T^2 - T_r^2)}{2} + \frac{c(T^3 - T_r^3)}{3} + \frac{d(T^4 - T_r^4)}{4} + e\ln(T/T_r) \\ &- f\left(\frac{1}{T} - \frac{1}{T_r}\right) - \frac{g}{2}\left(\frac{1}{T^2} - \frac{1}{T_r^2}\right) + \frac{2h}{3}\left(T^{3/2} - T_r^{3/2}\right) + 2i\left(\sqrt{T} - \sqrt{T_r}\right) \\ &+ j\left[T(\ln T - 1) - T_r(\ln T_r - 1)\right] + \frac{k}{2}\left[T^2(\ln T - \frac{1}{2}) - T_r^2(\ln T_r - \frac{1}{2})\right]\end{aligned} \qquad \text{(Eq. 6-9)}$$

and

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

Substitution of these results into the generalized retrieval equation then yields the apparent standard molar Gibbs 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 $SiO_2(aq)$. 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 analogue species for use in the specialized spreadsheets discussed below.

The basis species data consisted of the apparent Gibbs energy of formation on the standard EQ3/6 temperature grid (0-25-60-100-150-200-250-300°C). These data were used to compute reaction properties for species whose individual thermodynamic properties are developed entirely in the spreadsheets. Analogue species data are needed to facilitate temperature extrapolations using the isocoulombic/isoelectric method described below. The requisite data for analogue species (which include many if not most basis species) are the standard Gibbs energy of formation and standard entropy, both at 298.15 K 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 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 *sprons98.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886]). The sources of data in this file were described in *Data Qualification Report for Thermodynamic Data File, Data0.ympR0 for Geochemical Code, EQ3/6* (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: MO0302SPATHDYN.001 [DIRS 161886]), 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 SiO_2(aq) (significant change). Both data files are included in DTN: MO0302SPATHDYN.001 [DIRS 161886].

The thermodynamic data for steam (H_2O(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 H_2O 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 H_2O(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: MO0302SPATHDYN.001 [DIRS 161886]). 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 H_2O(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 to develop the log K grids for the data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), data0.ymp.R4 (Output DTN: SN0410T0510404.002), and data0.ymp.R5 (Output DTN: SN0612T0502404.014) databases. 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. All the spreadsheets used in developing the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]) are included in DTN: MO0302SPATHDYN.001 [DIRS 161886]. All of those used to generate additional or changed data for data0.ymp.R4 (Output DTN: SN0410T0510404.002) are included in Output DTN: SN0410T0510404.001. All of those used to generate additional or changed data for data0.ymp.R5 (Output DTN: SN0612T0502404.014) are included in Output DTN: SN0702T0502404.015.

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 are 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 analogue 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 *Minerals_cal.xls*, *Minerals_j.xls*, *Solids_cal.xls*, and *Solids_j.xls*. 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 energy and standard entropy of a species at 298.15 K and 1 bar pressure along with the heat capacity coefficients. The apparent Gibbs energy (the same Gibbs energy used in SUPCRT92) is then calculated on the EQ3/6 temperature grid (0-25-60-100-150-200-250-300°C). The retrieval equation for this is given in the heat capacity discussion (Section 6.1.1, Equation 6-6). This Gibbs 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 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 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 *sprons98.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886]). 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, SiO_2(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 to 127; Puigdomenech et al. 1999 [DIRS 159205], p. 65) to obtain the apparent Gibbs 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 and earlier report (CRWMS M&O 2000 [DIRS 152575], pp. 13 to 17). Comments on the Criss-Cobble method are provided by Puigdomenech et al. (1999 [DIRS 159205], pp. 64 and 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 energy and standard entropy at 298.15 K and 1 bar for the species in question as well as for other species (basis or analogue) 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:

$$PuO_2SO_4(aq) + UO_2^{2+} = UO_2SO_4(aq) + PuO_2^{2+} \quad \text{(Eq. 6-11)}$$

As suggested by this example, most of the best isocoulombic reactions are exchange reactions. Here the properties of $PuO_2SO_4(aq)$ could be extrapolated if sufficient data (entropies at 298.15 K and full Gibbs energy grids) were available for $UO_2SO_4(aq)$ (an "analogue" species) and two basis species, UO_2^{2+} and PuO_2^{2+}. 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:

$$HSO_4^{-} + OH^{-} = SO_4^{2-} + H_2O \quad \text{(Eq. 6-12)}$$

Normally an isoelectric reaction is required to deal with very highly charged species for which there are few usable analogues. Note also that most EQ3/6 reactions are not isocoulombic/isoelectric (for example: $CdSO_4(aq) = SO_4^{2-} + Cd^{2+}$). 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 energy of reaction and entropy of reaction at 298.15 K and 1 bar for the isocoulombic or isoelectric reaction. The Gibbs 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 energy grid for the species in question is then extracted from the Gibbs energy of reaction grid in a calculation that resembles but partially inverts the process of calculating a Gibbs energy of reaction grid from the Gibbs energy grids for the species in the reaction. This requires copying Gibbs energy grids for basis and analogue 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 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:

$$C_p^0 = a + bT + c / T^2 \quad \text{(Eq. 6-13)}$$

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 (Equation 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:

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

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

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

where $\nu_{j,i}$ is the number of moles of the j^{th} oxide formula unit in one mole of the i^{th} solid.

The Maier-Kelley coefficients of most oxides given in Table 2 in the study by Helgeson et al. (1978 [DIRS 101596]) were used in the estimation. Note that the Maier-Kelley equation in the study by Helgeson et al. (1978 [DIRS 101596]) differs from Equation 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

Equations 55, 56, and 57 in the report by 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 the report by 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 Energies of Formation at 25°C from Measurements at Other Temperatures

To obtain ΔG_f° (T = 298.15 K) of a solid from solubility measurements at temperatures other than 25°C (say 30°C), ΔG_f° (T = 303.15 K) has to be obtained first. This requires the ΔG_f° (T = 303.15 K) data for involved species. Those ΔG_f° (T = 303.15 K) data were obtained by running SUPCRT92 with the *sprons98.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886]) or its modified version *speq02.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886]).

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

6.1.5 Aqueous Silica and 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]), data0.ymp.R4 (Output DTN: SN0410T0510404.002), and data0.ymp.R5 (Output DTN: SN0612T0502404.014) 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 by 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 [SiO_2(aq)]. These properties have long been somewhat controversial, particularly at temperatures near 25°C (Walther and Helgeson 1977 [DIRS 133240], pp. 1324 to 1328).

In general, the properties of SiO_2(aq) (or the alternative species H_4SiO_4(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 of 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 of 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 SiO_2 (about 1.83×10^{-4} molal). As support for these higher results, he cites both a problem with data from Morey et al. (1962 [DIRS 159198]) 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 SiO_2 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 SiO_2(aq) and quartz were put in the SUPCRT92 data file *speq02.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886]). Gibbs energy grids (values of the Gibbs 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 energy grid as a function of temperature calculated for SiO_2(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: MO0302SPATHDYN.001 [DIRS 161886]). The log K values from the relevant SUPCRT92 "plot" (.kxy) files were then pasted into the relevant mineral data blocks for data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]).

Table 6-1. Comparison of $\Delta G_f°$ Obtained from data0.ymp.R2 with the $\Delta G_f°$ from Gunnarsson and Arnórsson for $SiO_2(aq)$

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	**$\Delta G_f°$ (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. The SUPCRT92 data file properties for species like $HSiO_3^-$ could have been reevaluated; SUPCRT92 calculations would then have produced new log K values identical to the old ones. For the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), that was not carried out as it was an unnecessary step. Calculation of the appropriate old log K values with the current SUPCRT92 data file (*speq02.dat*; DTN: MO0302SPATHDYN.001 [DIRS 161886]) can be performed by specifying the "SiO2(aq)(Fournier)" species for $SiO_2(aq)$ in the relevant reactions. It is noted that the predominance of silica species such as $HSiO_3^-$ is restricted to alkaline pH values greater than 9 to 10. The predicted pH values for waters of interest to YMP are lower (BSC 2004 [DIRS 169860]).

The revision as carried out for the silicate minerals assumed a calorimetric or equivalent origin of the constraining data that is independent of any assumptions about the enthalpy of formation of $SiO_2(aq)$. 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 by 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 to 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 $HSiO_3^-$). The appropriate log K values can be calculated using the *speq02.dat* data file (DTN: MO0302SPATHDYN.001 [DIRS 161886]) 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 by Helgeson et al. (1978 [DIRS 101596]) to obtain the reported values for the standard Gibbs 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 by Helgeson et al. (1978 [DIRS 101596]) to determine the standard Gibbs 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 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 298.15 K and the Gibbs energies of formation then extracted, a significant further correction would be necessary. However, the exact calculational path was not given by 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 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 to 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 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 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 and 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

SiO_2(aq). Therefore, multiplying these differences by the number of SiO_2 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 DTN: MO0302SPATHDYN.001 [DIRS 161886], spreadsheet: *silica.xls*.

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 by 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 by Gunnarsson and Arnórsson (2000 [DIRS 160465]), who also follow 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]. Also DTN: MO0302SPATHDYN.001 [DIRS 161886], SUPCRT92 data file *speq02.dat*; DTN: MO0302SPATHDYN.001 [DIRS 161886], spreadsheet calculation given in *Rimstidt_Silica_TJW.xls*.

It is noted that 28 silicon-bearing solids (all but "Silicon", Si, are silicates) and 2 such gas species were not corrected to the Rimstidt paradigm in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). Most of these species (the uranium mineral coffinite, $USiO_4$ is an exception) do occur rarely or not at all in natural geologic systems but may be encountered in interactions with engineered materials. The resulting difference in log K is generally about 0.25 unit per Si in the chemical formula. The basic thermodynamic data for these species were carried over from data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]) into the revised data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]). The affected species have been 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]). The process was to find all species with reactions involving SiO_2(aq) for which the data are unchanged, and removing the two special cases discussed earlier in this subsection (amorphous silica and sepiolite) for which the log K data should be unchanged. A list of the affected unrevised species is given in Table 7-2. The data for these species have not been subsequently revised in data0.ymp.R4 (Output DTN: SN0410T0510404.002) or data0.ymp.R5 (Output DTN: SN0612T0502404.014).

6.1.6 Clarification of the Discrepancy in $\Delta G_f°$ Data for Ca-Bearing Silicates

In comparing thermodynamic parameters such as $\Delta G_f°$ for Ca-bearing silicates against their given source in the database (i.e., Helgeson et al. 1978 [DIRS 101596], Table 8, pp. 120 to 125), a discrepancy was found between these values and those listed in the former source. The $\Delta G_f°$ values are correct in the databases *sprons98.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886]), *speq02.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886]), and accordingly in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). Moreover, these $\Delta G_f°$ values for Ca-bearing silicates are also internally consistent with other species. It is not clear why the values given by 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 energy of formation data for most of the minerals in the SUPCRT92 database (e.g., *sprons98.dat*, DTN: MO0302SPATHDYN.001 [DIRS 161886] and *speq02.dat,* DTN: MO0302SPATHDYN.001 [DIRS 161886]) 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 energies of formation (i.e., $\Delta G_f°$) 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. Other 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 energies of formation of the minerals, such that only the values at 298.15 K 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 ($CaCO_3$, the stable form at 298.15 K and 1 bar pressure) was used instead. The Gibbs energy of formation at 298.15 K and 1 bar pressure for calcite was itself regressed by Helgeson et al. (1978 [DIRS 101596], pp. 87 and 88) from a solubility experiment. This required the assumption of values for the Gibbs energies of formation of the Ca^{2+} and CO_3^{2-} ions at 298.15 K and 1 bar pressure as detailed in Helgeson et al. (1978 [DIRS 101596]). Aragonite (a less stable form of $CaCO_3$ at ambient conditions) was treated in a similar manner, using solubility data from the same sources. The data for lime (CaO) and monticellite ($CaMgSiO_4$) 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 by 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 energies of formation of the ions (including Ca^{2+} and CO_3^{2-}) had occurred. In order to obtain the original equilibrium constant for calcite dissolution (and hence a consistent set of saturation indices), the Gibbs energy of formation of calcite at 298.15 K and 1 bar pressure needed to be recalculated. The corresponding Gibbs energy of formation of every mineral linked to calcite (directly or indirectly) therefore also needed to be recalculated (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 energy of formation of calcite at 298.15 K 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" in the spreadsheet *SUPCRT92 Ca Minerals Analysis.xls* (Output 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 energies of formation of the ions at 298.15 K 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 energy of formation of aragonite is 192 cal/mol, not 220 cal/mol. The affected Ca-bearing silicates along with the corrected Gibbs 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 the study by 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 to Updated Ca^{2+} 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	$CaCO_3$	-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	$Ca_2Al_2SiO_7$	-903588	-903148	220	L
Grossular	$Ca_3Al_2Si_3O_{12}$	-1496967	-1496307	220	L
Andradite	$Ca_3Fe_2Si_3O_{12}$	-1297479	-1296819	220	L
Monticellite	$CaMgSiO_4$	-512829	-512829	0	NL
Merwinite	$Ca_3Mg(SiO_4)_2$	-1037186	-1036526	220	L
Akermanite	$Ca_2MgSi_2O_7$	-879802	-879362	220	L
Clinozoisite	$Ca_2Al_3Si_3O_{12}(OH)$	-1549680	-1549240	220	L
Zoisite	$Ca_2Al_3Si_3O_{12}(OH)$	-1549619	-1549179	220	L
Ordered Epidote	$Ca_2FeAl_2Si_3O_{12}(OH)$	-1451346	-1450906	220	L
Epidote	$Ca_2FeAl_2Si_3O_{12}(OH)$	-1451346	-1450906	220	L
Lawsonite	$CaAl_2Si_2O_7(OH)_2{\cdot}H_2O$	-1073628	-1073408	220	L
Wollastonite	$CaSiO_3$	-369445	-369225	220	L
Ca-Al Pyroxene	$CaAl_2SiO_6$	-742287	-742067	220	L
Diopside	$CaMg(SiO_3)_2$	-724000	-723780	220	L
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	-2770685	-2770245	220	L
Pargasite	$NaCa_2Mg_4Al(Al_2Si_6O_{22})(OH)_2$	-2847168	-2846728	220	L
Anorthite	$CaAl_2Si_2O_8$	-954298	-954078	220	L
Wairakite	$CaAl_2Si_4O_{12}{\cdot}2H_2O$	-1477652	-1477432	220	L
Laumontite	$CaAl_2Si_4O_{12}{\cdot}4H_2O$	-1597043	-1596823	220	L
Prehnite	$Ca_2Al(AlSi_3O_{10})(OH)_2$	-1390537	-1390097	220	L
Margarite	$CaAl_2(Al_2Si_2O_{10})(OH)_2$	-1394370	-1394150	220	L

Sources: Column 3: Helgeson et al. 1978 [DIRS 101596], Table 8, pp. 120 to 125.
Column 4: *sprons98.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886]); data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]).

NOTE: 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.

The thermodynamic data published by 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 (273.16 K to 573.15 K) (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 Grids for Neptunium and Plutonium Aqueous Species Used in data0.ymp.R2

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	-	-	-	-	-	-
$(NpO_2)_2CO_3(OH)_3^-$	$(NpO_2)_2CO_3(OH)_3^- + 4H^+ = 2NpO_2^{++} + HCO_3^- + 3H_2O$	-	13.2180	-	-	-	-	-	-
$(NpO_2)_3(CO_3)_6^{(-6)}$	$(NpO_2)_3(CO_3)_6^{(-6)} + 6H^+ = 3NpO_2^{++} + 6HCO_3^-$	-	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	-	-	-	-	-	-
$Np(CO_3)_3^{---}$	$Np(CO_3)_3^{---} + 3H^+ = Np^{+++} + 3HCO_3^-$	-	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	-	-	-	-	-	-
$NpCl^{+++}$	$NpCl^{+++} = Np^{++++} + Cl^-$	-	- 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	-	-	-	-	-	-
$NpO_2(CO_3)_2OH^{----}$	$NpO_2(CO_3)_2OH^{----} + 3H^+ = NpO_2^{++} + 2HCO_3^- + H_2O$	-	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 Grids for Neptunium and Plutonium Aqueous Species Used in data0.ymp.R2 (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	-	-	-	-	-	-
$NpO_2(OH)_2^{-}$	$NpO_2(OH)_2^{-} + 2H^{+} = NpO_2^{+} + 2H_2O$	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_2Cl^{+}	$NpO_2Cl^{+} = NpO2^{++} + Cl^{-}$	-	-0.4000	-	-	-	-	-	-
$NpO_2CO_3^{-}$	$NpO_2CO_3^{-} + H^{+} = NpO_2^{+} + HCO_3^{-}$	-	5.3814	-	-	-	-	-	-
$NpO_2CO_3(aq)$	$NpO_2CO_3(aq) + H^{+} = NpO_2^{++} + HCO_3^{-}$	-	1.0229	-	-	-	-	-	-
$NpO_2F(aq)$	$NpO_2F(aq) = NpO_2^{+} + F^{-}$	-	-1.2000	-	-	-	-	-	-
NpO_2F^{+}	$NpO_2F^{+} = NpO_2^{++} + F^{-}$	-	-4.5700	-	-	-	-	-	-
$NpO_2F_2(aq)$	$NpO_2F_2(aq) = NpO_2^{++} + 2F^{-}$	-	-7.6000	-	-	-	-	-	-
$NpO_2H_2PO_4^{+}$	$NpO_2H_2PO_4^{+} = NpO_2^{++} + H^{+} + HPO_4^{--}$	-	-11.7320	-	-	-	-	-	-
$NpO_2HPO_4^{-}$	$NpO_2HPO_4^{-} = NpO_2^{+} + HPO_4^{--}$	-	-2.9500	-	-	-	-	-	-
$NpO_2HPO_4(aq)$	$NpO_2HPO_4(aq) = NpO_2^{++} + HPO_4^{--}$	-	-6.2000	-	-	-	-	-	-
$NpO_2IO_3(aq)$	$NpO_2IO_3(aq) = NpO_2^{+} + IO_3^{-}$	-	-0.5000	-	-	-	-	-	-
$NpO_2IO_3^{+}$	$NpO_2IO_3^{+} = NpO_2^{++} + IO_3^{-}$	-	-1.2000	-	-	-	-	-	-
$NpO_2OH(aq)$	$NpO_2OH(aq) + H^{+} = NpO_2^{+} + H_2O$	12.3159	11.3072	10.0823	8.9121	7.7057	6.7012	5.8331	5.0502
NpO_2OH^{+}	$NpO_2OH^{+} + H^{+} = NpO_2^{++} + H_2O$	-	5.1000	-	-	-	-	-	-
$NpO_2SO_4^{-}$	$NpO_2SO_4^{-} = NpO_2^{+} + SO_4^{--}$	- 0.0950	-0.3604	- 0.9237	- 1.6673	- 2.6546	- 3.6824	- 4.7698	- 5.9887
$NpO_2SO_4(aq)$	$NpO_2SO_4(aq) = NpO_2^{++} + SO_4^{--}$	- 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	-	-	-	-	-	-
$NpOH^{+++}$	$NpOH^{+++} + H^{+} = Np^{++++} + H_2O$	-	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 Grids for Neptunium and Plutonium Aqueous Species Used in data0.ymp.R2 (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	-	-	-	-	-	-
$PuCl^{+++}$	$PuCl^{+++} = Pu^{++++} + Cl^-$	-	- 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
$PuH_3PO_4^{++++}$	$PuH_3PO_4^{++++} = Pu^{++++} + HPO_4^{--} + 2H^+$	-	- 12.9512	-	-	-	-	-	-
PuI^{++}	$PuI^{++} = Pu^{+++} + I^-$	-	- 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_2Cl^+	$PuO_2Cl^+ = PuO_2^{++} + Cl^-$	-	- 0.7000	-	-	-	-	-	-
$PuO_2Cl_2(aq)$	$PuO_2Cl_2(aq) = PuO_2^{++} + 2Cl^-$	-	0.6000	-	-	-	-	-	-
$PuO_2CO_3^-$	$PuO_2CO_3^- + H^+ = PuO_2^+ + HCO_3^-$	-	5.2234	-	-	-	-	-	-
$PuO_2CO_3(aq)$	$PuO_2CO_3(aq) + H^+ = PuO_2^{++} + HCO_3^-$	-	- 1.2567	-	-	-	-	-	-
PuO_2F^+	$PuO_2F^+ = PuO_2^{++} + F^-$	-	- 4.5600	-	-	-	-	-	-
$PuO_2F_2(aq)$	$PuO_2F_2(aq) = PuO_2^{++} + 2F^-$	-	- 7.2500	-	-	-	-	-	-
$PuO_2OH(aq)$	$PuO_2OH(aq) + H^+ = PuO_2^+ + H_2O$	-	9.7300	-	-	-	-	-	-
PuO_2OH^+	$PuO_2OH^+ + H^+ = PuO_2^{++} + H_2O$	5.9780	5.5073	5.0185	4.6203	4.2718	4.0208	3.8200	3.6358
$PuO_2SO_4(aq)$	$PuO_2SO_4(aq) = PuO_2^{++} + SO_4^{--}$	- 3.0878	- 3.3003	- 3.6596	- 4.0955	- 4.6821	- 5.3562	- 6.1948	- 7.3529

Table 6-5. Log K Grids for Neptunium and Plutonium Aqueous Species Used in data0.ymp.R2 (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
$PuOH^{++}$	$PuOH^{++} + H^+ = Pu^{+++} + H_2O$	-	6.9000	-	-	-	-	-	-
$PuOH^{+++}$	$PuOH^{+++} + H^+ = Pu^{++++} + H_2O$	1.3638	0.7872	0.1266	- 0.4703	- 1.0585	- 1.5380	- 1.9561	- 2.3367
$PuSCN^{++}$	$PuSCN^{++} = Pu^{+++} + SCN^-$	-	- 1.3000	-	-	-	-	-	-
$PuSO_4^+$	$PuSO_4^+ = Pu^{+++} + SO_4^{--}$	- 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	-	-	-	-	-	-

Source: 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 Data for Some Miscellaneous Aqueous Species

Based on isocoulombic/isoelectric spreadsheet calculations (See Section 6.1.3), the log K grids required for some miscellaneous other aqueous species were calculated (Table 6-6). The first set of grids is for some secondary (redox) species for actinides. These species are used as "auxiliary" or secondary basis species in EQ3/6. 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]). A second set of log K grids was calculated for some titanium hydrolysis species (which are non-basis species) using data taken from Knauss et al. (2001 [DIRS 158998]). A third set of log K grids was calculated for two non-basis molybdenum species (H_2MoO_4(aq) and $HMoO_4^-$) using data from Smith and Martell (1982 [DIRS 159196]). The inputs to all of these calculations are summarized in Table 4-3 in Section 4.1.2.

The calculations for the actinide redox species listed in Table 6-6 are somewhat unusual in that it was necessary to employ isopiestic/isoelectric reactions including solids. It was necessary to employ such calculations to obtain the apparent Gibbs energies of the "strict" basis species Am^{3+}, NpO_2^+, and PuO_2^+ on the standard EQ3/6 temperature grid (0-25-60-100-150-200-250-300°C). As these are strict basis species, they have no associated reactions. For example, the reaction $NpO_2^+ + UO_2 = UO_2^+ + NpO_2$ was employed to obtain the requisite data for NpO_2^+. Then the reaction $Np^{4+} + UO_2 = U^{4+} + NpO_2$ was employed to obtain the apparent Gibbs energy of Np^{4+} on the EQ3/6 temperature grid, and that in turn was used with the results obtained for NpO_2^+ to obtain the log K grid for the EQ3/6 data file reaction $Np^{4+} + 1.5\ H_2O + 0.25\ O_2(g) = NpO_2^+ + 3\ H^+$. The calculations for the other species and reactions were handled analogously. The apparent Gibbs energy grids for the strict and secondary basis species addressed here are not shown in this report, but are incorporated in the library worksheet "Basis Species 4," which appears in most of the *AqueousSpecies_j*.xls* workbooks in folder *\CD\Spreadsheets\Aqueous* of DTN: MO0302SPATHDYN.001 [DIRS 161886]. A potential issue is the use of solid species in isocoulombic/isoelectric reactions, which is somewhat unusual. Where possible, alternative isopiestic/isoelectric reactions were examined, such as $Np^{4+} + CeO_2 = Ce^{4+} + NpO_2$ in place of $Np^{4+} + UO_2 = U^{4+} + NpO_2$. These were found to give generally similar results, usually bounded by a few 100 J/mol. Comparisons are not shown here, but results can be found in workbooks in folder *\CD\Spreadsheets\Basis* of DTN: MO0302SPATHDYN.001 [DIRS 161886]. The data actually used for actinide basis species in the EQ3/6 data file were based on uranium analogues for all oxidation states except the trivalent, for which a chromium analogue was used.

The basis species for titanium is $Ti(OH)_4$(aq). The requisite Gibbs energy grid was obtained using the isocoulombic reaction $Ti(OH)_4$(aq) + Quartz = SiO_2(aq) + Rutile + 2 H_2O. Quartz is the SiO_2 mineral used, while rutile is the TiO_2 mineral employed.

The results summarized by 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 TiO_2 (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 298.15 K. The authors warned that the three-parameter temperature functions were over-fits (fitting function detail not fully supported by the discrete values). The approach taken for data0.ymp.R2 (DTN: MO0302SPATHDYN.000

[DIRS 161756]), data0.ymp.R4 (Output DTN: SN0410T0510404.002), and data0.ymp.R5 (Output DTN: SN0612T0502404.014) 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 298.15 K reaction properties (Gibbs energy of reaction, entropy of reaction) to fit that log K grid. The desired species properties at 298.15 K were then extracted and used in a normal isocoulombic/isoelectric temperature extrapolation to obtain the needed apparent Gibbs 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 H_2O equivalent to that present in *speq02.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886]) 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 from Knauss et al. (2001 [DIRS 158998]) through data corroboration. The extrapolation to 298.15 K (25°C) for this reaction as described above generates a log K value of −1.2859 (Table 6-6) which is larger than that listed in Table 6-7. The range of estimated Gibbs 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 (TiO_2) thermodynamic data were also updated in 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 ($TiO_2(s) + 2\ H_2O = Ti(OH)_4(aq)$) (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 the same rutile solubility reaction present in data0.ymp.R0 (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 Grids for Actinide Redox Species and Titanium Species Used in data0.ymp.R2

		Temperature (ºC)							
Species	**Reaction**	**0.01**	**25**	**60**	**100**	**150**	**200**	**250**	**300**
Secondary Basis Species (Redox)									
Am^{2+} [a]	$Am^{2+} + H^+ + 0.25O_2(g) = Am^{3+} + 0.5H_2O$	66.1230	59.6550	52.1783	45.3165	38.5253	33.1271	28.7110	25.0128
Am^{4+} [a]	$Am^{4+} + 0.5H_2O = Am^{3+} + H^+ + 0.25O_2(g)$	24.4899	23.4320	22.1496	20.9176	19.6484	18.6122	17.7614	17.0643
AmO_2^+ [a]	$AmO_2^+ + 2H^+ = Am^{3+} + 0.5O_2(g) + H_2O$	18.4277	16.8332	15.0507	13.4700	11.9471	10.7457	9.7386	8.8443
AmO_2^{2+} [a]	$AmO_2^{2+} + H^+ = Am^{3+} + 0.75O_2(g) + 0.5H_2O$	24.7620	23.0358	21.0145	19.1413	17.2626	15.7368	14.4484	13.3263
Np^{3+} [b]	$Np^{3+} + H_2O + 0.5O_2(g) = NpO_2^+ + 2H^+$	30.2579	27.6311	24.5634	21.7116	18.8682	16.6225	14.8388	13.4272
$N4^+$ [b]	$Np^{4+} + 1.5H_2O + 0.25O_2(g) = NpO_2^+ + 3H^+$	10.3964	10.5500	10.6102	10.5572	10.4156	10.2690	10.1733	10.1622
NpO_2^{2+} [b]	$NpO_2^{2+} + 0.5H_2O = NpO_2^+ + H^+ + 0.25O_2(g)$	-1.6314	-1.1851	-0.7603	-0.4470	-0.2064	-0.0606	0.0386	0.1247
Pu^{3+} [c]	$Pu^{3+} + H_2O + 0.5O_2(g) = PuO_2^+ + 2H^+$	6.8918	6.3912	5.7651	5.1429	4.4937	3.9785	3.5945	3.3384
Pu^{4+} [c]	$Pu^{4+} + 1.5H_2O + 0.25O_2(g) = PuO_2^+ + 3H^+$	2.3229	3.3087	4.3247	5.1444	5.8616	6.3924	6.8445	7.2858
PuO_2^{2+} [c]	$PuO_2^{2+} + 0.5H_2O = PuO_2^+ + H^+ + 0.25O_2(g)$	-5.8743	-4.9576	-3.9924	-3.1857	-2.4595	-1.9308	-1.5218	-1.1800
Titanium Species									
$Ti(OH)_3^+$ [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									
$H_2MoO_4(aq)$ [f]	$H_2MoO_4(aq) = 2H^+ + MoO_4^{2-}$	-8.9145	-8.2400	-7.8007	-7.7233	-8.0273	-8.6485	-9.5498	-10.8062
$HMoO_4^-$ [f]	$HMoO_4^- = H^+ + MoO_4^{2-}$	-4.0079	-4.2400	-4.6473	-5.1536	-5.8146	-6.5084	-7.2615	-8.1413

Source: 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]); Output DTN: SN0410T0510404.001, spreadsheet: *AqueousSpecies_j_TJW_2_CFJC.xls*
$Ti(OH)_5^- + H^+ = Ti(OH)_4(aq) + H_2O$	-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]); Output DTN: SN0410T0510404.001, spreadsheet: *AqueousSpecies_j_TJW_2_CFJC.xls* ()
$H_2O = H^+ + OH^-$	-	-13.9951	data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576])

Species	**ΔG_f° (25°C) (kJ/mol)**	**Source**
$Ti(OH)_3^+$	-1086.7	Stefánsson 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	Stefánsson 2001 [DIRS 159208], Table 3, p. 229
$Ti(OH)_4(aq)$ [b]	-1309.0	Stefánsson 2001 [DIRS 159208], p. 235
$Ti(OH)_4(aq)$	-1322.7	DTN: MO0302SPATHDYN.001 [DIRS 161886], spreadsheet: *AqueousSpecies_j_TJW_2.xls*
$Ti(OH)_5^-$ [a]	-1479.2	Stefánsson 2001 [DIRS 159208], p. 235
$Ti(OH)_5^-$	-1482.9	DTN: MO0302SPATHDYN.001 [DIRS 161886], spreadsheet: *AqueousSpecies_j_TJW_2.xls*
TiO_2(rutile)	-890.7	Robie et al. 1979 [DIRS 107109]; DTN: MO0302SPATHDYN.001 [DIRS 161886], spreadsheet: *Minerals_j_ERP_rutile.xls* ()
TiO_2(rutile)	-888.8	Robie and Hemingway 1995 [DIRS 153683], p. 222
H_2O	-237.181	Output DTN: SN0410T0510404.001, spreadsheet: *AqueousSpecies_j_TJW_2_CFJC.xls*
H^+	0.0	Output DTN: SN0410T0510404.001, spreadsheet: *AqueousSpecies_j_TJW_2_CFJC.xls*

Output DTN: SN0410T0510404.001 (log K values calculated in spreadsheet *AqueousSpecies_j_TJW_2_CFJC.xls*).

[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 H_2O equivalent to that in *speq02.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886]).

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 to 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 by 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 by Helgeson et al. (1978 [DIRS 101596]). The missing data in such cases consisted of the Gibbs energy of formation and the enthalpy of formation, both at 298.15 K and 1 bar pressure. In other cases, the minerals were ignored by 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 comprise 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^{2+}, and Mg^{2+}.

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 energy of formation (ΔG_f^o) at 298.15 K and 1 bar pressure using an algorithm proposed by Tardy and Garrels (1974 [DIRS 159209]). This is a linear approach that assumes that the Gibbs energy of a sheet silicate is the sum of the product of the Gibbs 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 SiO_2 was identical to that of quartz. This result was dependent on their usage of data for a sepiolite of composition $Mg_2Si_3O_6(OH)_4$ in conjunction with data for talc and chrysotile to regress the Gibbs energies of silicated $Mg(OH)_2$, MgO, and SiO_2. The present regressions use data from Helgeson et al. (1978 [DIRS 101596]). They included data (p. 124) for a sepiolite of composition “$Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$.” 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 Fe_2O_3 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 Fe_2O_3 should have a Gibbs 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 energies of both octahedral and tetrahedral silicated Fe_2O_3. Tardy and Garrels did not distinguish between octahedral and tetrahedral Al_2O_3. 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 Al_2O_3 and Fe_2O_3 was ignored. Nothing in this work addressed the Gibbs energies of silication of SiO_2 and Fe_2O_3 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 H_2O. The Gibbs energies of these silicated components were derived from a regression of known Gibbs 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:

$$CaO(ex) + 2Na^+ = Na_2O(ex) + Ca^{2+} \quad \text{(Eq. 6-17)}$$

They were then adjusted as recommended by Tardy and Garrels (1974 [DIRS 159209]) so that the silicated $K_2O(ex)$ had the same Gibbs energy as silicated K_2O (Wolery 1978 [DIRS 151346], pp. 236 and 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 $\Delta G_f°$ 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 $\Delta G_f°(K_2O(ex)) - \Delta G_f°(K_2O)$ and adding this difference to each of the original $\Delta G_f°$ values in Table 4-5 (see DTN: MO0302SPATHDYN.001 [DIRS 161886], spreadsheet: *Clays_TJW_1_Rev1b.xls*, worksheet: "G matrix").

Table 6-8. $\Delta G_f°$ of Silicated Exchangeable Components

Silicated Component	**Original** **$\Delta G_f°$ (cal/mol)**	**Corrected*** **$\Delta G_f°$ (cal/mol)**
CaO(ex)	-180200	-180062.7
H_2O(ex)	-56000	-55862.7
K_2O(ex)	-185440	-185302.7
Li_2O(ex)	-188000	-187862.7
MgO(ex)	-156900	-156762.7
Na_2O(ex)	-172800	-172662.7

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 energy of formation the same for the K_2O and K_2O(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 298.15 K and 1 bar pressure was obtained using a method described by Helgeson et al. (1978 [DIRS 101596], pp. 43 to 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* of DTN: MO0302SPATHDYN.001 [DIRS 161886]). Next, for a reference reaction involving a similar mineral (Equation 6-18), the changes in the entropy ($\Delta S_s°$) and molar volume ($\Delta V_s°$) 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 spreadsheet *Clays_TJW_1_Rev1b.xls* of DTN: MO0302SPATHDYN.001 [DIRS 161886]). The entropy for the clay ($S°$) was then calculated by:

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

where $\nu_{Fe(III)}$ 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 to 66) that used mostly real oxide components. In both the entropy and heat capacity coefficient estimation schemes, a "structural H_2O" component was used in addition to the real oxide components. Helgeson et al. (1978 [DIRS 101596]) also employed a "zeolitic" H_2O component, though this has no relevance to sheet silicates.

The enthalpy of formation at 298.15 K and 1 bar pressure (ΔH_f^o) was calculated from the corresponding Gibbs 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:

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

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 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 energies with any mixing effects taken out, then when estimating Gibbs energies for other minerals, adding any such effects back in at the end of the process). But mixing corrections were not implemented in the reestimation for data0.ymp.R2 (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 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:

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

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 [$KAl_2AlSi_3O_{10}(OH)_2$] in which an aluminum substitutes for one of what would be four tetrahedral silicons. Assuming that the mixing entities are just Al^{3+} and Si^{4+} (ignoring vacancies and any potential pairing/ordering effects), the Gibbs energies of mixing on the tetrahedral site would be:

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

Taking R to be 1.9872 cal/mol-K (Weast and Astle 1979 [DIRS 102865], p. F-108) and T to be 298.15 K, this Gibbs energy of mixing evaluates to −1,333 cal/mol (−5,577 joule/mol). In contrast, the difference in Gibbs energies of 7Å and 14Å clinochlores as given by 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 energies of the minerals used in the regression. Uncertainties in calorimetric determinations of the Gibbs 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* of 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 Al_2O_3 component was split into separate octahedral and tetrahedral forms. The values obtained by Wolery (1978 [DIRS 151346], p. 236, Table 3b) for these two components were almost identical: −380.08 kcal/mol for Al_2O_{3tetr}, −380.69 kcal/mol for Al_2O_{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 by Tardy and Garrels (1974 [DIRS 159209]) that the Gibbs 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 the study by 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 $\Delta G_f°$ for a suite of minerals against the stoichiometric coefficients of the component oxides. The fitted parameters were the $\Delta G_f°$ 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 energy regression (worksheet "G matrix 0" in spreadsheet *Clays_TJW_0_Rev1b.xls* of DTN: MO0302SPATHDYN.001 [DIRS 161886]) exactly duplicated that reported by 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" in spreadsheet *Clays_TJW_0_Rev1b.xls* of 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 differed. The standard errors of the component values in the Excel output in worksheet "V matrix 0" of spreadsheet *Clays_TJW_0_Rev1b.xls* (DTN: MO0302SPATHDYN.001 [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 (DTN: MO0302SPATHDYN.001 [DIRS 161886], spreadsheet: *Clays_TJW_0_Rev1b.xls*, worksheet: "V matrix 1") 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 of Wolery (1978 [DIRS 151346]) or the first attempted re-creation described above. A second attempt (DTN: MO0302SPATHDYN.001 [DIRS 161886], spreadsheet: *Clays_TJW_0_Rev1b.xls*, worksheet: "V matrix 2") adding instead quartz and hematite (which are not sheet silicates, but which were included in the Gibbs 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 (DTN: MO0302SPATHDYN.001 [DIRS 161886], spreadsheet: *Clays_TJW_0_Rev1b.xls*, worksheet: "V matrix 3") 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 Al_2O_3 components (37.629 cm^3/mol for Al_2O_{3tetr}, 4.099 cm^3/mol for Al_2O_{3oct}). This result had been used to justify a proportionally large difference for analogous Fe_2O_3 components (only a value for a "mean" Fe_2O_3 component could be obtained from the regression itself). In the first attempt to re-create the original regression (DTN: MO0302SPATHDYN.001 [DIRS 161886], spreadsheet: *Clays_TJW_0_Rev1b.xls*, worksheet: "V matrix 0"), an even larger difference between the values for the two Al_2O_3 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 (DTN: MO0302SPATHDYN.001 [DIRS 161886], spreadsheet: *Clays_TJW_0_Rev1b.xls*, worksheet: "V matrix 1") as previously discussed resulted in notably different results. In particular, the values obtained for the two Al_2O_3 components were very close (26.461 ±4.443 cm^3/mol for Al_2O_{3tetr}, 25.030 ±2.802 cm^3/mol for Al_2O_{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 (DTN: MO0302SPATHDYN.001 [DIRS 161886], spreadsheet: *Clays_TJW_0_Rev1b.xls*, worksheets: "Delta Ss Calc," "Delta Vs Calc," and "S calc") 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 (DTN: MO0302SPATHDYN.001 [DIRS 161886], spreadsheet: *Clays_TJW_0_Rev1b.xls*, worksheets: "Cp a Calc," "Cp b Calc," and "Cp c Calc").

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:

$$\begin{gathered} Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 0.33\ SiO_2 = \\ Al_2Si_4O_{10}(OH)_2 + 0.165\ Na_2O(ex) + 0.165\ Al_2O_3 \end{gathered} \qquad \text{(Eq. 6-22)}$$

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 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 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 (cm^3/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 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 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 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 energies of the ripidolites to the physical mixture values and then applied a correction for the ideal Gibbs 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 energy of mixing relation given previously holds at all temperatures, another consideration not included by Wolery (1978 [DIRS 151346]). The appropriate mixing correction is given by:

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

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 energy of a ripidolite. This is close to the Gibbs 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 of Wolery (1978 [DIRS 151346]) are summarized in 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 (Al_2O_3 in the Gibbs energy regression, Al_2O_3 and Fe_2O_3 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 energy method, as the Gibbs energies for the two distinct Al_2O_3 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 by 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 of 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 by Wolery (1978 [DIRS 151346]) in spreadsheet *Clays_TJW_0_Rev1b.xls* of 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* of 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 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 by Helgeson et al. (1978 [DIRS 101596]). These included the Gibbs energy, enthalpy, and entropy for quartz and the Gibbs energy and enthalpy for margarite. These changes were the only ones found by comparing the data from the SUPCRT92 data *speq02.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886]) with the data given by Helgeson et al. (1978 [DIRS 101596], pp. 120 to 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 by Helgeson et al. (1978 [DIRS 101596]). (Note: this increase in solubility is due more to changes in the stability of $SiO_2(aq)$ 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 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 $\Delta G_f°$ and the Recalculated $\Delta G_f°$ Value

	$\Delta G_f°$ (cal/mol)	Source	Temperature (ºC)							
			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

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

Using these new data, the $\Delta G_f°$ values for the silicated oxide components were recalculated in worksheet “G matrix” in spreadsheet *Clays_TJW_1_Rev1b.xls* (DTN: MO0302SPATHDYN.001 [DIRS 161886]). These $\Delta G_f°$ 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 Na_2O values (see Table 6-12). The $\Delta V_f°$ of the silicated oxide components were recalculated in worksheet “V matrix” in spreadsheet *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 $\Delta G_f°$ Values for the Silicated Oxide Components That Are Used to Calculate the $\Delta G_f°$ of the Clay Phases

Oxide	Calculated Silicated $\Delta G_f°$ (cal/mol)	Reported Silicated $\Delta G_f°$ (cal/mol)	Difference (cal/mol)
Al_2O_3	-380339.5	-382400	2060.5
CaO	-166129.9	-	-
Fe_2O_3	-178155.0	-177700	-455.0
FeO	-64098.1	-64100	1.9
H_2O	-57942.1	-59200	1257.9
K_2O	-185302.7	-188000	2697.3
$Mg(OH)_2$	-204224.2	-203300	-924.2
MgO	-148071.6	-149200	1128.4
Na_2O	-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 $\Delta V_f°$ Values for the Silicated Oxide Components That Will Be Used to Calculate the $\Delta G_f°$ of the Clays

Oxide	Calculated Silicated $\Delta V°$ (cm^3/mol)
Al_2O_3	25.483
CaO	19.228
Fe_2O_3	31.567
FeO	13.677
H_2O	14.056
K_2O	45.809
$Mg(OH)_2$	26.975
MgO	8.578
Na_2O	25.050
SiO_2	22.575

Source: DTN: MO0302SPATHDYN.001 [DIRS 161886], spreadsheet: *Clays_TJW_1_Rev1b.xls*, worksheet: "V matrix."

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 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 energies of formation and associated thermodynamic properties. Changes in the Gibbs 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 $SiO_2(aq)$ 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 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

Source: 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 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: data0.ymp.R0, 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 ($K_2Fe^{2+}{}_2Fe^{3+}{}_2Si_8O_{20}(OH)_4$) and ferroaluminoceladonite ($K_2Fe^{2+}{}_2Al_2Si_8O_{20}(OH)_4$). 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 ($\Delta G_f°$, $S°$, $\Delta V_f°$, and the heat capacity coefficients "a," "b," and "c") were summarized in worksheet "Results Summary" of spreadsheet *Clays_TJW_1_Rev1b.xls* (DTN: MO0302SPATHDYN.001 [DIRS 161886]), and are presented in Table 6-16. The "reestimated" $\Delta G_f°$ 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 sprons98*.dat* database (DTN: MO0302SPATHDYN.001 [DIRS 161886]). These thermodynamic data were used in spreadsheet *Minerals_cal_sea_clays1a.xls* (DTN: MO0302SPATHDYN.001 [DIRS 161886]) to calculate the log K for each reaction for the EQ3/6 temperature grid from 0.01 up to 300ºC. These results are summarized in Table 6-18.

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

					Heat Capacity Coefficients*		
Phase	**Formula**	**$\Delta G_f°$ (cal/mol)**	**S° (cal/mol-K)**	**V° (cm^3/mol)**	**a (cal/mol-K)**	**b × 10^3 (cal/mol-K^2)**	**c × 10^{-5} (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	$Ca_{0.165}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2$	-1272306.883	59.845	133.070	80.1811	39.5011	16.6451
Ca-Nontronite	$Ca_{0.165}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1079810.475	67.549	135.850	78.1908	52.9315	13.2011
Ca-Saponite	$Ca_{0.165}Mg_3Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1345103.557	62.328	134.359	85.2388	39.5475	14.0891
Ferroaluminoceladonite	$KFeAlSi_4O_{10}(OH)_2$	-1223659.186	76.901	153.678	87.062	44.199	14.282
Ferroceladonite	$KFeFeSi_4O_{10}(OH)_2$	-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	$Na_{0.1}K_{0.2}Ca_{0.025}(Mg_{1.15}Fe^{3+}{}_{0.2}Fe^{2+}{}_{0.5}Al_{0.75})$ $(Al_{0.5}Si_{3.5})O_{10}(OH)_2$	-1262124.787	68.395	139.510	86.6845	40.089	15.493
H-Montmorillonite	$H_{0.33}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2$	-1251813.883	59.786	132.216	79.4287	40.6825	16.3877
H-Nontronite	$H_{0.33}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1059317.475	67.482	134.996	77.4384	54.1129	12.9437
H-Saponite	$H_{0.33}Mg_3Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-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	$K_{0.33}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2$	-1273171.483	62.108	137.455	81.3097	40.75015	16.5329
K-Nontronite	$K_{0.33}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1080675.075	69.821	140.235	79.3194	54.18055	13.0889
K-Saponite	$K_{0.33}Mg_3Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1345968.157	64.585	138.745	86.3674	40.79655	13.9769
Low Fe-Mg Smectite	$Na_{0.15}K_{0.2}Ca_{0.02}(Mg_{0.9}Fe^{3+}{}_{0.16}Fe^{2+}{}_{0.29}Al)$ $(Al_{0.25}Si_{3.75})O_{10}(OH)_2$	-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	$Mg_{0.495}Al_{1.67}Si_4O_{10}(OH)_2$	-1268462.383	59.309	132.029	79.93525	39.61	16.6319
Mg-Nontronite	$Mg_{0.165}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-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*		
Name	**Formula**	**$\Delta G_f°$ (cal/mol)**	**S° (cal/mol-K)**	**V° (cm^3/mol)**	**a (cal/mol-K)**	**b × 10^3 (cal/mol-K^2)**	**c × 10^{-5} (cal-K/mol)**
Na-Montmorillonite	$Na_{0.33}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2$	-1271085.883	61.157	134.030	81.2668	40.12975	16.86455
Na-Nontronite	$Na_{0.33}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1078589.475	68.852	136.810	79.2765	53.56015	13.42055
Na-Saponite	$Na_{0.33}Mg_3Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1343882.557	63.623	135.320	86.3245	40.17615	14.30855
Reykjanes Smectite	$Na_{0.33}K_{0.03}Ca_{0.66}(Mg_{1.29}Fe^{3+}_{0.35}Fe^{2+}_{0.33}Mn_{0.01}Al_{0.28})(Al_{0.83}Si_{3.17})O_{10}(OH)_2$	-1310547.875	71.115	142.853	90.2311	39.0046	15.6183

Source: DTN: MO0302SPATHDYN.001 [DIRS 161886], spreadsheet: *Clays_TJW_1_Rev1b.xls*, worksheet: "Results Summary."

* Coefficients defined in Equation 4-1.

Table 6-17. $\Delta G_f°$ Data for Additional Clay Minerals

Phase	Formula	$\Delta G_f°$ (cal/mol)
14A-Amesite	$Mg_4Al_4Si_2O_{10}(OH)_8$	-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	$Fe_2Al_2SiO_5(OH)_4$	-826814.2
7A-Cronstedtite	$Fe_2Fe_2SiO_5(OH)_4$	-624629.6
7A-Daphnite	$Fe_5Al_2Si_3O_{10}(OH)_8$	-1544391.7
Celadonite	$KMgAlSi_4O_{10}(OH)_2$	-1305843.2
Greenalite	$Fe_3Si_2O_5(OH)_4$	-716529.6
Minnesotaite	$Fe_3Si_4O_{10}(OH)_2$	-1070057.2

Source: 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: MO0302SPATHDYN.001 [DIRS 161886]) are from Helgeson et al. (1978 [DIRS 101596]) and were included in the *sprons98.dat* database (DTN: MO0302SPATHDYN.001 [DIRS 161886]).

Some additional comments are appropriate concerning the accuracy of the estimated values presented here. These are primarily directed toward values for Gibbs 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 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 energy of margarite itself is not zero.

A minimum measure of uncertainty in estimated Gibbs 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 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^{4+}, Al^{3+}) 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 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 Grids for Clay Minerals Used in data0.ymp.R2

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

Table 6-18. Log K Grids for Clay Minerals Used in data0.ymp.R2 (Continued)

Mineral	**Reaction**	**Temperature (ºC)**							
		0.01	**25**	**60**	**100**	**150**	**200**	**250**	**300**
Greenalite	Greenalite + $6H^+$ = $5H_2O + 3Fe^{2+} + 2SiO_2(aq)$	26.0534	23.1624	19.7179	16.5850	13.5453	11.1388	9.0868	7.1439
Illite	Illite + $8H^+$ = $2.3Al^{3+} + 0.25Mg^{2+} + 5H_2O + 0.6\ K^+ + 3.5SiO_2(aq)$	11.1913	8.3706	4.7199	1.2042	-2.3885	-5.3930	-8.0973	-10.7757
Minnesotaite	Minnesotaite + $6H^+$ = $4H_2O + 3Fe^{2+} + 4SiO_2(aq)$	17.1553	15.0002	12.2222	9.6380	7.1347	5.1629	3.4582	1.7440
H-Montmorillonite	H-Montmorillonite + $5.67H^+$ = $0.33\ Mg^{2+} + 1.67Al^{3+} + 4H_2O + 4SiO_2(aq)$	3.1333	1.4445	-0.9146	-3.2347	-5.6069	-7.5864	-9.3859	-11.2358
Na-Montmorillonite	Na-Montmorillonite + $6H^+$ = $0.33\ Na^+ + 0.33\ Mg^{2+} + 1.67Al^{3+} + 4H_2O + 4SiO_2(aq)$	4.1752	2.4583	0.0686	-2.2746	-4.6636	-6.6516	-8.4568	-10.3142
K-Montmorillonite	K-Montmorillonite + $6H^+$ = $0.33\ K^+ + 0.33\ Mg^{2+} + 1.67Al^{3+} + 4H_2O + 4SiO_2(aq)$	3.7554	2.1194	-0.1824	-2.4524	-4.7777	-6.7228	-8.4982	-10.3337
Ca-Montmorillonite	Ca-Montmorillonite + $6H^+$ = $0.165\ Ca^{2+} + 0.33\ Mg^{2+} + 1.67Al^{3+} + 4H_2O + 4SiO_2(aq)$	4.2226	2.4024	-0.1121	-2.5786	-5.1015	-7.2081	-9.1212	-11.0793
Mg-Montmorillonite	Mg-Montmorillonite + $6H^+$ = $0.495\ Mg^{2+} + 1.67Al^{3+} + 4H_2O + 4SiO_2(aq)$	4.2348	2.3643	-0.2067	-2.7218	-5.2890	-7.4277	-9.3650	-11.3418
H-Nontronite	H-Nontronite + $6.99H^+$ = $2Fe^{3+} + 0.33Al^{3+} + 4.66H_2O + 3.67SiO_2(aq)$	-11.2178	-12.0580	-13.3804	-14.7103	-16.0807	-17.2650	-18.4365	-19.7989
Na-Nontronite	Na-Nontronite + $7.32H^+$ = $0.33Na^+ + 2Fe^{3+} + 0.33Al^{3+} + 4.66H_2O + 3.67SiO_2(aq)$	-10.1759	-11.0442	-12.3972	-13.7502	-15.1373	-16.3301	-17.5073	-18.8772
K-Nontronite	K-Nontronite + $7.32H^+$ = $0.33K^+ + 2Fe^{3+} + 0.33Al^{3+} + 4.66H_2O + 3.67SiO_2(aq)$	-10.5953	-11.3831	-12.6486	-13.9288	-15.2526	-16.4027	-17.5503	-18.8986
Ca-Nontronite	Ca-Nontronite + $7.32H^+$ = $0.165\ Ca^{2+} + 2Fe^{3+} + 0.33Al^{3+} + 4.66H_2O + 3.67SiO_2(aq)$	-10.1283	-11.1001	-12.5781	-14.0546	-15.5758	-16.8873	-18.1725	-19.6432
Mg-Nontronite	Mg-Nontronite + $7.32H^+$ = $0.165\ Mg^{2+} + 2Fe^{3+} + 0.33Al^{3+} + 4.66H_2O + 3.67SiO_2(aq)$	-10.1162	-11.1382	-12.6726	-14.1977	-15.7631	-17.1067	-18.4161	-19.9055

Table 6-18. Log K Grids for Clay Minerals Used in data0.ymp.R2 (Continued)

Mineral	Reaction	Temperature (ºC)							
		0.01	**25**	**60**	**100**	**150**	**200**	**250**	**300**
Ripidolite-7A	Ripidolite-7A + $16H^+$ = $2Al^{3+}$ + $3Mg^{2+}$ + $12H_2O$ + 2 Fe^{2+} + $3SiO_2(aq)$	71.9986	62.5511	51.3031	40.8781	30.4819	22.0378	14.7716	8.0641
Ripidolite-14A	Ripidolite-14A + $16H^+$ = $2Al^{3+}$ + $3Mg^{2+}$ + $12H_2O$ + 2 Fe^{2+} + $3SiO_2(aq)$	68.4043	59.1778	48.1896	38.0078	27.8567	19.6105	12.5078	5.9378
H-Saponite	H-Saponite + $6.99H^+$ = 3 Mg^{2+} + $0.33Al^{3+}$ + $4.66H_2O$ + $3.67SiO_2(aq)$	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^{2+} + $0.33Al^{3+}$ + $4.66H_2O$ + $3.67SiO_2(aq)$	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^{2+} + $0.33Al^{3+}$ + $4.66H_2O$ + $3.67SiO_2(aq)$	30.2295	26.7202	22.3686	18.3310	14.3787	11.2413	8.5634	6.0136
Ca-Saponite	Ca-Saponite + $7.32H^+$ = $0.165Ca^{2+}$ + 3 Mg^{2+} + $0.33Al^{3+}$ + $4.66H_2O$ + $3.67SiO_2(aq)$	30.6968	27.0032	22.4387	18.2045	14.0545	10.7554	7.9397	5.2674
Mg-Saponite	Mg-Saponite + $7.32H^+$ = 3.165 Mg^{2+} + $0.33Al^{3+}$ + $4.66H_2O$ + $3.67SiO_2(aq)$	30.7058	26.9651	22.3479	18.0685	13.8775	10.5490	7.7110	5.0214
Low Fe-Mg Smectite	Low Fe-Mg Smectite + $7H^+$ = $0.15Na^+$ + $0.2K^+$ + $0.02Ca^{2+}$ + 0.9 Mg^{2+} + $0.16Fe^{3+}$ + $0.29Fe^{2+}$ + $1.25Al^{3+}$ + $4.5H_2O$ + $3.75SiO_2(aq)$	13.7198	11.1541	7.8261	4.6537	1.4698	-1.1361	-3.4437	-5.7296
High Fe-Mg Smectite	High Fe-Mg Smectite + $8H^+$ = $0.1Na^+$ + $0.2K^+$ + $0.025Ca^{2+}$ + 1.15 Mg^{2+} + $0.2Fe^{3+}$ + $0.5Fe^{2+}$ + $1.25Al^{3+}$ + $5H_2O$ + $3.5SiO_2(aq)$	20.8773	17.4595	13.1723	9.1326	5.0925	1.7976	-1.0908	-3.8865
Reykjanes Smectite	Reykjanes Smectite + $9.32H^+$ = $0.33Na^+$ + $0.03K^+$ + $0.66Ca^{2+}$ + 1.29 Mg^{2+} + $0.35Fe^{3+}$ + $0.33Fe^{2+}$ + $0.01Mn^{2+}$ + $1.11Al^{3+}$ + 5.66 H_2O + $3.17SiO_2(aq)$	26.1136	22.1615	17.2950	12.7445	8.2070	4.5112	1.2779	-1.8342

Source: DTN: MO0302SPATHDYN.001 [DIRS 161886], spreadsheet: *Minerals_cal_sea_clays1a.xls*.

Actual uncertainties in estimated Gibbs 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 cm^3/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 to 52 for entropies, pp. 52 to 66 for heat capacity coefficients). Unlike molar volumes, these properties are basically of interest only when they affect Gibbs energies or log K values at elevated temperature. Generally the uncertainty in the Gibbs 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 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 K_2O(ex) and non-exchangeable K_2O, following the assumption of equality of Gibbs 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 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 $[(K_{0.65}Na_{0.03})(Al_{1.83}Fe_{0.03}{}^{3+}Fe_{0.04}{}^{2+}Mg_{0.1}Mn)(Si_{3.59}Al_{0.41})O_{10}(OH)_{1.8}F_{0.07}]$ 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 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 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, pp. 462 to 463.

* No equivalent mineral in Vieillard 2000 [DIRS 171586].

Other estimation schemes for the Gibbs 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 in this section) and those determined for data0.ymp.R2

(DTN: MO0302SPATHDYN.000 [DIRS 161756]). This comparison of corroborative 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 500 K (226.85°C). Only Cs-clinoptilolite has a lower temperature limit for heat capacity of 350 K (76.85°C). For the other zeolites described by this source the upper temperature limits for heat capacity data range from 470 K to 1,000 K (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 with experimental data. More important for the data0.ymp.R2 database (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* in 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 the spreadsheets *Zeolite_Solids_j_CFJC_fix.xls*, *Zeolite_2_Solids_cal_CFJC_fix.xls*, and *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 are the same as in Table 6-20 (Output DTN: SN0410T0510404.001, spreadsheet: *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., Δlog 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 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" H_2O in the mineral structure, the overall differences in estimated and measured Gibbs 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., $\Delta G_f°$ and $\Delta H_f°$) 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% (2σ) for Gibbs 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 to 124) provide further discussion of the model comparisons with reported thermodynamic data on zeolites. For 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 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 energies. Therefore, as with other zeolites, these differences are deemed reasonable for use by the YMP.

Table 6-20. Log K Grids for Zeolite Minerals Used in data0.ymp.R2

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

Source: DTN: MO0302SPATHDYN.001 [DIRS 161886], spreadsheets: *Zeolite Solids_j.xls*, *Zeolite #2 Solids_cal.xls*, and *Zeolite #3 Solids_j.xls*.

Table 6-21. Corrected log K Grids for Zeolite Minerals Used in data0.ymp.R4

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

Source: 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. Δlog K (Difference between Incorrect and Corrected Values) for Zeolite Minerals in Table 6-21

Mineral	Δlog K 0.01°C	Δlog K 25°C	Δlog K 60°C	Δlog K 100°C	Δlog K 150°C	Δlog K 200°C	Δlog K 250°C	Δlog 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

Source: 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-H_2O 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 the formation constants and direct inclusion into the data0.ymp.R2 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 to 66). For more details, see Sections 6.3.3.1 and 6.3.3.4. The log K grid generated for the cement 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 data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), data0.ymp.R4 (Output DTN: SN0410T0510404.002), and data0.ymp.R5 (Output DTN: SN0612T0502404.014). However, these phases are discussed in detail and qualified in this report (in actuality, previously qualified and verified in this report) as possible additions to future calculations.

Table 6-23. Thermodynamic Data for Additional Zeolite Minerals Included in data0.ymp.R2

						Empirical Coefficients for the Heat Capacity Equation[a]						
Phase	**ΔG_f° (J/mol)**	**ΔH_f° (J/mol)**	**S° (J/mol-K)**	**V° (cm^3/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	-	-	-	-	-	-	-	-	-	-	4
Clinoptilolite-Na[e]	-18,978,314	-	1,507.16	632.050	77.62	6.365	4.616E-03	-	-	-	-	1
Clinoptilolite-Na[f]	-18,803,700	-	-	-	-	-	-	-	-	-	-	5
Clinoptilolite-Na[g]	-18,903,791	-	-	-	-	-	-	-	-	-	-	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	-	-	-	-	-	-	-	-	6
Chabazite[i]	-13,780,159[i]	-	-	-	-	-	-	-	-	-	-	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

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).

[b] Chemical formula for this analcime phase as tabulated in Neuhoff et al. (2004 [DIRS 172354], Tables 6 and 7, p. 40 and 44): $(NaAl)_{1.05}Si_{1.95}O_6 \cdot 0.975H_2O$.

[c] Chemical formula for this analcime phase as tabulated in Neuhoff et al. (2004 [DIRS 172354], Tables 6 and 7, p. 40 and 44): $(NaAl)_{1.05}Si_{1.95}O_6 \cdot 0.975H_2O$.

[d] Chemical formula for this analcime phase as tabulated in Mattigod and McGrail (1999 [DIRS 172343], Table 3, p. 44): $(NaAl)_{0.96}Si_{2.04}O_6 \cdot H_2O$, 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.

[f] Chemical formula for Na-clinoptilolite as given in Wilkin and Barnes (1998 DIRS 172351], Table 7, p. 753): $Na_{1.1}Al_{1.1}Si_{4.9}O_{12}\cdot 3.48H_2O$. 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 H_2O per fractional formula unit) by 3 for comparison with the phase stoichiometry adopted in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]).

[g] Value corrected by adding the equivalent ΔG_f° of 0.422 moles of H_2O 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.

[h] Thermodynamic data for the chemical formula of chabazite as given in Ogorodova et al. (2004 [DIRS 172353], Table 3, p. 193): $(Ca_{1.65}Na_{0.24}K_{0.10})[Al_{3.79}Si_{8.25}O_{24}]\cdot 12.47H_2O$.

[i] Value corrected by substracting the equivalent ΔG_f° of 2.47 moles of H_2O 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 J/mol – (2.47)*(−237182.6 J/mol) = −13,780,159 J/mol.

[j] Thermodynamic data for the chemical formula of stellerite as given in Fridriksson et al. (2001 [DIRS 160460], Table 4, p. 4002): $Ca_2Al_4Si_{14}O_{36}\cdot 14H_2O$. Values in the source given in cal/mol units and converted in J/mol in this table.

[k] Thermodynamic data for the chemical formula of stellerite as given in Kiseleva et al. (2001 [DIRS 172352], Table 5, p. 174): $Ca_2Al_4Si_{14}O_{36}\cdot 14H_2O$. 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	X		x				x	x			Y
Allite (C_3S)	x	x					x				Y
Anhydrite	x	x							x		Y
Bellite (C_2S)	x	x					x				Y
Brucite	x	x		x					x		Y
$C_{12}A_7$	x						x				Y
C_2AH_8	x					x	x				y
C_3A	x	x					x				y
C_4AF	x	x									y
C_4AH_{13}	x	x		x		x	x	x			y
C_4AH_{19}	x						x				y
CA	x						x				y
CA_2	x						x				y
CAH_{10}	x						x				y
CSH[a]	x	x		x	x	x	x	x		x	y
Ettringite	x	x		x	x	x	x	x			y
Ferrite-Ca	x						x				y
Ferrite-Dicalcium	x						x				y
Foshagite			x				x				y
Friedl Salt[b]	x					x	x	x			y
Gehlenite Hydrate[c]	x			x				x		x	25[d]
Gibbsite	x	x		x							y
Gismondine-Na								x			25[d]
Gismondine-Ca								x			25[d]
Gypsum	x			x					x		y
Gyrolite	x		x				x				y
Hillebrandite	x		x				x				y
Hydrogarnet	x	x		x	x		x	x		x	y
Hydrotalcite[e]	x	x		x	x			x		x	25[d]
Jennite	x							x			
Monocarboaluminate		x				x		x			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	x		x		x	x	x			y
Nekoite			x								
Okenite			x				x				y
Periclase	x	x									y
Plombierite[f]	x		x				x				y
Portlandite	x	x		x	x				x		y
Reyerite			x								
Riversideite[g]			x				x				y
Syngenite	x	x				x			x		25[d]
Thaumasite	x										
Tobermorite-11A[h]	x		x	x			x	x			y
Truscottite	x		x								
Xonotlite	x		x				x				y
$CaSO_4 \cdot 0.5H_2O$ (beta)											y
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 $C_3AlCaCl_2 \cdot 10H_2O$ 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 $(Mg_{0.75}Al_{0.25}[OH]_2)](CO_3)_{0.125}(H_2O)_{0.5}$.

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

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

[h] This is "normal" Tobermorite.

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

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).

Table 6-25. Log K Grids for Cement Mineral Phases Used in data0.ymp.R2

		Temperature (°C)							
Mineral	**Reaction**	**0.01**	**25**	**60**	**100**	**150**	**200**	**250**	**300**
$(C_{12}A_7)$[a]	$(C_{12}A_7) + 66H^+ =$ $12Ca^{2+} + 33H_2O + 14Al^{3+}$	550.4886	487.2030	414.0713	346.9265	280.0183	225.8021	179.8050	138.9111
(C_2AH_8)[a]	$(C_2AH_8) + 10H^+ =$ $2Ca^{2+} + 2Al^{3+} + 13H_2O$	66.1489	59.2699	51.4645	44.4608	37.6368	32.1948	27.5826	23.4125
(C_3A)[a]	$(C_3A) + 12H^+ =$ $3Ca^{2+} + 6H_2O + 2Al^{3+}$	130.3127	116.7717	101.1568	86.8476	72.6344	61.1837	51.5545	43.0912
(C_4AF)[a]	$(C_4AF) + 20H^+ =$ $4Ca^{2+} + 2Al^{3+} + 10H_2O + 2Fe^{3+}$	157.6612	139.8695	119.3314	100.5049	81.7809	66.6349	53.7907	42.3452
(C_4AH_{13})[a]	$(C_4AH_{13}) + 14H^+ =$ $4Ca^{2+} + 2Al^{3+} + 20H_2O$	110.8317	100.6293	89.1050	78.8149	68.8522	60.9746	54.3629	48.4368
(C_4AH_{19})[a]	$(C_4AH_{19}) + 14H^+ =$ $4Ca^{2+} + 2Al^{3+} + 26H_2O$	109.9718	100.6045	90.1529	80.9597	72.1928	65.3429	59.6128	54.4408
(CA)[a]	$(CA) + 8H^+ =$ $Ca^{2+} + 4H_2O + 2Al^{3+}$	52.4679	45.7317	37.9299	30.7511	23.5715	17.7179	12.7075	8.2047
(CA_2)[a]	$(CA_2) + 14H^+ =$ $Ca^{2+} + 7H_2O + 4Al^{3+}$	72.3522	61.7708	49.4921	38.1739	26.8205	17.5151	9.4887	2.2092
(CAH_{10})[a]	$(CAH_{10}) + 8H^+ =$ $Ca^{2+} + 2Al^{3+} + 14H_2O$	43.6796	39.0445	33.8558	29.2831	24.9053	21.4541	18.5237	15.8339
Afwillite	Afwillite $+ 6H^+ =$ $3Ca^{2+} + 2SiO_2(aq) + 6H_2O$	65.8852	60.5586	54.3512	48.7177	43.2335	38.9119	35.3174	32.0963
Allite (C_3S)	Allite $+ 6H^+ =$ $SiO_2(aq) + 3Ca^{2+} + 3H_2O$	80.7463	73.6625	65.4520	57.9399	50.5253	44.6084	39.6786	35.3514
Bellite (C_2S)[a]	Bellite $+ 4H^+ =$ $2Ca^{2+} + 2H_2O + SiO_2(aq)$	42.5902	38.8242	34.4238	30.3903	26.4097	23.2289	20.5608	18.1770
CSH:1.7[1, a]	CSH $+ 3.4H^+ =$ $1.7Ca^{2+} + SiO_2(aq) + 4.317H_2O$	31.9548	29.5255	26.7220	24.2206	21.8439	20.0241	18.5492	17.2455
Ettringite	Ettringite (B) $+ 12H^+ =$ $6Ca^{2+} + 2Al^{3+} + 38H_2O + 3SO_4^{2-}$	62.1144	56.8823	50.7600	45.1311	39.3132	34.0737	28.7003	22.3823
Cr-ettringite	Cr-ettringite $+ 12H^+ =$ $6Ca^{2+} + 2Al^{3+} + 3CrO_4^{2-} + 38H_2O$	-[b]	59.0000	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]

Table 6-25. Log K Grids for Cement Mineral Phases Used in data0.ymp.R2(Continued)

		Temperature (°C)							
Mineral	**Reaction**	**0.01**	**25**	**60**	**100**	**150**	**200**	**250**	**300**
Foshagite	Foshagite + $8H^+$ = $4Ca^{2+} + 3SiO_2(aq) + 5.5H_2O$	72.8341	66.6910	59.4664	52.8906	46.4921	41.4558	37.2600	33.4631
Friedl Salt[a]	Friedl Salt + $6H^+$ = $4Ca^{2+} + 2Cl^- + 19H_2O$	-178.8322	-160.3061	-138.9735	-119.3986	-100.0899	-84.9403	-72.9462	-63.5893
Gehlenite Hydrate[2]	$Ca_2Al_2SiO_7{\cdot}8H_2O + 10H^+$ = $2Ca^{2+} + 2Al^{3+} + SiO_2 + 13H_2O$	-[b]	49.2204	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]
Gismondine-Ca	$CaAl_2Si_2O_8\ 4H_2O + 8H^+$ = $Ca^{2+} + 2Al^{3+} + 2SiO_2 + 8H_2O$	-[b]	20.8686	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]
Gismondine-Na	$Na_2Al_2Si_2O_8\ 4H_2O + 8H^+$ = $2Na^+ + 2Al^{3+} + 2SiO_2 + 8H_2O$	-[b]	21.8596	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]
Gyrolite	Gyrolite + $4H^+$ = $2Ca^{2+} + 3SiO_2(aq) + 4.5H_2O$	25.3869	23.6797	21.5505	19.6199	17.7964	16.4002	15.2205	14.0407
Hemicarbo-aluminate[3]	Hemicarboaluminate + $13.5H^+$ = $4Ca^{2+} + 2Al^{3+} + 0.5HCO_3^- + 17.5H_2O$	-[b]	88.3235	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]
Hillebrandite	Hillebrandite + $4H^+$ = $2Ca^{2+} + SiO_2(aq) + 3.17H_2O$	40.4592	37.0757	33.1420	29.5650	26.0671	23.2950	20.9782	18.9002
Hydrogarnet[a]	Hydrogarnet + $12H^+$ = $3Ca^{2+} + 2Al^{3+} + 6H_2O$	-180.8116	-169.1024	-155.8511	-143.9549	-132.5681	-124.0078	-117.6057	-112.9719
Hydrotalcite[4]	$4MgO{\cdot}Al_2O_3{\cdot}10H_2O + 14H^+$ = $4Mg^{2+} + 2Al^{3+} + 17H_2O$	-[b]	73.7800	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]
Monocarbo-aluminate[3]	$3CaO{\cdot}Al_2O_3{\cdot}CaCO_3{\cdot}10H_2O + 13H^+$ = $4Ca^{2+} + 2Al^{3+} + HCO_3^- + 16H_2O$	-[b]	77.3538	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]
Monosulphate	Monosulphate + $12H^+$ = $4Ca^{2+} + 2Al^{3+} + 18H_2O + SO_4^{2-}$	80.7137	72.4704	62.9530	54.2551	45.5660	38.3842	31.9936	25.7834
Okenite	Okenite + $2H^+$ = $Ca^{2+} + 2SiO_2(aq) + 3H_2O$	11.4698	10.8948	10.1470	9.5024	8.9579	8.5978	8.3158	7.9937
Plombierite	Plombierite + $10H^+$ = $5Ca^{2+} + 6SiO_2(aq) + 15.5H_2O$	69.8789	65.3842	59.9716	55.1602	50.6830	47.3017	44.4797	41.6996
Riversideite	Riversideite + $10H^+$ = $5Ca^{2+} + 6SiO_2(aq) + 8H_2O$	76.6335	70.6194	63.3144	56.6105	50.0934	44.9615	40.6267	36.5343
Syngenite[5]	$K_2Ca(SO_4)_2{\cdot}H_2O$ = $Ca^{2+} + 2K^+ + 2SO_4^{2-} + H_2O$	-[b]	-7.6001[c]	-[b]	-[b]	-[b]	-[b]	-[b]	--[b]

Table 6-25. Log K Grids for Cement Mineral Phases Used in data0.ymp.R2 (Continued)

		Temperature (°C)							
Mineral	**Reaction**	**0.01**	**25**	**60**	**100**	**150**	**200**	**250**	**300**
Syngenite[d]	$K_2Ca(SO_4)_2{\cdot}H_2O =$ $Ca^{2+} + 2K^+ + 2SO_4^{2-} + H_2O$	-7.5463	-7.2618	-7.1520	-7.2929	-7.7579	-8.6663	-10.6136	-[b]
Tobermorite	$\text{Tobermorite} + 10H^+ =$ $5Ca^{2+} + 6SiO_2(aq) + 10.5H_2O$	72.5004	67.1518	60.6578	54.7498	49.0777	44.6609	40.9360	37.3654
Xonotlite	$\text{Xonotlite} + 12H^+ =$ $6Ca^{2+} + 6SiO_2(aq) + 7H_2O$	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_j_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 298.15 K.
[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]), data0.ymp.R4 (Output DTN: SN0410T0510404.002), and data0.ymp.R5 (Output DTN: SN0612T0502404.014). 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 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 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)	***ΔG°$_f$* (kJ/mol)**	***V*°(cm^3/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 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 $CaCrO_4(aq) = Ca^{2+} + CrO_4^{2-}$ consistent with the solubility data for Cr-ettringite.

Table 6-27. Values of Gibbs 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 × 10^3 (cal/ mol-K^2)**	**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

The Na and Ca-gismondine species are active in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), data0.ymp.R4 (Output DTN: SN0410T0510404.002), and data0.ymp.R5 (Output DTN: SN0612T0502404.014). 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 $\Delta G°_f$ 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* in DTN: MO0302SPATHDYN.001 [DIRS 161886]) to determine the log K values at 25°C based on the following reactions:

$$Na_2Al_2Si_2O_8 \cdot 4\ H_2O + 8\ H^+ = 2\ Na^+ + 2\ Al^{3+} + 2\ SiO_2(aq) + 8\ H_2O \qquad \text{(Eq. 6-24)}$$

$$CaAl_2Si_2O_8 \cdot 4\ H_2O + 8\ H^+ = Ca^{2+} + 2\ Al^{3+} + 2\ SiO_2(aq) + 8\ H_2O \qquad \text{(Eq. 6-25)}$$

Calculation of the log K grid was done in 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 [DIRS 172005]). So far, these are the only thermodynamic data available to conduct a 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 adopted in this report. The only difference is that the Ca-Gismondine composition ($CaAl_2Si_2O_8 \cdot 4.5H_2O$) reported by Ogorodova et al. (2003 [DIRS 172005]) has 4.5 instead of 4 moles of H_2O relative to that reported by Atkins et al. (1993 [DIRS 131758]). To correct for this difference, it was assumed that H_2O is loosely bound to the zeolite structure (not treated as zeolitic H_2O) so this difference is subtracted (see spreadsheet *Cement_phases_Gismon_fixed_CFJC.xls* in Output DTN: SN0410T0510404.001) from the $\Delta G°_f$ 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 $\Delta G°_f$ 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 $\Delta H°_f$ data for Ca-gismondine ($CaAl_2Si_2O_8 \cdot 4.5H_2O$) having the same compositions as that reported by Ogorodova et al. (2003 [DIRS 172005]). The $\Delta H°_f$ 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 $\Delta H°_f$ 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 $\Delta G°_f$ obtained by Atkins et al. (1993 [DIRS 131758]) data between Na-gismondine and Ca-gismondine, their data for Na-gismondine is also questionable.

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

Mineral	Formula	$\Delta G°_f$ (kcal/mol)	log K (25°C)	Source
Gismondine-Na	$Na_2Al_2Si_2O_8{\cdot}4H_2O$	−1179.16	21.8596	Atkins et al. 1993 [DIRS 131758]
Gismondine-Ca	$CaAl_2Si_2O_8{\cdot}4H_2O$	−1187.45	20.8686	Atkins et al. 1993 [DIRS 131758]
Gismondine-Ca	$CaAl_2Si_2O_8{\cdot}4.5H_2O$	−1234.70	-	Ogorodova et al. 2003 [DIRS 172005], Table 3, p.1545
Gismondine-Ca*	$CaAl_2Si_2O_8{\cdot}4H_2O$	−1236.32	−14.9557	Ogorodova et al. 2003 [DIRS 172005], Table 3, p.1545

* $\Delta G°_f$ estimated by subtracting half of the $\Delta G°_f$ associated with one H_2O, assuming it is loosely bound to the zeolite structure (see spreadsheet *Cement_phases_Gismon_fixed_CFJC.xl* in 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]), data0.ymp.R4 (Output DTN: SN0410T0510404.002), and data0.ymp.R5 (Output DTN: SN0612T0502404.014). 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]), data0.ymp.R4 (Output DTN: SN0410T0510404.002), and data0.ymp.R5 (Output DTN: SN0612T0502404.014) 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 $CaCl_2$. The needed heat capacity values were taken from Chase (1998 [DIRS 157874]) and calculated in 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 calculations were conducted in spreadsheet *DJ Cp and Vm calculations.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 Equation 6-26, shown as inactive data in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), data0.ymp.R4 (Output DTN: SN0410T0510404.002), and data0.ymp.R5 (Output DTN: SN0612T0502404.014), are relevant to cement calculations only and the low solubilities cause extreme precipitation if activated and not suppressed in an EQ3/6 run.

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

Subsequent revisiting of thermodynamic data for this Ca-oxychloride hydrate cement phase indicate that the Gibbs energy of formation and standard entropy values given in 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" ($CaCl_2(CaO)_3 \cdot 13H_2O$) 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 $Ca(OH)_2$-$CaCl_2$-H_2O and advanced a predictive model using the Pitzer approach. They obtained values for standard chemical potentials that can be converted to Gibbs energies of formation (see spreadsheet *Minerals_cal_DJ_Cement_CFJC_fix.xls* in 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 energy of formation is –1745.14 kcal/mol. The difference in Gibbs 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]), data0.ymp.R4 (Output DTN: SN0410T0510404.002), and data0.ymp.R5 (Output DTN: SN0612T0502404.014) 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 salt 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 ($Ca_2Al_2SiO_7 \cdot 8H_2O$)

Bennett et al. (1992 [DIRS 116990]) reported an average log K value of 49.16 for gehlenite hydrate ($Ca_2Al_2SiO_7 \cdot 8H_2O$) based on the following reaction:

$$Ca_2Al_2SiO_7 \cdot 8H_2O + 10\ H^+ = 2\ Ca^{2+} + 2\ Al^{3+} + H_4SiO_4 + 11\ H_2O \qquad \text{(Eq. 6-27)}$$

Table 6-29. Gibbs Energy of Formation and log K Values for the Dissociation Reaction Represented by Equation 6-26 for “Friedl Salt” in data0.ymp.R2 Database

Mineral	**Formula**	***ΔG°_f*** **(kcal/mol)**	**log K[a]**	**Source**
Ca-oxychloride Hydrate (R2)[b]	$CaCl_2 \cdot 3CaO \cdot 16H_2O$	−1887	−160.3061	spreadsheet *Minerals_cal_DJ_Cement_CFJC_fix.xls* (Output DTN: SN0410T0510404.001)
Ca-oxychloride Hydrate (New)[b]	$CaCl_2 \cdot 3CaO \cdot 16H_2O$	−1745.14	−56.3238	Harvie et al. 1984 [DIRS 118163]

Sources: Output DTN: SN0410T0510404.001, spreadsheet: *Minerals_cal_DJ_Cement_CFJC_fix.xls*. 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.

[a] See spreadsheet *Minerals_cal_DJ_Cement_CFJC_fix.xls* (Output DTN: SN0410T0510404.001]) for details of the log K calculations.

[b] 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.

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 within spreadsheet *Solids_j_DJ_Cement.xls* (DTN: MO0302SPATHDYN.001 [DIRS 161886]) and calculating log K gave a result of 49.22 based on the following reaction:

$$Ca_2Al_2SiO_7 \cdot 8H_2O + 10\ H^+ = 2\ Ca^{2+} + 2\ Al^{3+} + SiO_2(aq) + 13\ H_2O \qquad \text{(Eq. 6-28)}$$

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

An alternate way of corroborating these data is to take the Gibbs energy of formation values for anhydrous gehlenite ($Ca_2Al_2SiO_7$) 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 energy of formation of eight moles of H_2O to the value for the anhydrous phase. This of course represents an approximation and implicitly assumes that H_2O is weakly bound to the mineral structure (i.e., no “structural” H_2O). The resulting values are given in Table 6-30. Vieillard and Rassineux (1992 [DIRS 120508], Table 2, p. 130) also provide a Gibbs 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.

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

Mineral	Formula	ΔG°_f (kJ/mol)	Source
Gehlenite Hydrate	$Ca_2Al_2SiO_7 \cdot 8H_2O$[a]	–5703.22	Babushkin et al. 1985 [DIRS 116981]
Gehlenite Hydrate	$Ca_2Al_2SiO_7 \cdot 8H_2O$	–5673.5	Vieillard and Rassineux 1992 [DIRS 120508]
Gehlenite Hydrate	$Ca_2Al_2SiO_7 \cdot 8H_2O$[a]	–5682.95	Robie and Hemingway 1995 [DIRS 153683]
Gehlenite Hydrate	$Ca_2Al_2SiO_7 \cdot 8H_2O$[b]	–5710.28[b]	Atkins et al. 1992 [DIRS 100700]

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.

[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.

6.3.3.6 Hydrotalcite ($4MgO \cdot Al_2O_3 \cdot 10H_2O$)

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

$$4MgO \cdot Al_2O_3 \cdot 10\ H_2O + 14\ H^+ = 4\ Mg^{2+} + 2\ Al^{3+} + 17\ H_2O \qquad \text{(Eq. 6-29)}$$

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 ($3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 10H_2O$)

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:

$$3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 10H_2O + 13\ H^+ = 4\ Ca^{2+} + 2\ Al^{3+} + HCO_3^- + 16\ H_2O \qquad \text{(Eq. 6-30)}$$

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 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 CO_3^{2-} to HCO_3^- 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 $\Delta G°_f$ at 25°C for the Ca-carboaluminate phase with the stoichiometry $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 12H_2O$. This value of $\Delta G°_f$ is –7598.1 kJ/mol. This stoichiometry has two additional waters relative to that of Damidot et al. (1994 [DIRS 144866]) given in Equation 6-30. Assuming an enthalpy of reaction equal to zero (i.e., $\Delta H°_r = 0$) and subtracting the $\Delta G°_f$ for two moles of H_2O (i.e., −474.363 kJ/mol) from the $\Delta G°_f$ given by Vieillard and Rassineux (1992 [DIRS 120508]) yields a value of −7123.737 kJ/mol. The $\Delta G°_f$ value for the monocarboaluminate phase of Damidot et al. (1994 [DIRS 144866]) obtained from the recalculated log K of reaction (77.3538) of Equation 6-30 and $\Delta G°_f$ data for the aqueous species and H_2O from 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 ($3CaO \cdot Al_2O_3 \cdot 0.5CaCO_3 \cdot 0.5Ca(OH)_2 \cdot 10.5H_2O$)

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:

$$\begin{aligned} &3CaO \cdot Al_2O_3 \cdot 0.5CaCO_3 \cdot 0.5Ca(OH)_2 \cdot 10.5H_2O + 13.5\ H^+ = \\ &\quad 4\ Ca^{2+} + 2\ Al^{3+} + 0.5\ HCO_3^- + 17.5\ H_2O \end{aligned} \qquad \text{(Eq. 6-31)}$$

The recalculated log K value (see *final carboaluminate solubility.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 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 CO_3^{2-} to HCO_3^- to give the value of 88.3235 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 estimate if ΔG°_f for Ca-carboaluminate phase with the stoichiometry $3CaO{\cdot}Al_2O_3{\cdot}CaCO_3{\cdot}12H_2O$ 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:

$$3CaO{\cdot}Al_2O_3{\cdot}0.5CaCO_3{\cdot}0.5Ca(OH)_2{\cdot}10.5H_2O = 3CaO{\cdot}Al_2O_3{\cdot}CaCO_3{\cdot}12H_2O + 0.5\ Ca(OH)_2 - 0.5\ CaCO_3 - 1.5\ H_2O \qquad \text{(Eq. 6-32)}$$

Using the ΔG°_f data reported by Vieillard and Rassineux (1992 [DIRS 120508], Table 2, p. 130) for $3CaO{\cdot}Al_2O_3{\cdot}CaCO_3{\cdot}12H_2O$ (–7598.1 kJ/mol), $Ca(OH)_2$ (–898.49 kJ/mol), and $CaCO_3$ (–1128.76 kJ/mol) plus that of H_2O (–237.181 kJ/mol) from data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]), the resulting ΔG°_f at 25°C of the hemicarboaluminate phase obtained using the relation given by Equation 6-32 yields a value of –7127.193 kJ/mol. The values for the phases $CaCO_3$ (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 H_2O 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]).

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

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 25ºC of –7.45; different from the one present in data0.ymp.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 (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 25ºC 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 ± 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 ± 0.6 log units (one standard deviation). Using two standard deviations or ± 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 ± 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 $\Delta G°_r$ (standard Gibbs energy of reaction), which was then used to calculate the $\Delta G°_f$ (standard Gibbs energy of formation). The $\Delta G°_f$ was then used to calculate the temperature dependent log K values used in the database (calculations in spreadsheet *Usilicates_yc_tls_ch.xls* in DTN: MO0302SPATHDYN.001 [DIRS 161886]). Extrapolation of $\Delta G°$ 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 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).

Table 6-31. Sources of Soddyite Thermodynamic Data

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]*	$\Delta G°_f$	–3654.41 kJ/mol	Inclusion in data0.ymp.R2 (DTN: MO0302SPATHDYN. 000 [DIRS 161756])
Chen et al. 1999 [DIRS 123270], Table 9, p. 658	$\Delta G°_f$ (predicted)	–3653.0 kJ/mol	Corroborative data
Chen et al. 1999 [DIRS 123270], Table 5, p. 657	$\Delta G°_f$ (measured)	–3652.8 kJ/mol	Corroborative data

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

Finch 1997 [DIRS 106347], Table II, p. 1187; Nguyen et al. 1992 [DIRS 100809]	$\Delta G°_f$	–3658.0 kJ/mol	Corroborative data
McKenzie et al. 2001 [DIRS 172346], Table 1, p. 303	$\Delta G°_f$	–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 N_2 atmosphere experiments was selected for data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), as it seems the N_2 atmosphere experiments might be better controlled (as shown in Figure 2 of Moll et al. 1996 [DIRS 106349]: the results in the N_2 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 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 $\Delta G°_f$ 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_yc_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_yc_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.

Table 6-32. Sources of Uranophane Thermodynamic 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	ΔG°_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]	ΔG°_f	–6210.6 kJ/mol	Corroborative data
McKenzie et al. 2001 [DIRS 172346], Table 1, p. 303	ΔG°_f	–6213 kJ/mol	Corroborative data

* Value shown is calculated using input from Perez et al. (2000 [DIRS 157910]), in spreadsheet *Usilicates_yc_tls_ch.xls* (DTN: MO0302SPATHDYN.000 [DIRS 161756]), with unit conversion from cal/mol.

There have been several solubility studies conducted for uranophane. The Gibbs 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]).

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 is synthesized uranophane. Their average measured log K value at infinite dilution is 11.7 (± 0.6). Pérez et al. (2000 [DIRS 157910]) also compared the Gibbs 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 energy based on input from Perez et al. (2000 [DIRS 157910]), and thermodynamic data from data0.ymp.R2, is –6195.6 kJ/mol (DTN: MO0302SPATHDYN.000 [DIRS 161756], spreadsheet: *Usilicates_yc_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 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. The 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 the source spreadsheet *Minerals_cal_YC_Usilicates.xls* (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 S° values are computed in spreadsheet *Usilicates_yc_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 for the S° value for uranophane was identified in spreadsheet *Minerals_cal_YC_Usilicates.xls* by comparison to the other source spreadsheet *Usilicates_yc_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 ($Na_2(UO_2)_2(Si_5O_{13})\cdot 3H_2O$) 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* in DTN: MO0302SPATHDYN.001 [DIRS 161886]). The extracted Gibbs 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 energies of formation between these two, which is much smaller than the Gibbs energy of formation of one mole of H_2O, 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 a 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 log K values for Na-weeksite. 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 0.003 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 ($Na(UO_2)(SiO_3)(OH)\cdot 1.5H_2O$)

The reported log K value for this phase at 30°C by Nguyen et al. (1992 [DIRS 100809]) is ≥ 5.82 ± 0.16 for a formula of $Na(H_3O)(UO_2)(SiO_4)\cdot H_2O$. 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 ($Na(UO_2)(SiO_3)(OH)\cdot 1.5H_2O$) be adopted. With this formula, the log K value was rederived from the original experimental data reported in Nguyen et al. (1992 [DIRS 100809]) and extrapolated to infinite dilution, as ≥ 5.97 at 25°C (there is no significant change in log K because of the different formula) (DTN: MO0302SPATHDYN.001 [DIRS 161886], spreadsheet: *Minerals_cal_YC_Usilicates.xls*, worksheet: “Na-boltwoodite 30Cto25C”). The extracted Gibbs energy of formation based on this log K value is –2845.42 kJ/mol (at 25°C). The predicted value for Gibbs 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 a 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 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 (Output DTN: MO0302SPATHDYN.000) 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.

Evaluation and Correction of Associated Errors Present in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). Subsequent to the completion of data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), some errors were found. First, transcription errors in the heat capacity coefficients were uncovered for Np and Pu solids as obtained from Lemire (2001 [DIRS 159027]). Second, transcription errors related to the "c" heat capacity coefficient for several solids species from Binnewies and Milke (1999

[DIRS 158955]) were found. In both cases, the problem stems from the incorrect scaling of heat capacity coefficients when implemented in the corresponding log K grid calculations in the associated spreadsheets (which are included in DTN: MO0302SPATHDYN.001 [DIRS 161886]). These errors are corrected in log K grid calculations in updated versions of the affected spreadsheets. The updated spreadsheets are included in Output DTN: SN0410T0510404.001. The corresponding log K grids for the first group of affected species (Np and Pu solids) are corrected in data0.ymp.R4 (Output DTN: SN0410T0510404.002). The corresponding log K grids for the second group of affected species (hereafter the "non-Np, non-Pu" group) were not corrected in data0.ymp.R4 (Output DTN: SN0410T0510404.002), due to late discovery of the problem affecting this group. The corrected log K grids were developed in Rev. 00 of this analysis report with the intention of including them in the next revision of the thermodynamic database. With a couple of exceptions, these corrected data are included in data0.ymp.R5 (Output DTN: SN0612T0502404.014). Evaluation and correction of these errors is discussed below. The exceptions (eskolaite, Cr_2O3:$NiCO_3$) regarding incorporation in data0.ymp.R5 (Output DTN: SN0612T0502404.014) are associated with later calculations described in Section 6.7.

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 (Equation 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 Equation 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 25ºC 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 (NpF_6 and PuF_6) 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 Δlog K of approximately 0.3 in the worst case. The corrected values can be located in the source 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.ymp.R4 (Output DTN: SN0410T0510404.002).

Additional errors were subsequently uncovered that affect both data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) and data0.ymp.R4 (Output DTN: SN0410T0510404.002). These were discovered too late to correct in data0.ymp.R4, though they were noted in Rev. 00 of this analysis report and corrected log K grids were presented in that document. These corrections have since been implemented in data0.ymp.R5 (Output DTN: SN0612T0502404.014), though some errors have since been found in that implementation (see Section 6.8).

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., $\Delta G_f°$ and log K). In this report, two types of thermodynamic data ($\Delta G_f°$ and $\Delta H_f°$; $S°$ and $C_p°$) 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 $\Delta G_f°$ values were obtained from Barin and Platzki (1995 [DIRS 157865]) and the heat capacity data ($C_p°$) used to extrapolate the apparent Gibbs 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 $\Delta G_f°$ (i.e., $\Delta H_f°$ and $S°$) are identical or at least very close within the uncertainty reported in each source. Table 6-39 show a comparison of $\Delta H_f°$ 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 $\Delta H_f°$ is approximately 41 kJ/mol (the case for Ferrite-Ca). The majority of the differences in $\Delta H_f°$ 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 $\Delta H_f°$ 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 Grids for Solid Phases Used in data0.ymp.R2

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**
$(NH_4)_4NpO_2(CO_3)_3$	$(NH_4)_4NpO_2(CO_3)_3 = NpO_2^{2+} + H^+ + 4NH_3(aq) + 3HCO_3^-$	-	-32.7086	-	-	-	-	-	-
Portlandite	$Ca(OH)_2 + 2H^+ = Ca^{2+} + 2H_2O$	24.6086	22.5444	20.1812	18.0331	15.9215	14.2416	12.8472	11.6332
Ferrite-Dicalcium	$Ca_2Fe_2O_5 + 10H^+ = 2Ca^{2+} + 2Fe^{3+} + 5H_2O$	64.4019	56.8114	48.0430	40.0003	31.9910	25.4933	19.9542	14.9759
$Ca_3Al_2O_6$	$Ca_3Al_2O_6 + 12H^+ = 3Ca^{2+} + 2Al^{3+} + 6H_2O$	124.6741	111.6139	96.5236	82.6676	68.8804	57.7558	48.3914	40.1572
$CaAl_2O_4$	$CaAl_2O_4 + 8H^+ = Ca^{2+} + 2Al^{3+} + 4H_2O$	52.2849	45.5699	37.7772	30.5932	23.3999	17.5331	12.5163	8.0178
Pseudowollastonite	$CaSiO_3 + 2H^+ = Ca^{2+} + SiO_2(aq) + H_2O$	15.4002	14.0344	12.3769	10.8345	9.3058	8.0809	7.0433	6.0865
Titanite	$CaSiTiO_5 + 2H^+ + H_2O = Ti(OH)_4 + Ca^{2+} + SiO_2(aq)$	2.8906	1.9918	0.7864	-0.3694	-1.5167	-2.4339	-3.2249	-4.0075
Perovskite	$CaTiO_3 + 2H^+ + H_2O = Ti(OH)_4 + Ca^{2+}$	12.8665	11.0419	8.8548	6.8252	4.8119	3.1997	1.8439	0.6201
$Co(OH)_2$	$Co(OH)_2 + 2H^+ = Co^{2+} + 2H_2O$	14.5818	13.0671	11.3386	9.7790	8.2566	7.0476	6.0355	5.1363
Spinel-Co	$Co_3O_4 + 8H^+ = Co^{2+} + 2Co^{3+} + 4H_2O$	-8.7738	-10.4344	-12.3917	-14.2060	-16.0687	-17.6943	-19.2575	-20.8940
$CoCl_2$	$CoCl_2(s) = Co^{2+} + 2Cl^-$	9.4850	8.2904	6.7186	5.0820	3.2084	1.4315	-0.3634	-2.3549
CoF_3[b]	$CoF_3 = Co^{3+} + 3F^-$	0.5298	-1.3201	-3.7465	-6.2538	-9.1083	-11.8169	-14.5685	-17.6326
Sphaerocobaltite	$CoCO_3(s) + H^+ = Co^{2+} + HCO_3^-$	1.3201	0.7971	0.1047	-0.6184	-1.4547	-2.2664	-3.1146	-4.0936
$CoCr_2O_4$	$CoCr_2O_4 + 8H^+ = Co^{2+} + 2Cr^{3+} + 4H_2O$	19.2781	15.0442	10.1278	5.6052	1.0693	-2.6715	-5.9511	-9.0071
CoF_2	$CoF_2 = Co^{2+} + 2F^-$	-0.6816	-1.5187	-2.6692	-3.9012	-5.3543	-6.7866	-8.3009	-10.0662
$CoFe_2O_4$	$CoFe_2O_4 + 8H^+ = Co^{2+} + 2Fe^{3+} + 4H_2O$	13.4374	10.0104	6.0324	2.3757	-1.2984	-4.3496	-7.0622	-9.6472
CoO	$CoO + 2H^+ = Co^{2+} + H_2O$	15.2509	13.5557	11.6049	9.8261	8.0691	6.6585	5.4696	4.4118
$CoTiO_3$	$CoTiO_3 + 2H^+ + H_2O = Co^{2+} + Ti(OH)_4(aq)$	18.2260	17.0136	15.5294	14.1469	12.7758	11.6719	10.7238	9.8303
$CoWO_4$	$CoWO_4 = Co^{2+} + WO_4^{2-}$	-11.9847	-11.7760	-11.7291	-11.8788	-12.2822	-12.8981	-13.7588	-14.9905

Table 6-33. Log K Grids for Solid Phases Used in data0.ymp.R2 (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	$Cr_2O_3 + 2H_2O + 1.5O_2(g) = 2CrO_4^{2-} + 4H^+$	-11.5436	-12.2116	-13.4372	-15.0171	-17.1381	-19.4062	-21.9006	-24.8658
$CrCl_3$	$CrCl_3(s) = Cr^{3+} + 3Cl^-$	22.9486	19.9413	16.1747	12.4178	8.3039	4.5844	1.0134	-2.7177
CrF_3	$CrF_3(s) = Cr^{3+} + 3F^-$	-7.8776	-9.0957	-10.7894	-12.6210	-14.8039	-16.9783	-19.2950	-21.9974
CrI_3	$CrI_3 = Cr^{3+} + 3I^-$	30.7636	27.4198	23.2699	19.1619	14.7015	10.7132	6.9359	3.0557
CrO_3	$CrO_3 + H_2O = CrO_4^{2-} + 2H^+$	-3.2049	-3.2201	-3.4762	-3.9529	-4.7213	-5.6408	-6.7279	-8.0893
$Cs_2NaPuCl_6$	$Cs_2NaPuCl_6 = Pu^{3+} + Na^+ + 2Cs^+ + 6Cl^-$	12.6910	11.9903	10.7216	9.1448	7.0406	4.7083	1.9462	-1.6789
Cs_2NpBr_6	$Cs_2NpBr_6 = Np^{4+} + 2Cs^+ + 6Br^-$	-	13.8968	-	-	-	-	-	-
Cs_2NpCl_6	$Cs_2NpCl_6 = Np^{4+} + 2Cs^+ + 6Cl^-$	-	5.2219	-	-	-	-	-	-
Cs_2PuBr_6	$Cs_2PuBr_6 = Pu^{4+} + 2Cs^+ + 6Br^-$	-	8.9929	-	-	-	-	-	-
Cs_2PuCl_6	$Cs_2PuCl_6 = Pu^{4+} + 2Cs^+ + 6Cl^-$	-	1.8950	-	-	-	-	-	-
Cs_3PuCl_6	$Cs_3PuCl_6 = Pu^{2+} + 3Cs^+ + 6Cl^-$	76.2003	70.6870	63.7161	56.7397	49.1001	42.2114	35.6138	28.7057
$CsPu_2Cl_7$	$CsPu_2Cl_7 = 2Pu^{3+} + Cs^+ + 7Cl^-$	31.8161	28.1392	23.2011	17.9835	11.9216	6.0813	0.0880	-6.6516
Ferrite-Cu	$CuFe_2O_4 + 8H^+ = Cu^{2+} + 2Fe^{3+} + 4H_2O$	13.0021	9.5266	5.4967	1.7969	-1.9118	-4.9806	-7.6956	-10.2679
Iron	$Fe + 2H^+ + 0.5O_2(g) = Fe^{2+} + H_2O$	63.6422	57.5836	50.6277	44.2848	38.0433	33.1025	29.0637	25.6580
$Fe(OH)_2$	$Fe(OH)_2(s) + 2H^+ = Fe^{2+} + 2H_2O$	15.3413	13.8214	12.0765	10.4910	8.9312	7.6838	6.6348	5.7012
$Fe(OH)_3$	$Fe(OH)_3(s) + 3H^+ = Fe^{3+} + 3H_2O$	6.9977	5.6581	4.1257	2.7413	1.3775	0.2679	-0.7022	-1.6141
$Fe_2(SO_4)_3$	$Fe_2(SO_4)_3(s) = Fe^{3+} + 3SO_4^{2-}$	4.5147	0.8936	-3.9957	-9.1664	-15.1498	-20.8688	-26.6630	-33.0596
hercynite	$FeAl_2O_4 + 8H^+ = Fe^{2+} + 2Al^{3+} + 4H_2O$	27.2135	22.4207	16.8317	11.6611	6.4509	2.1479	-1.6071	-5.0680
lawrencite	$FeCl_2 = Fe^{2+} + 2Cl^-$	10.3376	9.0646	7.4040	5.6877	3.7361	1.8968	0.0484	-1.9931
molysite	$FeCl_3(s) = Fe^{3+} + 3Cl^-$	15.8514	13.5217	10.5451	7.5206	4.1357	0.9961	-2.1068	-5.4602
chromite	$FeCr_2O_4 + 8H^+ = Fe^{2+} + 2Cr^{3+} + 4H_2O$	21.4464	16.9730	11.7841	7.0157	2.2433	-1.6773	-5.0937	-8.2518
FeF_2	$FeF_2(s) = Fe^{2+} + 2F^-$	-0.5959	-1.4320	-2.5782	-3.8024	-5.2429	-6.6604	-8.1584	-9.9065
FeF_3	$FeF_3(s) = Fe^{3+} + 3F^-$	-19.1368	-19.2386	-19.6397	-20.2803	-21.2782	-22.5050	-24.0432	-26.0946
Goethite	$FeOOH(s) + 3H^+ = Fe^{3+} + 2H_2O$	1.5251	0.5347	-0.6066	-1.6494	-2.7014	-3.5942	-4.4184	-5.2402
Ferrite-Ca	$CaFe_2O_4 + 8H^+ = 2Fe^{3+} + Ca^{2+} + 4H_2O$	25.8281	21.5945	16.7003	12.2140	7.7348	4.0632	0.8671	-2.0967
Ferrite-Ni	$NiFe_2O_4 + 8H^+ = 2Fe^{3+} + Ni^{2+} + 4H_2O$	13.1975	9.7959	5.8444	2.2106	-1.4416	-4.4763	-7.1766	-9.7520
$FeSO_4$	$FeSO_4(s) = Fe^{2+} + SO_4^{2-}$	3.0095	1.9396	0.4732	-1.0933	-2.9213	-4.6831	-6.4843	-8.4996

Table 6-33. Log K Grids for Solid Phases Used in data0.ymp.R2 (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**
Ilmenite	$FeTiO_3 + 2H^+ + H_2O = Ti(OH)_4 + Fe^{2+}$	4.7306	3.3187	1.6078	0.0209	-1.5482	-2.8051	-3.8743	-4.8659
$K_4NpO_2(CO_3)_3$	$K_4NpO_2(CO_3)_3 + 3H^+ = NpO_2^{2+} + 4K^+ + 3HCO_3^-$	-	4.5920	-	-	-	-	-	-
$MgBr_2$	$MgBr_2 = Mg^{2+} + 2Br^-$	30.5643	27.6871	24.1881	20.8077	17.2423	14.1551	11.3222	8.4951
Chloromagnesite	$MgCl_2 = Mg^{2+} + 2Cl^-$	24.2691	21.8099	18.7942	15.8518	12.7075	9.9394	7.3482	4.7003
$MgSO_4$	$MgSO_4 = Mg^{2+} + SO_4^{2-}$	6.2374	4.8818	3.0998	1.2626	-0.8107	-2.7478	-4.6772	-6.7870
Bixbyite	$Mn_2O_3 + 6H^+ = 2Mn^{3+} + 3H_2O$	2.5123	0.0527	-2.8289	-5.5008	-8.2129	-10.4932	-12.5452	-14.5141
Tephroite	$Mn_2SiO_4 + 4H^+ = 2Mn^{2+} + SiO_2(aq) +2H_2O$	26.8129	24.2091	21.1411	18.3322	15.5705	13.3635	11.4914	9.7712
Scacchite	$MnCl_2 = Mn^{2+} + 2Cl^-$	10.3334	9.2222	7.7576	6.2301	4.4744	2.7984	1.0891	-0.8326
$MnSO_4$	$MnSO_4 = Mn^{2+} + SO_4^{2-}$	4.0667	3.1105	1.7833	0.3516	-1.3374	-2.9856	-4.6947	-6.6381
MoO_2Cl_2	$MoO_2Cl_2 + 2H_2O = MoO_4^{2-} + 2Cl^- + 4H^+$	1.0071	0.5936	-0.2793	-1.4889	-3.2010	-5.1125	-7.2954	-9.9885
Na_2CO_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_2CrO_4	$Na_2CrO_4 = 2Na^+ + CrO_4^{2-}$	3.8172	3.5616	3.0862	2.4882	1.6936	0.8277	-0.1710	-1.4480
Na_3NpF_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
$Na_3NpO_2(CO_3)_2$	$Na_3NpO_2(CO_3)_2 + 2H^+ = NpO_2^+ + 3Na^+ + 2HCO_3^-$	-	5.9485	-	-	-	-	-	-
Nahcolite	$NaHCO_3 = Na^+ + HCO_3^-$	-1.0584	-0.7061	-0.3492	-0.0651	0.1539	0.2439	0.1989	-0.0343
$NaNpO_2CO_3$	$NaNpO_2CO_3 + H^+ = NpO_2^+ + Na^+ + HCO_3^-$	-	-1.3265	-	-	-	-	-	-
$NaNpO_2CO_3{\cdot}3.5H_2O$	$NaNpO_2CO_3{\cdot}3.5H_2O + H^+ = NpO_2^+ + Na^+ + HCO_3^- + 3.5H_2O$	-	-0.8000	-	-	-	-	-	-
Heazlewoodite	$Ni_3S_2 + 4H^+ + 0.5O_2(g) = 3Ni^{2+} + 2HS^- + H_2O$	28.6004	24.4693	19.5027	14.7638	9.8201	5.5688	1.6743	-2.2027
$NiCl_2$	$NiCl_2(s) = Ni^{2+} + 2Cl^-$	9.8343	8.5926	6.9613	5.2662	3.3313	1.5025	-0.3371	-2.3675
$NiCO_3$	$NiCO_3 + H^+ = Ni^{2+} + HCO_3^-$	3.3189	2.5700	1.6085	0.6310	-0.4648	-1.4889	-2.5152	-3.6457
$NiCr_2O_4$	$NiCr_2O_4 + 8H^+ = Ni^{2+} + 2Cr^{3+} + 4H_2O$	28.7772	23.6681	17.7383	12.2829	6.8212	2.3437	-1.5369	-5.0928
NiF_2	$NiF_2(s) = Ni^{2+} + 2F^-$	0.7826	-0.2087	-1.5390	-2.9364	-4.5527	-6.1140	-7.7328	-9.5842

Table 6-33. Log K Grids for Solid Phases Used in data0.ymp.R2 (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**
Trevorite	$NiFe_2O_4 + 8H^+ = Ni^{2+} + 2Fe^{3+} + 4H_2O$	13.1975	9.7959	5.8444	2.2106	-1.4395	-4.4690	-7.1591	-9.7170
$NiSO_4$	$NiSO_4 = Ni^{2+} + SO_4^{2-}$	6.7405	5.3469	3.4997	1.5773	-0.6099	-2.6624	-4.7049	-6.9235
$NiTiO_3$	$NiTiO_3 + 2H^+ + H_2O = Ti(OH)_4 + Ni^{2+}$	3.5707	2.2603	0.6583	-0.8359	-2.3208	-3.5179	-4.5440	-5.5036
$NiWO_4$	$NiWO_4 = Ni^{2+} + WO_4^{2-}$	-11.3005	-11.1792	-11.2395	-11.4931	-12.0046	-12.7110	-13.6490	-14.9474
Np	$Np + 3H^+ + 0.75O_2(g) = Np^{3+} + 1.5H_2O$	167.5198	152.1799	134.5685	118.5020	102.6895	90.1833	79.9918	71.4644
Np_2C_3	$Np_2C_3 + 3H^+ + 4.5O_2(g) = 2Np^{3+} + 3HCO_3^-$	-	454.4742	-	-	-	-	-	-
Np_2O_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
$NpBr_3$	$NpBr_3 = Np^{3+} + 3Br^-$	23.3944	20.9379	17.8033	14.6332	11.1113	7.8740	4.7046	1.3143
$NpBr_4$	$NpBr_4 = Np^{4+} + 4Br^-$	34.0066	29.8101	24.6456	19.5826	14.1296	9.2708	4.6508	-0.1567
$NpC_{0.91}$[c]	$NpC_{0.91} + 2.09H^+ + 1.66O_2(g) = Np^{3+} + 0.91HCO_3^- + 0.59H_2O$	214.6543	194.6217	171.5153	150.3170	129.3115	112.5628	98.7826	87.0847
$NpCl_3$	$NpCl_3 = Np^{3+} + 3Cl^-$	15.4616	13.4766	10.8967	8.2378	5.2187	2.3732	-0.4864	-3.6310
$NpCl_4$	$NpCl_4 = Np^{4+} + 4Cl^-$	24.9789	21.2634	16.6639	12.1176	7.1657	2.6901	-1.6343	-6.2149
NpF_3	$NpF_3 = Np^{3+} + 3F^-$	-17.9938	-17.9369	-18.1661	-18.6598	-19.5272	-20.6659	-22.1483	-24.1670
NpF_4	$NpF_4 = Np^{4+} + 4\ F^-$	-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	$NpF_6 + 2H_2O = NpO_2^{2+} + 4H^+ + 6\ F^-$	34.9278	29.8193	23.4792	17.2248	10.4509	4.3751	-1.4543	-7.6196
NpI_3	$NpI_3 = Np^{3+} + 3I^-$	30.2029	27.3544	23.7833	20.2153	16.2960	12.7396	9.3101	5.7084
NpN	$NpN + 3H^+ = Np^{3+} + NH_3(aq)$	52.2385	47.2199	41.4250	36.1113	30.8387	26.6081	23.0814	20.0350
NpO_2	$NpO_2 + 4H^+ = Np^{4+} + 2H_2O$	-8.8615	-9.7398	-10.7021	-11.5341	-12.3305	-12.9874	-13.6028	-14.2445
NpO_2(am, hyd)	$NpO_2 + 4H^+ = Np^{4+} + 2H_2O$	-	1.5445	-	-	-	-	-	-
$NpO_2(NO_3)_2{\cdot}6H_2O$	$NpO_2(NO_3)_2{\cdot}6H_2O = NpO_2^{2+} + 2NO_3^- + 6H_2O$	-	2.2370	-	-	-	-	-	-
NpO_2CO_3	$NpO_2CO_3 + H^+ = NpO_2^{2+} + HCO_3^-$	-	242.0251	-	-	-	-	-	-
NpO_2OH(am)	$NpO_2OH + H^+ = NpO_2^+ + H_2O$	-	4.7072	-	-	-	-	-	-
NpO_2OH(am, aged)	$NpO_2OH + H^+ = NpO_2^+ + H_2O$	-	5.3074	-	-	-	-	-	-
$NpO_3{\cdot}H_2O$	$NpO_3{\cdot}H_2O + 2H^+ = NpO_2^{2+} + 2H_2O$	-	5.4844	-	-	-	-	-	-

Table 6-33. Log K Grids for Solid Phases Used in data0.ymp.R2 (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**
$NpOBr_2$	$NpOBr_2 + 2H^+ = Np^{4+} + 2\ Br^- + H_2O$	7.3740	5.2794	2.7147	0.2116	-2.4896	-4.9259	-7.2945	-9.8236
$NpOCl_2$	$NpOCl_2 + 2H^+ = Np^{4+} + 2Cl^- + H_2O$	7.6908	5.4117	2.6464	-0.0340	-2.9065	-5.4782	-7.9587	-10.5850
Pu	$Pu + O_2(g) + 4H^+ = Pu^{4+} + 2H_2O$	184.6832	166.8458	146.4193	127.8270	109.5673	95.1509	83.4149	73.5976
$Pu(HPO_4)_2$ (am,hyd)	$Pu(HPO_4)_2 = Pu^{4+} + 2HPO_4^{2-}$	-	-32.8499	-	-	-	-	-	-
$Pu(OH)_3$	$Pu(OH)_3 + 3H^+ = Pu^{3+} + 3H_2O$	-	15.8218	-	-	-	-	-	-
Pu_2C_3[c]	$Pu_2C_3 +3H^+ +4.5O_2(g) = 2Pu^{3+} + 3HCO_3^-$	533.5333	483.9154	426.6236	373.9963	321.7747	280.0729	245.7040	216.4445
Pu_2O_3	$Pu_2O_3 + 6H^+ = 3H_2O + 2Pu^{3+}$	56.7969	50.6550	43.5378	36.9885	30.4486	25.1389	20.6280	16.6232
Pu_3C_2	$Pu_3C_2 + 7H^+ +4.25O_2(g) = 3Pu^{3+} +2HCO_3^- + 2.5H_2O$	652.3279	592.2086	522.9563	459.5238	396.7967	346.9117	306.0016	271.4409
PuAs	$PuAs + 2O_2(g) + 2H^+ = Pu^{3+} + H_2AsO_4^-$	-	191.0895	-	-	-	-	-	-
PuBi	$PuBi + 6H^+ +1.5\ O_2(g) = Pu^{3+} + Bi^{3+} + 3H_2O$	-	188.3637	-	-	-	-	-	-
$PuBi_2$	$PuBi_2 + 8H^+ + 3O_2(g) = PuO_2^{2+} + 2Bi^{3+} + 4H_2O$	-	244.4113	-	-	-	-	-	-
$PuBr_3$	$PuBr_3 = Pu^{3+} + 3Br^-$	24.2043	21.6939	18.5470	15.4240	12.0179	8.9338	5.9388	2.7339
$PuC_{0.84}$[c]	$PuC_{0.84} + 1.59O_2(g) + 2.16H^+ = 0.84HCO_3^- + 0.66H_2O + Pu^{3+}$	227.5352	206.5054	182.2538	160.0100	137.9775	120.4229	105.9970	93.7775
$PuCl_3$	$PuCl_3 = Pu^{3+} + 3Cl^-$	16.2123	14.1989	11.5854	8.8960	5.8478	2.9809	0.1054	-3.0511
$PuCl_3{\cdot}6H_2O$	$PuCl_3{\cdot}6H_2O = Pu^{3+} + 3Cl^- + 6H_2O$	-	5.3599	-	-	-	-	-	-
$PuCl_4$	$PuCl_4 = Pu^{4+} + 4Cl^-$	-	21.6853	-	-	-	-	-	-
PuF_3	$PuF_3 = Pu^{3+} + 3F^-$	-16.2624	-16.3164	-16.6721	-17.2795	-18.2556	-19.4767	-21.0227	-23.0916
PuF_6	$PuF_6 +2H_20 = 6F^- + PuO_2^{2+} + 4H^+$	49.7872	43.5597	35.9292	28.4915	20.5480	13.5459	6.9645	0.1760
PuI_3	$PuI_3 = Pu^{3+} + 3I^-$	30.1003	27.2872	23.7566	20.2269	16.3475	12.8253	9.4258	5.8508
PuN	$PuN + 3H^+ = NH_3(aq) + Pu^{3+}$	-	58.1593	-	-	-	-	-	-
$PuO_{1.61}$	$PuO_{1.61} + 0.195O_2(g) + 4H^+ = Pu^{4+} + 2H_2O$	24.3995	20.5992	16.2792	12.3796	8.5623	5.5209	2.9735	0.7320
PuO_2[c]	$PuO_2 + 4H^+ = Pu^{4+} + 2H_2O$	-7.1094	-8.0173	-9.0228	-9.9038	-10.7586	-11.4701	-12.1362	-12.8255
PuO_2(hyd, aged)	$PuO_2(hyd, aged) + 4H^+ = Pu^{4+} + 2H_2O$	-	-1.9803	-	-	-	-	-	-

Table 6-33. Log K Grids for Solid Phases Used in data0.ymp.R2 (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**
$PuO_2(NO_3)_2 \cdot 6H_2O$	$PuO_2(NO_3)_2 \cdot 6H_2O = PuO_2^{2+} + 6H_2O + 2NO_3^-$	-	2.4443	-	-	-	-	-	-
$PuO_2(OH)_2 \cdot H_2O$[d]	$PuO_2(OH)_2 \cdot H_2O + 2H^+ = PuO_2^{2+} + 3H_2O$	-	5.5000-	-	-	-	-	-	-
PuO_2CO_3	$PuO_2CO_3 + H^+ = PuO_2^{2+} + HCO_3^-$	-	-3.8567	-	-	-	-	-	-
$PuO_2OH(am)$	$PuO_2OH(am) + H^+ = PuO_2^+ + H_2O$	-	5.0073	-	-	-	-	-	-
PuOBr	$PuOBr + 2H^+ = Pu^{3+} + Br^- + H_2O$	16.3616	14.3427	11.9072	9.5748	7.1268	5.0040	3.0407	1.0763
PuOCl	$PuOCl + 2H^+ = Pu^{3+} + Cl^- + H_2O$	13.1692	11.3957	9.2448	7.1717	4.9765	3.0494	1.2404	-0.6016
PuOF[c]	$PuOF + 2H^+ = Pu^{3+} + F^- + H_2O$	2.2336	1.1116	-0.2857	-1.6605	-3.1569	-4.5256	-5.8808	-7.3490
PuOI[c]	$PuOI + 2H^+ = Pu^{3+} + I^- + H_2O$	18.1012	16.0237	13.5298	11.1490	8.6571	6.5028	4.5174	2.5390
PuP	$PuP + H^+ + 2O_2(g) = Pu^{3+} + HPO_4^{2-}$	-	237.2760	-	-	-	-	-	-
$PuPO_4(s, hyd)$	$PuPO_4(s, hyd) + H^+ = Pu^{3+} + HPO_4^{2-}$	-	-13.4500	-	-	-	-	-	-
PuSb	$PuSb + 2H^+ + 1.5\ O_2(g) = Pu^{3+} + SbO_2^- + H_2O$	-	176.7466	-	-	-	-	-	-
Ti_2O_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_3O_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
$TiBr_3$	$TiBr_3 + 3.5H_2O + 0.25O_2(g) = Ti(OH)_4(aq) + 3Br^- + 3H^+$	54.0865	48.8970	42.5601	36.4515	30.0678	24.6382	19.7839	15.0958
$TiBr_4$	$TiBr_4 + 4H_2O = Ti(OH)_4(aq) + 4Br^- + 4H^+$	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
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

Table 6-33. Log K Grids for Solid Phases Used in data0.ymp.R2 (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**
TiI_4	$TiI_4 + 4H_2O = Ti(OH)_4(aq) + 4I^- + 4H^+$	40.4343	36.9635	32.5191	28.0374	23.1169	18.6929	14.4885	10.1176
TiO	$TiO(s) + 2H_2O + 0.5O_2 = Ti(OH)_4(aq)$	65.1565	58.6942	51.1924	44.3201	37.5613	32.2405	27.9350	24.3501
Uranium	$U + 2H^+ + 1.5O_2(g) = UO_2^{2+} + H_2O$	229.3696	208.4445	184.4377	162.5347	140.9842	123.9704	110.1644	98.6912
$U(SO_4)_2$	$U(SO_4)_2 = U^{3+} + 2SO_4^{2-}$	-10.6470	-11.9785	-13.8994	-16.0361	-18.6520	-21.3227	-24.2285	-27.6849
U_2S_3	$U_2S_3 + 3H^+ = 2U^{3+} + 3HS^-$	13.0324	10.4341	7.0450	3.5631	-0.3624	-4.0266	-7.6673	-11.6110
UBr_3	$UBr_3 = U^{3+} + 3Br^-$	22.2645	19.9367	16.9090	13.7994	10.3020	7.0598	3.8722	0.4518
UBr_4	$UBr_4 = U^{4+} + 4Br^-$	35.4871	31.2328	25.9892	20.8389	15.2802	10.3192	5.5990	0.6917
UCl_3	$UCl_3 = U^{3+} + 3Cl^-$	14.9578	13.0401	10.4960	7.8326	4.7734	1.8720	-1.0474	-4.2567
UCl_4	$UCl_4 = U^{4+} + 4Cl^-$	25.6364	21.9229	17.3180	12.7569	7.7768	3.2649	-1.1027	-5.7335
UCl_5	$UCl_5 + 2H_2O = UO_2^+ + 5Cl^- + 4H^+$	37.2989	33.8207	29.2712	24.5499	19.1927	14.2091	9.3248	4.1144
UCl_6	$UCl_6 + 2H_2O = UO_2^{2+} + 6Cl^- + 4H^+$	58.6497	53.1432	46.2494	39.3547	31.7911	24.9671	18.4514	11.6658
UF_3	$UF_3 = U^{3+} + 3F^-$	-21.2939	-20.9385	-20.8561	-21.0915	-21.7266	-22.6949	-24.0446	-25.9613
UF_4	$UF_4 = U^{4+} + 4F^-$	-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	$UF_6 + 2H_2O = UO_2^{2+} + 6F^- + 4H^+$	21.5553	17.5678	12.4557	7.2463	1.3981	-4.0509	-9.4686	-15.3832
UI_3	$UI_3 = U^{3+} + 3I^-$	32.9911	29.9408	26.0968	22.2421	18.0049	14.1734	10.5065	6.6935
UI_4	$UI_4 = U^{4+} + 4I^-$	45.2686	40.4934	34.6660	28.9791	22.8794	17.4804	12.3999	7.1975
UO_2Br_2	$UO_2Br_2 = UO_2^{2+} + 2Br^-$	18.4072	16.4880	14.0969	11.7192	9.1185	6.7682	4.5068	2.1241
UO_2Cl_2	$UO_2Cl_2 = UO_2^{2+} + 2Cl^-$	13.7845	12.1037	9.9923	7.8698	5.5163	3.3543	1.2376	-1.0345
UO_2F_2	$UO_2F_2 = UO_2^{2+} + 2F^-$	-5.6669	-6.2647	-7.1248	-8.0882	-9.2818	-10.5178	-11.8836	-13.5398
UO_2SO_4	$UO_2SO_4 = UO_2^{2+} + SO_4^{2-}$	3.6829	2.4282	0.7802	-0.9327	-2.8940	-4.7579	-6.6467	-8.7462
UO_3(gamma)	$UO_3(gamma) + 2H^+ = UO_2^{2+} + H_2O$	9.1979	7.8659	6.3470	4.9650	3.5935	2.4792	1.5215	0.6449
$UOBr_2$	$UOBr_2 + 2H^+ = U^{4+} + 2Br^- + H_2O$	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
UOCl	$UOCl + 2H^+ = U^{3+} + Cl^- + H_2O$	-9.8816	-9.7309	-9.7123	-9.8415	-10.1594	-10.6310	-11.2776	-12.1751
$UOCl_2$	$UOCl_2 + 2H^+ = U^{4+} + 2Cl^- + H_2O$	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

Table 6-33. Log K Grids for Solid Phases Used in data0.ymp.R2 (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**
$WCl_2(s)$	$WCl_2(s) + 2H_2O + O_2(g) = WO_4^{2-} + 2Cl^- + 4H^+$	93.6338	84.5211	73.6761	63.3790	52.7437	43.8115	35.9624	28.6009
$WCl_4(s)$	$WCl_4(s) + 3H_2O + 0.5O_2 = WO_4^{2-} + 4Cl^- + 6H^+$	71.3689	64.5388	56.1177	47.8276	38.9055	31.0428	23.7400	16.3841
$WCl_5(s)$	$WCl_5(s) + 3.5H_2O + 0.25O_2 = WO_4^{2-} + 5Cl^- + 7H^+$	65.4016	59.3442	51.7106	44.0347	35.5828	27.9461	20.6622	13.0949
$WCl_6(s)$	$WCl_6(s) + 4H_2O = WO_4^{2-} + 6Cl^- + 8H^+$	57.2682	52.1561	45.5135	38.6433	30.8566	23.6054	16.4742	8.8097
$WO_2Cl_2(s)$	$WO_2Cl_2(s) + 2H_2O = WO_4^{2-} + 2Cl^- + 4H^+$	0.6693	-0.0612	-1.2805	-2.7892	-4.7792	-6.8982	-9.2424	-12.0657
$WOCl_4(s)$	$WOCl_4(s) + 3H_2O = WO_4^{2-} + 4Cl^- + 6H^+$	34.4557	31.2806	27.0555	22.5950	17.4379	12.5397	7.6296	2.2438
$WOF_4(s)$	$WOF_4(s) + 3H_2O = WO_4^{2-} + 4F^- + 6H^+$	10.1133	7.7357	4.4528	0.8968	-3.3209	-7.4485	-11.7279	-16.5992

Source: 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 CoF_3 is corrected from the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), which gives an equation for $CoCl_3$.

[c] 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).

[d] The formula for $PuO_2(OH)_2{\cdot}H_2O$ is corrected from the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), which gives $PuO_2(OH)_2{\cdot}2H_2O$. The corrected form is consistent with Lemire (2001 [DIRS 159027], Section 17.2.2.1).

Table 6-34. Corrected log K Grids for Np and Pu Solid Phases Implemented in data0.ymp.R4

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_3NpF_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	$Np + 3H^+ + 0.75O_2(g) = Np^{3+} + 1.5H_2O$	167.5129	152.1799	134.5579	118.4599	102.5893	90.0115	79.7396	71.1257
Np_2O_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
$NpBr_3$	$NpBr_3 = Np^{3+} + 3Br^-$	23.3940	20.9379	17.8023	14.6289	11.0996	7.8519	4.6698	1.2647
$NpBr_4$	$NpBr_4 = Np^{4+} + 4Br^-$	34.0049	29.8101	24.6427	19.5708	14.1006	9.2201	4.5750	-0.2600
$NpC_{0.91}$*	$NpC_{0.91} + 2.09H^+ + 1.66O_2(g) = Np^{3+} + 0.91HCO_3^- + 0.59H_2O$	214.6573	194.6217	171.5199	150.3350	129.3544	112.6364	98.8906	87.2297
$NpCl_3$	$NpCl_3 = Np^{3+} + 3Cl^-$	15.4590	13.4766	10.8928	8.2227	5.1830	2.3122	-0.5754	-3.7500
$NpCl_4$	$NpCl_4 = Np^{4+} + 4Cl^-$	24.9771	21.2634	16.6608	12.1047	7.1338	2.6337	-1.7192	-6.3314
NpF_3	$NpF_3 = Np^{3+} + 3F^-$	-17.9914	-17.9369	-18.1629	-18.6483	-19.5023	-20.6271	-22.0960	-24.1022
NpF_4	$NpF_4 = Np^{4+} + 4\ F^-$	-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	$NpF_6 + 2H_2O = NpO_2^{2+} + 4H^+ + 6\ F^-$	34.9067	29.8193	23.4454	17.0862	10.1113	3.7797	-2.3444	-8.8333
NpI_3	$NpI_3 + Np^{3+} + 3I^-$	30.2017	27.3544	23.7814	20.2075	16.2767	12.7058	9.2596	5.6395
NpN	$NpN + 3H^+ = Np^{3+} + NH_3(aq)$	52.2383	47.2199	41.4246	36.1091	30.8326	26.5962	23.0622	20.0070
$NpOBr_2$	$NpOBr_2 + 2H^+ = Np^{4+} + 2\ Br^- + H_2O$	7.3768	5.2794	2.7183	0.2240	-2.4643	-4.8887	-7.2475	-9.7693
$NpOCl_2$	$NpOCl_2 + 2H^+ = Np^{4+} + 2Cl^- + H_2O$	7.6917	5.4117	2.6473	-0.0317	-2.9041	-5.4784	-7.9642	-10.5985
Cs_3PuCl_6	$Cs_3PuCl_6 = Pu^{3+} + 3Cs^+ + 6Cl^-$	76.2000	70.6870	63.7152	56.7349	49.0858	42.1827	35.5667	28.6366
$CsPu_2Cl_7$	$CsPu_2Cl_7 = 2Pu^{3+} + Cs^+ + 7Cl^-$	31.8127	28.1392	23.1957	17.9614	11.8680	5.9881	-0.0505	-6.8394
Pu	$Pu + O_2(g) + 4H^+ = Pu^{4+} + 2H_2O$	184.6805	166.8458	146.4150	127.8093	109.5241	95.0752	83.3017	73.4433
Pu_2C_3*	$Pu_2C_3 +3H^+ +4.5O_2(g) = 2Pu^{3+} +3HCO_3^-$	533.5625	483.9329	426.6540	374.0675	321.9198	280.3062	246.0339	216.8757
Pu_2O_3	$Pu_2O_3 + 6H^+ = 3H_2O + 2Pu^{3+}$	56.8079	50.6550	43.5537	37.0502	30.5909	25.3763	20.9682	17.0707
Pu_3C_2	$Pu_3C_2 + 7H^+ +4.25O_2(g) = 3Pu^{3+} +2HCO_3^- + 2.5H_2O$	652.3246	592.2086	522.9512	459.5030	396.7466	346.8247	305.8727	271.2665

Table 6-34. Corrected log K Grids for Np and Pu Solid Phases Implemented in data0.ymp.R4 (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
$PuBr_3$	$PuBr_3 = Pu^{3+} + 3Br^-$	24.1856	21.6939	18.5185	15.3107	11.7509	8.4824	5.2862	1.8718
$PuC_{0.84}$*	$PuC_{0.84} + 1.59O_2(g) + 2.16H^+ = 0.84HCO_3^- + 0.66H_2O + Pu^{3+}$	227.5412	206.5054	182.2628	160.0451	138.0603	120.5633	106.2012	94.0495
$PuCl_3$	$PuCl_3 = Pu^{3+} + 3Cl^-$	16.2103	14.1989	11.5823	8.8837	5.8185	2.9307	0.0318	-3.1500
PuF_3	$PuF_3 = Pu^{3+} + 3F^-$	-16.2599	-16.3164	-16.6688	-17.2675	-18.2297	-19.4362	-20.9682	-23.0240
PuF_6	$PuF_6 + 2H_20 = 6F^- + PuO_2^{2+} + 4H^+$	49.7680	43.5597	35.8984	28.3650	20.2382	13.0028	6.1526	-0.9311
PuI_3	$PuI_3 = Pu^{3+} + 3I^-$	30.0992	27.2872	23.7547	20.2190	16.3282	12.7915	9.3753	5.7819
$PuO_{1.61}$	$PuO_{1.61} + 0.195O_2(g) + 4H^+ = Pu^{4+} + 2H_2O$	24.4008	20.5992	16.2807	12.3845	8.5714	5.5327	2.9861	0.7435
PuO_2*	$PuO_2 + 4H^+ = Pu^{4+} + 2H_2O$	-7.1053	-8.0173	-9.0177	-9.8854	-10.7201	-11.4116	-12.0598	-12.7335
PuOBr	$PuOBr + 2H^+ = Pu^{3+} + Br^- + H_2O$	16.3619	14.3427	11.9073	9.5742	7.1237	4.9960	3.0258	1.0526
PuOCl	$PuOCl + 2H^+ = Pu^{3+} + Cl^- + H_2O$	13.1696	11.3957	9.2450	7.1719	4.9750	3.0439	1.2289	-0.6210
PuOF*	$PuOF + 2H^+ = Pu^{3+} + F^- + H_2O$	2.2342	1.1116	-0.2852	-1.6594	-3.1564	-4.5278	-5.8875	-7.3622
PuOI*	$PuOI + 2H^+ = Pu^{3+} + I^- + H_2O$	18.0993	16.0237	13.5267	11.1361	8.6251	6.4461	4.4321	2.4222

Source: 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. Δlog 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_3NpF_8	$Na_3NpF_8 + 2H_2O = NpO_2^+ + 3Na^+ + 4H^+ + 8F^-$	-0.0002	0.0000	-0.0012	-0.0068	-0.0212	-0.0433	-0.0723	-0.1069
Np	$Np + 3H^+ + 0.75O_2(g) = Np^{3+} + 1.5H_2O$	-0.0069	0.0000	-0.0105	-0.0420	-0.1002	-0.1718	-0.2522	-0.3387
Np_2O_5	$Np_2O_5 + 2H^+ = 2NpO_2^+ + H_2O$	-0.0059	0.0000	-0.0095	-0.0388	-0.0950	-0.1665	-0.2489	-0.3394
$NpBr_3$	$NpBr_3 = Np^{3+} + 3Br^-$	-0.0004	0.0000	-0.0009	-0.0043	-0.0117	-0.0221	-0.0348	-0.0495
$NpBr_4$	$NpBr_4 = Np^{4+} + 4Br^-$	-0.0018	0.0000	-0.0029	-0.0118	-0.0289	-0.0507	-0.0757	-0.1033
$NpC_{0.91}$	$NpC_{0.91} + 2.09H^+ + 1.66O_2(g) = Np^{3+} + 0.91HCO_3^- + 0.59H_2O$	0.0030	0.0000	0.0045	0.0180	0.0429	0.0736	0.1080	0.1450
$NpCl_3$	$NpCl_3 = Np^{3+} + 3Cl^-$	-0.0025	0.0000	-0.0038	-0.0151	-0.0357	-0.0609	-0.0890	-0.1190
$NpCl_4$	$NpCl_4 = Np^{4+} + 4Cl^-$	-0.0019	0.0000	-0.0031	-0.0129	-0.0319	-0.0564	-0.0849	-0.1165
NpF_3	$NpF_3 = Np^{3+} + 3F^-$	0.0024	0.0000	0.0032	0.0115	0.0249	0.0388	0.0523	0.0648
NpF_4	$NpF_4 = Np^{4+} + 4\ F^-$	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	$NpF_6 + 2H_2O = NpO_2^{2+} + 4H^+ + 6\ F^-$	-0.0210	0.0000	-0.0338	-0.1387	-0.3396	-0.5954	-0.8901	-1.2137
NpI_3	$NpI_3 + Np^{3+} + 3I^-$	-0.0012	0.0000	-0.0019	-0.0079	-0.0193	-0.0338	-0.0505	-0.0689
NpN	$NpN + 3H^+ = Np^{3+} + NH_3(aq)$	-0.0002	0.0000	-0.0004	-0.0021	-0.0061	-0.0119	-0.0193	-0.0279
NpO_2	$NpO_2 + 4H^+ = Np^{4+} + 2H_2O$	0.0004	0.0000	0.0001	-0.0007	-0.0046	-0.0120	-0.0226	-0.0362
$NpOBr_2$	$NpOBr_2 + 2H^+ = Np^{4+} + 2\ Br^- + H_2O$	0.0029	0.0000	0.0035	0.0124	0.0253	0.0372	0.0469	0.0543
$NpOCl_2$	$NpOCl_2 + 2H^+ = Np^{4+} + 2Cl^- + H_2O$	0.0009	0.0000	0.0009	0.0023	0.0024	-0.0002	-0.0055	-0.0135
Cs_3PuCl_6	$Cs_3PuCl_6 = Pu^{3+} + 3Cs^+ + 6Cl^-$	-0.0002	0.0000	-0.0009	-0.0048	-0.0144	-0.0287	-0.0471	-0.0691
$CsPu_2Cl_7$	$CsPu_2Cl_7 = 2Pu^{3+} + Cs^+ + 7Cl^-$	-0.0035	0.0000	-0.0054	-0.0221	-0.0536	-0.0932	-0.1385	-0.1878
Pu	$Pu + O_2(g) + 4H^+ = Pu^{4+} + 2H_2O$	-0.0027	0.0000	-0.0043	-0.0176	-0.0432	-0.0757	-0.1132	-0.1543
Pu_2C_3	$Pu_2C_3 + 3H^+ + 4.5O_2(g) = 2Pu^{3+} + 3HCO_3^-$	0.0292	0.0175	0.0304	0.0712	0.1451	0.2334	0.3299	0.4312
Pu_2O_3	$Pu_2O_3 + 6H^+ = 3H_2O + 2Pu^{3+}$	0.0110	0.0000	0.0159	0.0617	0.1423	0.2374	0.3403	0.4475
Pu_3C_2	$Pu_3C_2 + 7H^+ + 4.25O_2(g) = 3Pu^{3+} + 2HCO_3^- + 2.5H_2O$	-0.0033	0.0000	-0.0051	-0.0207	-0.0501	-0.0870	-0.1289	-0.1745
$PuBr_3$	$PuBr_3 = Pu^{3+} + 3Br^-$	-0.0187	0.0000	-0.0285	-0.1132	-0.2669	-0.4514	-0.6526	-0.8620
$PuC_{0.84}$	$PuC_{0.84} + 1.59O_2(g) + 2.16H^+ = 0.84HCO_3^- + 0.66H_2O + Pu^{3+}$	0.0060	0.0000	0.0089	0.0352	0.0828	0.1404	0.2042	0.2720

Table 6-35. Δlog 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
$PuCl_3$	$PuCl_3 = Pu^{3+} + 3Cl^-$	-0.0020	0.0000	-0.0031	-0.0123	-0.0293	-0.0502	-0.0736	-0.0989
PuF_3	$PuF_3 = Pu^{3+} + 3F^-$	0.0025	0.0000	0.0033	0.0120	0.0259	0.0404	0.0545	0.0676
PuF_6	$PuF_6 + 2H_20 = 6F^- + PuO_2^{2+} + 4H^+$	-0.0192	0.0000	-0.0309	-0.1265	-0.3098	-0.5431	-0.8119	-1.1071
PuI_3	$PuI_3 = Pu^{3+} + 3I^-$	-0.0012	0.0000	-0.0019	-0.0079	-0.0193	-0.0338	-0.0505	-0.0689
$PuO_{1.61}$	$PuO_{1.61} + 0.195O_2(g) + 4H^+ = Pu^{4+} + 2H_2O$	0.0013	0.0000	0.0015	0.0049	0.0091	0.0118	0.0126	0.0115
PuO_2	$PuO_2 + 4H^+ = Pu^{4+} + 2H_2O$	0.0040	0.0000	0.0051	0.0184	0.0385	0.0584	0.0764	0.0919
PuOBr	$PuOBr + 2H^+ = Pu^{3+} + Br^- + H_2O$	0.0003	0.0000	0.0000	-0.0006	-0.0032	-0.0080	-0.0149	-0.0237
PuOCl	$PuOCl + 2H^+ = Pu^{3+} + Cl^- + H_2O$	0.0004	0.0000	0.0002	0.0002	-0.0015	-0.0054	-0.0115	-0.0194
PuOF	$PuOF + 2H^+ = Pu^{3+} + F^- + H_2O$	0.0006	0.0000	0.0005	0.0011	0.0005	-0.0021	-0.0067	-0.0131
PuOI	$PuOI + 2H^+ = Pu^{3+} + I^- + H_2O$	-0.0019	0.0000	-0.0031	-0.0130	-0.0321	-0.0567	-0.0852	-0.1168

Source: 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 Various Non-Np, Non-Pu Solids with the Correct Scaling of the “c” Heat Capacity Coefficient

				Heat Capacity Coefficients[a]			
Name	**ΔG°_f (J/mol)**	**ΔH°_f (J/mol)**	**S° (J/mol-K)**	**a (J/mol-K)**	**$b \times 10^3$ (J/mol-K^2)**	**$c \times 10^{-6}$ (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 ($Ca_2Fe_2O_5$)[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
$Ca_3Al_2O_6$	-3,411,786	-3,587,800	205.90	260.580	19.1600	-5.030	1, 2
$CaAl_2O_4$	-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_3O_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
$CoCr_2O_4$	-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
$CoFe_2O_4$	-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_2O_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
CrI_3	-205,530	-205,000	199.60	105.440	20.9200	0.000	1, 2
CrO_3	-512,562	-587,000	73.20	71.760	87.8700	-1.670	1, 2
Ferrite-Cu ($CuFe_2O_4$)[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 $FeAl_2O_4$	-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 $FeCr_2O_4$	-1,355,891	-1,458,600	146.90	163.010	22.3400	-3.190	1, 2

Table 6-36. Thermodynamic Data Input for Various Non-Np, Non-Pu Solids with the Correct Scaling of the “c” Heat Capacitiy Coefficient (Continued)

				Heat Capacity Coefficients[a]			
Name	**ΔG°_f (J/mol)**	**ΔH°_f (J/mol)**	**S° (J/mol-K)**	**a (J/mol-K)**	**b × 10^3 (J/mol-K^2)**	**c × 10^{-6} (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	98.30	90.750	11.3100	-0.220	1, 2
Ferrite-Ca	-1,412,731	-1,479,400	145.20	164.930	19.9200	-1.530	1, 2
Ferrite-Ni	-972,893	-1,084,500	125.90	152.670	77.8200	-1.490	1, 2
$FeSO_4$	-824,892	-928,900	121.00	122.000	37.8200	-2.930	1, 2
Ilmenite $FeTiO_3$	-1,158,045	-1,239,200	105.90	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	89.50	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_2O_3	-881,114	-959,000	110.50	102.800	35.6700	-1.280	1, 2
Tephroite Mn_2SiO_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_2Cl_2	-623,302	-725,800	120.50	127.400	7.0300	-1.940	1, 2
Na_2CO_3	-1,048,005	-1,130,800	138.80	11.000	244.0500	2.450	1, 2
Na_2CrO_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_3S_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
$NiCr_2O_4$	-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 $NiFe_2O_4$	-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_2O_3	-1,433,824	-1,520,900	77.30	53.070	163.4400	--	1, 2
Ti_3O_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 –5,155)**	87.30	68.370	18.0300	-0.350	1, 2
$TiCl_3$	-654,451	-721,700	139.80	95.810	11.0600	-0.180	1, 2
TiF_3	-1,361,861	-1,435,500	87.90	79.080	29.2900	0.340	1, 2
TiF_4(am)	-1,559,179	-1,649,300	134.00	123.310	36.2400	-1.770	1, 2
TiI_4	-370,647	-375,700	246.20	71.420	181.8700	-	1, 2
TiO	-513,278	-542,700	34.80	44.220	15.0600	-0.780	1, 2

Table 6-36. Thermodynamic Data Input for Various Non-Np, Non-Pu Solids with the Correct Scaling of the “c” Heat Capacitiy Coefficient (Continued)

				Heat Capacity Coefficients[a]			
Name	**$\Delta G°_f$ (J/mol)**	**$\Delta H°_f$ (J/mol)**	**$S°$ (J/mol-K)**	**a (J/mol-K)**	**b × 10^3 (J/mol-K^2)**	**c × 10^{-6} (J-K/mol)**[b]	**Source**
Uranium U	0	0	50.30	27.590	-4.0400	-0.110	1, 2
$U(SO_4)_2$	-2,087,195	-2,318,000	164.00	104.600	230.9600	-	1, 2
U_2S_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
UCl_3	-794,530	-861,900	159.00	87.780	31.1300	0.490	1, 2
UCl_4	-929,927	-1,018,800	197.20	113.810	35.8600	-0.330	1, 2
UCl_5	-950,061	-1,041,500	246.90	140.040	35.4400	-0.540	1, 2
UCl_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
UF_4	-1,830,173	-1,914,200	151.70	123.560	9.6200	-0.930	1, 2
UF_5(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_2Br_2	-1,066,612	-1,137,600	169.50	117.950	17.5300	-1.070	1, 2
UO_2Cl_2	-1,146,105	-1,243,500	150.60	115.230	18.2000	-1.140	1, 2
UO_2F_2	-1,551,873	-1,651,400	135.60	122.880	8.6200	-1.990	1, 2
UO_2SO_4	-1,683,212	-1,845,100	154.80	112.470	108.7800	-	1, 2
UO_3(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
$UOBr_3$	-901,429	-954,000	205.00	130.540	20.5000	-1.380	1, 2
UOCl	-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
$UOCl_3$	-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
WCl_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_2Cl_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

Sources:
1. All values of $\Delta G°_f$ are from Barin and Platzki (1995 [DIRS 157865]).
2. All values of $\Delta H°_f$, $S°$, and heat capacity coefficients are from Binnewies and Milke (1999 [DIRS 158955]).

[a] Heat capacity coefficients a, b, and c defined in Equation 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.

[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 are developed in the following spreadsheets:

Ferrite-Dicalcium: spreadsheet: *Minerals_j_psd_8_DS_fix.xls*, worksheet: “Ferrite-Dicalcium (fix).”
Ferrite-Cu ($CuFe_2O_4$): spreadsheet: *Minerals_j_psd_9_DS_fix.xls*, worksheet: “Ferrite-Cu (fix).”
$TiCl_2$: spreadsheet: *Minerals_j_psd_1_DS_fix.xls*, worksheet: “TiCl2(s) (fix).”

Table 6-37. Corrected log K Grids for Solid Phases Implemented in data0.ymp.R5

Data0 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**
Witherite ($BaCO_3$)	$BaCO_3 + H^+ = Ba^{2+} + HCO_3^-$	1.9041	1.7639	1.5062	1.1717	0.7100	0.1917	-0.4144	-1.1855
Portlandite ($Ca(OH)_2$)	$Ca(OH)_2 + 2H^+ = Ca^{2+} + 2H_2O$	24.6125	22.5444	20.1862	18.0517	15.9616	14.3045	12.9323	11.7391
Ferrite Dicalcium ($Ca_2Fe_2O_5$)	$Ca_2Fe_2O_5 + 10H^+ = 2Ca^{2+} + 2Fe^{3+} + 5H_2O$	64.4136	56.8114	48.0584	40.0564	32.1116	25.6815	20.2076	15.2897
Ferrite-Mg ($MgFe_2O_4$)	Ferrite-Mg + $8H^+ = 2Fe^{3+} + Mg^{2+} + 4H_2O$	25.4526	20.9808	15.8346	11.1482	6.5052	2.7292	-0.5359	-3.5453
$Ca_3Al_2O_6$	$Ca_3Al_2O_6 + 12H^+ = 3Ca^{2+} + 2Al^{3+} + 6H_2O$	124.6852	111.6139	96.5383	82.7213	68.9964	57.9377	48.6374	40.4634
$CaAl_2O_4$	$CaAl_2O_4 + 8H^+ = Ca^{2+} + 2Al^{3+} + 4H_2O$	52.2923	45.5699	37.7870	30.6288	23.4767	17.6536	12.6792	8.2205
Pseudo-wollastonite ($CaSiO_3$)	$CaSiO_3 + 2H^+ = Ca^{2+} + SiO_2(aq) + H_2O$	15.4054	14.0344	12.3838	10.8597	9.3603	8.1663	7.1587	6.2301
Titanite ($CaSiTiO_5$)	$CaSiTiO_5 + 2H^+ + H_2O = Ti(OH)_4 + Ca_2^+ + SiO_2(aq)$	2.8995	1.9918	0.7981	-0.3263	-1.4237	-2.2881	-3.0278	-3.7622
Perovskite ($CaTiO_3$)	$CaTiO_3 + 2H^+ + H_2O = Ti(OH)_4 + Ca^{2+}$	12.8727	11.0419	8.8630	6.8551	4.8765	3.3010	1.9809	0.7905
$Co(OH)_2$	$Co(OH)_2 + 2H^+ = Co^{2+} + 2H_2O$	14.5818	13.0671	11.3386	9.7790	8.2566	7.0476	6.0355	5.1363
Spinel-Co (Co_3O_4)	$Co_3O_4 + 8H^+ = Co^{2+} + 2Co^{3+} + 4H_2O$	-8.7683	-10.4344	-12.3845	-14.1795	-16.0115	-17.6046	-19.1362	-20.7431
$CoCl_2$	$CoCl_2(s) = Co^{2+} + 2Cl^-$	9.4861	8.2904	6.7200	5.0870	3.2193	1.4485	-0.3404	-2.3262
CoF_3	$CoF_3 = Co^{3+} + 3F^-$	0.5317	-1.3201	-3.7439	-6.2444	-9.0880	-11.7850	-14.5255	-17.5790
Sphaerocobaltite ($CoCO_3$)	$CoCO_3(s) + H^+ = Co^{2+} + HCO_3^-$	1.3240	0.7971	0.1099	-0.5992	-1.4131	-2.2012	-3.0266	-3.9840
$CoCr_2O_4$	$CoCr_2O_4 + 8H^+ = Co^{2+} + 2Cr^{3+} + 4H_2O$	19.2812	15.0442	10.1319	5.6202	1.1016	-2.6209	-5.8826	-8.9219
CoF_2	$CoF_2 = Co^{2+} + 2F^-$	-0.6789	-1.5187	-2.6656	-3.8880	-5.3257	-6.7418	-8.2402	-9.9907
$CoFe_2O_4$	$CoFe_2O_4 + 8H^+ = Co^{2+} + 2Fe^{3+} + 4H_2O$	13.4446	10.0104	6.0420	2.4107	-1.2228	-4.2310	-6.9018	-9.4475
CoO	$CoO + 2H^+ = Co^{2+} + H_2O$	15.2495	13.5557	11.6031	9.8196	8.0552	6.6368	5.4402	4.3753
$CoTiO_3$	$CoTiO_3 + 2H^+ + H_2O = Co^{2+} + Ti(OH)_4(aq)$	18.2297	17.0136	15.5343	14.1645	12.8139	11.7316	10.8045	9.9308
$CoWO_4$	$CoWO_4 = Co^{2+} + WO_4^{2-}$	-11.9847	-11.7760	-11.7291	-11.8788	-12.2822	-12.8981	-13.7588	-14.9905

Table 6-37. Corrected log K Grids for Solid Phases Implemented in data0.ymp.R5 (Continued)

Data0 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_2O_3)	$Cr_2O_3 + 2H_2O + 1.5O_2(g) = 2CrO_4^{2-} + 4H^+$	-11.5436	-12.2116	-13.4372	-15.0171	-17.1381	-19.4062	-21.9006	-24.8658
$CrCl_3$	$CrCl_3(s) = Cr^{3+} + 3Cl^-$	22.9508	19.9413	16.1776	12.4285	8.3270	4.6206	1.0623	-2.6568
CrF_3	$CrF_3(s) = Cr^{3+} + 3F^-$	-7.8740	-9.0957	-10.7847	-12.6037	-14.7665	-16.9197	-19.2158	-21.8988
CrI_3	$CrI_3 = Cr^{3+} + 3I^-$	30.7636	27.4198	23.2699	19.1619	14.7015	10.7132	6.9359	3.0557
CrO_3	$CrO_3 + H_2O = CrO_4^{2-} + 2H^+$	-3.2012	-3.2201	-3.4714	-3.9351	-4.6827	-5.5804	-6.6462	-7.9877
Ferrite-Cu ($CuFe_2O_4$)	$CuFe_2O_4 + 8H^+ = Cu^{2+} + 2Fe^{3+} + 4H_2O$	12.8745	9.5266	5.6722	2.1613	-1.3333	-4.2134	-6.7633	-9.1921
Iron (Fe)	$Fe + 2H^+ + 0.5O_2(g) = Fe^{2+} + H_2O$	63.6419	57.5836	50.6273	44.2830	38.0396	33.0967	29.0558	25.6483
$Fe(OH)_2$	$Fe(OH)_2(s) + 2H^+ = Fe^{2+} + 2H_2O$	15.3477	13.8214	12.0849	10.5217	8.9974	7.7876	6.7751	5.8759
$Fe(OH)_3$	$Fe(OH)_3(s) + 3H^+ = Fe^{3+} + 3H_2O$	7.0070	5.6581	4.1380	2.7863	1.4749	0.4205	-0.4958	-1.3572
$Fe_2(SO_4)_3$	$Fe_3(SO_4)_3(s) = Fe^{3+} + 3SO_4^{2-}$	4.5382	0.8936	-3.9646	-9.0528	-14.9043	-20.4839	-26.1426	-32.4119
Hercynite ($FeAl_2O_4$)	$FeAl_2O_4 + 8H^+ = Fe^{2+} + 2Al^{3+} + 4H_2O$	27.2213	22.4207	16.8420	11.6987	6.5321	2.2752	-1.4349	-4.8537
Lawrencite ($FeCl_2$)	$FeCl_2(g) = Fe^{2+} + 2Cl^-$	10.3385	9.0646	7.4052	5.6922	3.7458	1.9119	0.0690	-1.9676
Molysite ($FeCl_3$)	$FeCl_3(s) = Fe^{3+} + 3Cl^-$	15.8516	13.5217	10.5454	7.5215	4.1378	0.9993	-2.1023	-5.4547
Chromite ($FeCr_2O_4$)	$FeCr_2O_4 + 8H^+ = Fe^{2+} + 2Cr^{3+} + 4H_2O$	21.4534	16.9730	11.7934	7.0498	2.3169	-1.5620	-4.9377	-8.0576
FeF_2	$FeF_2(s) = Fe^{2+} + 2F^-$	-0.5943	-1.4320	-2.5761	-3.7949	-5.2267	-6.6351	-8.1241	-9.8639
FeF_3	$FeF_3(s) = Fe^{3+} + 3F^-$	-19.1363	-19.2386	-19.6390	-20.2780	-21.2731	-22.4970	-24.0325	-26.0812
Ferrite-Ca ($CaFe_2O_4$)	Ferrite-Ca + $8H^+ = 2Fe^{3+} + Ca^{2+} + 4H_2O$	25.8315	21.5945	16.7047	12.2304	7.7701	4.1185	0.9419	-2.0036
Ferrite-Ni ($NiFe_2O_4$)	Ferrite-Ni + $8H^+ = 2Fe^{3+} + Ni^{2+} + 4H_2O$	13.2008	9.7959	5.8487	2.2265	-1.4072	-4.4224	-7.1037	-9.6613
$FeSO_4$	$FeSO_4(s) = Fe^{2+} + SO_4^{2-}$	3.0160	1.9396	0.4818	-1.0620	-2.8537	-4.5771	-6.3409	-8.3212
Ilmenite ($FeTiO_3$)	$FeTiO_3 + 2H^+ + H_2O = Ti(OH)_4 + Fe^{2+}$	4.7351	3.3187	1.6136	0.0422	-1.5020	-2.7328	-3.7765	-4.7442
$MgBr_2$	$MgBr_2 = Mg^{2+} + 2Br^-$	30.5646	27.6871	24.1884	20.8089	17.2448	14.1591	11.3276	8.5018
Chloromagnesite ($MgCl_2$)	$MgCl_2 = Mg^{2+} + 2Cl^-$	24.2706	21.8099	18.7962	15.8593	12.7237	9.9647	7.3824	4.7429
$MgSO_4$	$MgSO_4 = Mg^{2+} + SO_4^{2-}$	6.2422	4.8818	3.1062	1.2859	-0.7602	-2.6686	-4.5701	-6.6537
Bixbyite (Mn_2O_3)	$Mn_2O_3 + 6H^+ = 2Mn^{3+} + 3H_2O$	2.5151	0.0527	-2.8252	-5.4871	-8.1834	-10.4469	-12.4826	-14.4362
Tephroite (Mn_2SiO_4)	$Mn_2SiO_4 + 4H^+ = 2Mn^{2+} + SiO_2(aq) + 2H_2O$	26.8198	24.2091	21.1502	18.3654	15.6422	13.4760	11.6435	9.9606
Scacchite ($MnCl_2$)	$MnCl_2 = Mn^{2+} + 2Cl^-$	10.3344	9.2222	7.7590	6.2351	4.4853	2.8154	1.1121	-0.8040
$MnSO_4$	$MnSO_4 = Mn^{2+} + SO_4^{2-}$	4.0732	3.1105	1.7919	0.3831	-1.2693	-2.8789	-4.5504	-6.4586

Table 6-37. Corrected log K Grids for Solid Phases Implemented in data0.ymp.R5 (Continued)

Data0 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
MoO_2Cl_2	$MoO_2Cl_2 + 2H_2O = MoO_4^{2-} + 2Cl^- + 4H^+$	1.0114	0.5936	-0.2737	-1.4682	-3.1562	-5.0424	-7.2005	-9.8704
Na_2CO_3	$Na_2CO_3 + H^+ = 2Na^+ + HCO_3^-$	11.6028	10.9840	10.2335	9.5237	8.7862	8.1362	7.4957	6.7592
Na_2CrO_4	$Na_2CrO_4 = 2Na^+ + CrO_4^{2-}$	3.8172	3.5616	3.0862	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_3S_2)	$Ni_3S_2 + 4H^+ + 0.5O_2(g) = 3Ni^{2+} + 2HS^- + H_2O$	28.6021	24.4693	19.5049	14.7718	9.8374	5.5959	1.7110	-2.1571
$NiCl_2$	$NiCl_2(s) = Ni^{2+} + 2Cl^-$	9.8354	8.5926	6.9627	5.2714	3.3424	1.5199	-0.3136	-2.3383
$NiCO_3$	$NiCO_3 + H^+ = Ni^{2+} + HCO_3^-$	3.3217	2.5700	1.6121	0.6441	-0.4364	-1.4444	-2.4551	-3.5709
$NiCr_2O_4$	$NiCr_2O_4 + 8H^+ = Ni^{2+} + 2Cr^{3+} + 4H_2O$	28.7818	23.6681	17.7445	12.3055	6.8699	2.4200	-1.4337	-4.9644
NiF_2	$NiF_2(s) = Ni^{2+} + 2F^-$	0.7839	-0.2087	-1.5373	-2.9301	-4.5391	-6.0927	-7.7040	-9.5483
Trevorite ($NiFe_2O_4$)	$NiFe_2O_4 + 8H^+ = Ni^{2+} + 2Fe^{3+} + 4H_2O$	13.2008	9.7959	5.8487	2.2265	-1.4051	-4.4151	-7.0862	-9.6263
$NiSO_4$	$NiSO_4 = Ni^{2+} + SO_4^{2-}$	6.7477	5.3469	3.5093	1.6121	-0.5346	-2.5445	-4.5454	-6.7251
$NiTiO_3$	$NiTiO_3 + 2H^+ + H_2O = Ti(OH)_4 + Ni^{2+}$	3.5747	2.2603	0.6636	-0.8164	-2.2786	-3.4517	-4.4545	-5.3922
$NiWO_4$	$NiWO_4 = Ni^{2+} + WO_4^{2-}$	-11.2995	-11.1792	-11.2383	-11.4884	-11.9944	-12.6951	-13.6275	-14.9206
Ti_2O_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_3O_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 Grids for Solid Phases Implemented in data0.ymp.R5 (Continued)

Data0 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
TiI_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	$U + 2H^+ + 1.5O_2(g) = UO_2^{2+} + H_2O$	229.3698	208.4445	184.4380	162.5359	140.9867	123.9744	110.1697	98.6979
$U(SO_4)_2$	$U(SO_4)_2 = U^{4+} + 2SO_4^{2-}$	-10.6470	-11.9785	-13.8994	-16.0361	-18.6520	-21.3227	-24.2285	-27.6849
U_2S_3	$U_2S_3 + 3H^+ = 2U^{3+} + 3HS^-$	13.0332	10.4341	7.0461	3.5671	-0.3536	-4.0128	-7.6487	-11.5878
UBr_3	$UBr_3 = U^{3+} + 3Br^-$	22.2645	19.9367	16.9090	13.7994	10.3020	7.0598	3.8722	0.4518
UBr_4	$UBr_4 = U^{4+} + 4Br^-$	35.4896	31.2328	25.9925	20.8510	15.3063	10.3601	5.6542	0.7605
UCl_3	$UCl_3 = U^{3+} + 3Cl^-$	14.9568	13.0401	10.4946	7.8273	4.7621	1.8543	-1.0714	-4.2865
UCl_4	$UCl_4 = U^{4+} + 4Cl^-$	25.6371	21.9229	17.3189	12.7604	7.7844	3.2769	-1.0866	-5.7135
UCl_5	$UCl_5 + 2H_2O = UO_2^+ + 5Cl^- + 4H^+$	37.3001	33.8207	29.2728	24.5557	19.2052	14.2286	9.3512	4.1472
UCl_6	$UCl_6 + 2H_2O = UO_2^{2+} + 6Cl^- + 4H^+$	58.6513	53.1432	46.2515	39.3626	31.8081	24.9939	18.4876	11.7108
UF_3	$UF_3 = U^{3+} + 3F^-$	-21.2939	-20.9385	-20.8561	-21.0915	-21.7266	-22.6949	-24.0446	-25.9613
UF_4	$UF_4 = U^{4+} + 4F^-$	-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	$UF_6 + 2H_2O = UO_2^{2+} + 6F^- + 4H^+$	21.5553	17.5678	12.4557	7.2463	1.3981	-4.0509	-9.4686	-15.3832
UI_3	$UI_3 = U^{3+} + 3I^-$	32.9911	29.9408	26.0968	22.2421	18.0049	14.1734	10.5065	6.6935
UI_4	$UI_4 = U^{4+} + 4I^-$	45.2721	40.4934	34.6706	28.9961	22.9161	17.5379	12.4777	7.2943
UO_2Br_2	$UO_2Br_2 = UO_2^{2+} + 2Br^-$	18.4096	16.4880	14.1001	11.7306	9.1432	6.8069	4.5591	2.1893
UO_2Cl_2	$UO_2Cl_2 = UO_2^{2+} + 2Cl^-$	13.7870	12.1037	9.9956	7.8820	5.5426	3.3955	1.2934	-0.9651
UO_2F_2	$UO_2F_2 = UO_2^{2+} + 2F^-$	-5.6625	-6.2647	-7.1190	-8.0669	-9.2359	-10.4458	-11.7863	-13.4186
UO_2SO_4	$UO_2SO_4 = UO_2^{2+} + SO_4^{2-}$	3.6829	2.4282	0.7802	-0.9327	-2.8940	-4.7579	-6.6467	-8.7462
UO_3 (gamma)	$UO_3 + 2H^+ = UO_2^{2+} + H_2O$	9.2004	7.8659	6.3502	4.9769	3.6191	2.5193	1.5758	0.7124
$UOBr_2$	$UOBr_2 + 2H^+ = U^{4+} + 2Br^- + H_2O$	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
UOCl	$UOCl + 2H^+ = U^{3+} + Cl^- + H_2O$	-9.8798	-9.7309	-9.7099	-9.8326	-10.1403	-10.6010	-11.2370	-12.1246
$UOCl_2$	$UOCl_2 + 2H^+ = U^{4+} + 2Cl^- + H_2O$	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)	$WCl_2(s) + 2H_2O + O_2(g) = WO_4^{2-} + 2Cl^- + 4H^+$	93.6338	84.5211	73.6761	63.3790	52.7437	43.8115	35.9624	28.6009

Table 6-37. Corrected log K Grids for Solid Phases Implemented in data0.ymp.R5 (Continued)

Data0 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)	$WCl_4(s) + 3H_2O + 0.5O_2 = WO_4^{2-} + 4Cl^- + 6H^+$	71.3689	64.5388	56.1177	47.8276	38.9055	31.0428	23.7400	16.3841
WCl_5 (s)	$WCl_5(s) + 3.5H_2O + 0.25O_2 = WO_4^{2-} + 5Cl^- + 7H^+$	65.4019	59.3442	51.7110	44.0362	35.5861	27.9512	20.6691	13.1034
WCl_6 (s)	$WCl_6(s) + 4H_2O = WO_4^{2-} + 6Cl^- + 8H^+$	57.2682	52.1561	45.5135	38.6433	30.8566	23.6054	16.4742	8.8097
WO_2Cl_2 (s)	$WO_2Cl_2(s) + 2H_2O = WO_4^{2-} + 2Cl^- + 4H^+$	0.6699	-0.0612	-1.2796	-2.7861	-4.7725	-6.8877	-9.2282	-12.0481
$WOCl_4$ (s)	$WOCl_4(s) + 3H_2O = WO_4^{2-} + 4Cl^- + 6H^+$	34.4557	31.2806	27.0555	22.5950	17.4379	12.5397	7.6296	2.2438
WOF_4 (s)	$WOF_4(s) + 3H_2O = WO_4^{2-} + 4F^- + 6H^+$	10.1133	7.7357	4.4528	0.8968	-3.3209	-7.4485	-11.7279	-16.5992

Source: Output DTN: SN0410T0510404.001, spreadsheets: *Minerals_j_psd_1_DS_fix.xls* to *Minerals_j_psd_9_DS_fix.xls* and *Minerals_j_psd_10_U_DS_fix.xls*.

NOTE: The data given in this table for Eskolaite (Cr_2O_3) and $NiCO_3$ are not implemented in data0.ymp.R5 (Output DTN: SN0612T0502404.014). Data developed in Section 6.7 are used instead for these solids.

Table 6-38. Δlog K (Difference between Incorrect and Corrected Values) for Solid Phases

Data0.ymp.R2 Species Name	Reaction	Δlog K 0.01°C	Δlog K 25°C	Δlog K 60°C	Δlog K 100°C	Δlog K 150°C	Δlog K 200°C	Δlog K 250°C	Δlog K 300°C
Witherite ($BaCO_3$)	$BaCO_3 + H^+ = Ba^{2+} + HCO_3^-$	0.0027	0.0000	0.0035	0.0128	0.0277	0.0434	0.0587	0.0730
Portlandite ($Ca(OH)_2$)	$Ca(OH)_2 + 2H^+ = Ca^{2+} + 2H_2O$	0.0039	0.0000	0.0051	0.0186	0.0401	0.0629	0.0851	0.1059
Ferrite Dicalcium ($Ca_2Fe_2O_5$)	$Ca_2Fe_2O_5 + 10H^+ = 2Ca^{2+} + 2Fe^{3+} + 5H_2O$	0.0117	0.0000	0.0154	0.0561	0.1207	0.1883	0.2534	0.3139
Ferrite-Mg ($MgFe_2O_4$)	Ferrite-Mg + $8H^+ = 2Fe^{3+} + Mg^{2+} + 4H_2O$	0.0066	0.0000	0.0087	0.0319	0.0690	0.1082	0.1462	0.1820
$Ca_3Al_2O_6$	$Ca_3Al_2O_6 + 12H^+ = 3Ca^{2+} + 2Al^{3+} + 6H_2O$	0.0111	0.0000	0.0147	0.0537	0.1161	0.1819	0.2460	0.3062
$CaAl_2O_4$	$CaAl_2O_4 + 8H^+ = Ca^{2+} + 2Al^{3+} + 4H_2O$	0.0074	0.0000	0.0097	0.0356	0.0768	0.1205	0.1629	0.2027
Pseudo-wollastonite ($CaSiO_3$)	$CaSiO_3 + 2H^+ = Ca^{2+} + SiO_2(aq) + H_2O$	0.0052	0.0000	0.0069	0.0252	0.0545	0.0854	0.1154	0.1437
Titanite ($CaSiTiO_5$)	$CaSiTiO_5 + 2H^+ + H_2O = Ti(OH)_4 + Ca^{2+} + SiO_2(aq)$	0.0089	0.0000	0.0118	0.0430	0.0930	0.1458	0.1971	0.2453
Perovskite ($CaTiO_3$)	$CaTiO_3 + 2H^+ + H_2O = Ti(OH)_4 + Ca^{2+}$	0.0062	0.0000	0.0082	0.0299	0.0646	0.1013	0.1370	0.1704
$Co(OH)_2$	$Co(OH)_2 + 2H^+ = Co^{2+} + 2H_2O$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Spinel-Co (Co_3O_4)	$Co_3O_4 + 8H^+ = Co^{2+} + 2Co^{3+} + 4H_2O$	0.0055	0.0000	0.0072	0.0265	0.0572	0.0897	0.1213	0.1510
$CoCl_2$	$CoCl_2(s) = Co^{2+} + 2Cl^-$	0.0010	0.0000	0.0014	0.0050	0.0108	0.0170	0.0230	0.0286
CoF_3*	$CoF_3 = Co^{3+} + 3F^-$*	0.0019	0.0000	0.0026	0.0094	0.0203	0.0318	0.0430	0.0536
Sphaerocobaltite ($CoCO_3$)	$CoCO_3(s) + H^+ = Co^{2+} + HCO_3^-$	0.0040	0.0000	0.0053	0.0192	0.0415	0.0651	0.0880	0.1096
$CoCr_2O_4$	$CoCr_2O_4 + 8H^+ = Co^{2+} + 2Cr^{3+} + 4H_2O$	0.0031	0.0000	0.0041	0.0150	0.0323	0.0506	0.0685	0.0852
CoF_2	$CoF_2 = Co^{2+} + 2F^-$	0.0027	0.0000	0.0036	0.0132	0.0286	0.0449	0.0606	0.0755
$CoFe_2O_4$	$CoFe_2O_4 + 8H^+ = Co^{2+} + 2Fe^{3+} + 4H_2O$	0.0073	0.0000	0.0096	0.0350	0.0757	0.1186	0.1604	0.1997
CoO	$CoO + 2H^+ = Co^{2+} + H_2O$	-0.0013	0.0000	-0.0018	-0.0064	-0.0138	-0.0217	-0.0293	-0.0365
$CoTiO_3$	$CoTiO_3 + 2H^+ + H_2O = Co^{2+} + Ti(OH)_4(aq)$	0.0037	0.0000	0.0048	0.0176	0.0381	0.0597	0.0807	0.1004

Table 6-38. Δlog K (Difference between Incorrect and Corrected Values) for Solid Phases (Continued)

Data0.ymp.R2 Species Name	**Reaction**	**Δlog K 0.01°C**	**Δlog K 25°C**	**Δlog K 60°C**	**Δlog K 100°C**	**Δlog K 150°C**	**Δlog K 200°C**	**Δlog K 250°C**	**Δlog K 300°C**
$CoWO_4$	$CoWO_4 = Co^{2+} + WO_4^{2-}$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Eskolaite (Cr_2O_3)	$Cr_2O_3 + 2H_2O + 1.5O_2(g) = 2CrO_4^{2-} + 4H^+$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
$CrCl_3$	$CrCl_3(s) = Cr^{3+} + 3Cl^-$	0.0022	0.0000	0.0029	0.0107	0.0231	0.0362	0.0489	0.0609
CrF_3	$CrF_3(s) = Cr^{3+} + 3F^-$	0.0036	0.0000	0.0047	0.0173	0.0374	0.0586	0.0792	0.0986
CrI_3	$CrI_3 = Cr^{3+} + 3I^-$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CrO_3	$CrO_3 + H_2O = CrO_4^{2-} + 2H^+$	0.0037	0.0000	0.0049	0.0178	0.0385	0.0604	0.0817	0.1017
Ferrite-Cu ($CuFe_2O_4$)	$CuFe_2O_4 + 8H^+ = Cu^{2+} + 2Fe^{3+} + 4H_2O$	-0.1276	0.0000	0.1755	0.3644	0.5785	0.7672	0.9322	1.0758
Iron (Fe)	$Fe + 2H^+ + 0.5O_2(g) = Fe^{2+} + H_2O$	-0.0004	0.0000	-0.0005	-0.0017	-0.0037	-0.0058	-0.0078	-0.0097
$Fe(OH)_2$	$Fe(OH)_2(s) + 2H^+ = Fe^{2+} + 2H_2O$	0.0064	0.0000	0.0084	0.0307	0.0662	0.1038	0.1404	0.1747
$Fe(OH)_3$	$Fe(OH)_3(s) + 3H^+ = Fe^{3+} + 3H_2O$	0.0093	0.0000	0.0123	0.0451	0.0974	0.1526	0.2064	0.2569
$Fe_2(SO_4)_3$	$Fe_3(SO_4)_3(s) = Fe^{3+} + 3SO_4^{2-}$	0.0235	0.0000	0.0311	0.1137	0.2455	0.3849	0.5204	0.6477
Hercynite ($FeAl_2O_4$)	$FeAl_2O_4 + 8H^+ = Fe^{2+} + 2Al^{3+} + 4H_2O$	0.0078	0.0000	0.0103	0.0376	0.0812	0.1273	0.1722	0.2143
Lawrencite ($FeCl_2$)	$FeCl_2(g) = Fe^{2+} + 2Cl^-$	0.0009	0.0000	0.0012	0.0045	0.0097	0.0152	0.0205	0.0256
Molysite ($FeCl_3$)	$FeCl_3(s) = Fe^{3+} + 3Cl^-$	0.0002	0.0000	0.0003	0.0010	0.0021	0.0033	0.0044	0.0055
Chromite ($FeCr_2O_4$)	$FeCr_2O_4 + 8H^+ = Fe^{2+} + 2Cr^{3-} + 4H_2O$	0.0071	0.0000	0.0093	0.0341	0.0736	0.1154	0.1560	0.1942
FeF_2	$FeF_2(s) = Fe^{2+} + 2F^-$	0.0015	0.0000	0.0020	0.0075	0.0162	0.0253	0.0342	0.0426
FeF_3	$FeF_3(s) = Fe^{3+} + 3F^-$	0.0005	0.0000	0.0006	0.0024	0.0051	0.0080	0.0108	0.0134
Ferrite-Ca ($CaFe_2O_4$)	Ferrite-Ca + $8H^+ = 2Fe^{3+} + Ca^{2+} + 4H_2O$	0.0034	0.0000	0.0045	0.0163	0.0353	0.0553	0.0748	0.0931
Ferrite-Ni ($NiFe_2O_4$)	Ferrite-Ni + $8H^+ = 2Fe^{3+} + Ni^{2+} + 4H_2O$	0.0033	0.0000	0.0043	0.0159	0.0344	0.0539	0.0729	0.0907
$FeSO_4$	$FeSO_4(s) = Fe^{2+} + SO_4^{2-}$	0.0065	0.0000	0.0086	0.0313	0.0676	0.1060	0.1433	0.1784
Ilmenite ($FeTiO_3$)	$FeTiO_3 + 2H^+ + H_2O = Ti(OH)_4 + Fe^{2+}$	0.0044	0.0000	0.0058	0.0214	0.0461	0.0723	0.0978	0.1217
$MgBr_2$	$MgBr_2 = Mg^{2+} + 2Br^-$	0.0002	0.0000	0.0003	0.0012	0.0025	0.0040	0.0054	0.0067

Table 6-38. Δlog K (Difference between Incorrect and Corrected Values) for Solid Phases (Continued)

Data0.ymp.R2 Species Name	**Reaction**	**Δlog K 0.01°C**	**Δlog K 25°C**	**Δlog K 60°C**	**Δlog K 100°C**	**Δlog K 150°C**	**Δlog K 200°C**	**Δlog K 250°C**	**Δlog K 300°C**
Chloromagnesite ($MgCl_2$)	$MgCl_2 = Mg^{2+} + 2Cl^{-}$	0.0015	0.0000	0.0020	0.0075	0.0162	0.0253	0.0342	0.0426
$MgSO_4$	$MgSO_4 = Mg^{2+} + SO_4^{2-}$	0.0048	0.0000	0.0064	0.0234	0.0505	0.0792	0.1071	0.1333
Bixbyite (Mn_2O_3)	$Mn_2O_3 + 6H^+ = 2Mn^{3+} + 3H_2O$	0.0028	0.0000	0.0037	0.0137	0.0295	0.0463	0.0626	0.0779
Tephroite (Mn_2SiO_4)	$Mn_2SiO_4 + 4H^+ = 2Mn^{2+} + SiO_2(aq) +2H_2O$	0.0069	0.0000	0.0091	0.0332	0.0718	0.1125	0.1521	0.1893
Scacchite ($MnCl_2$)	$MnCl_2 = Mn^{2+} + 2Cl^{-}$	0.0010	0.0000	0.0014	0.0050	0.0108	0.0170	0.0230	0.0286
$MnSO_4$	$MnSO_4 = Mn^{2+} + SO_4^{2-}$	0.0065	0.0000	0.0086	0.0315	0.0681	0.1067	0.1443	0.1796
MoO_2Cl_2	$MoO_2Cl_2 + 2H_2O = MoO_4^{2-} + 2Cl^{-} + 4H^+$	0.0043	0.0000	0.0057	0.0207	0.0448	0.0702	0.0949	0.1181
Na_2CO_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_2CrO_4	$Na_2CrO_4 = 2Na^+ + CrO_4^{2-}$	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_3S_2)	$Ni_3S_2 + 4H^+ + 0.5O_2(g) = 3Ni^{2+} + 2HS^- + H_2O$	0.0017	0.0000	0.0022	0.0080	0.0173	0.0271	0.0367	0.0457
$NiCl_2$	$NiCl_2(s) = Ni^{2+} + 2Cl^{-}$	0.0011	0.0000	0.0014	0.0051	0.0111	0.0174	0.0235	0.0292
$NiCO_3$	$NiCO_3 + H^+ = Ni^{2+} + HCO_3^-$	0.0027	0.0000	0.0036	0.0131	0.0284	0.0445	0.0602	0.0749
$NiCr_2O_4$	$NiCr_2O_4 + 8H^+ = Ni^{2+} + 2Cr^{3+} + 4H_2O$	0.0047	0.0000	0.0062	0.0225	0.0487	0.0763	0.1032	0.1284
NiF_2	$NiF_2(s) = Ni^{2+} + 2F^-$	0.0013	0.0000	0.0017	0.0063	0.0136	0.0213	0.0289	0.0359
Trevorite ($NiFe_2O_4$)	$NiFe_2O_4 + 8H^+ = Ni^{2+} + 2Fe^{3+} + 4H_2O$	0.0033	0.0000	0.0043	0.0159	0.0344	0.0539	0.0729	0.0907
$NiSO_4$	$NiSO_4 = Ni^{2+} + SO_4^{2-}$	0.0072	0.0000	0.0095	0.0348	0.0752	0.1179	0.1595	0.1984
$NiTiO_3$	$NiTiO_3 + 2H^+ + H_2O = Ti(OH)_4 + Ni^{2+}$	0.0040	0.0000	0.0053	0.0195	0.0422	0.0662	0.0895	0.1114
$NiWO_4$	$NiWO_4 = Ni^{2+} + WO_4^{2-}$	0.0010	0.0000	0.0013	0.0047	0.0102	0.0159	0.0215	0.0268
Ti_2O_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_3O_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
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
$TiBr_3$	$TiBr_3 + 3.5H_2O + 0.25O_2(g) =$	-0.0002	0.0000	-0.0002	-0.0009	-0.0018	-0.0029	-0.0039	-0.0049

Table 6-38. Δlog K (Difference between Incorrect and Corrected Values) for Solid Phases (Continued)

Data0.ymp.R2 Species Name	Reaction	Δlog K 0.01°C	Δlog K 25°C	Δlog K 60°C	Δlog K 100°C	Δlog K 150°C	Δlog K 200°C	Δlog K 250°C	Δlog K 300°C
	$Ti(OH)_4 + 3Br^- + 3H^+$								
$TiBr_4$	$TiBr_4 + 4H_2O = Ti(OH)_4 + 4Br^- + 4H^+$	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
TiI_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	$U + 2H^+ + 1.5O_2(g) = UO_2^{2+} + H_2O$	0.0002	0.0000	0.0003	0.0012	0.0025	0.0040	0.0054	0.0067
$U(SO_4)_2$	$U(SO_4)_2 = U^{4+} + 2SO_4^{2-}$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
U_2S_3	$U_2S_3 + 3H^+ = 2U^{3+} + 3HS^-$	0.0008	0.0000	0.0011	0.0041	0.0088	0.0137	0.0186	0.0231
UBr_3	$UBr_3 = U^{3+} + 3Br^-$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
UBr_4	$UBr_4 = U^{4+} + 4Br^-$	0.0025	0.0000	0.0033	0.0121	0.0261	0.0409	0.0553	0.0688
UCl_3	$UCl_3 = U^{3+} + 3Cl^-$	-0.0011	0.0000	-0.0014	-0.0052	-0.0113	-0.0177	-0.0240	-0.0298
UCl_4	$UCl_4 = U^{4+} + 4Cl^-$	0.0007	0.0000	0.0010	0.0035	0.0076	0.0119	0.0161	0.0201
UCl_5	$UCl_5 + 2H_2O = UO_2^+ + 5Cl^- + 4H^+$	0.0012	0.0000	0.0016	0.0058	0.0125	0.0195	0.0264	0.0329
UCl_6	$UCl_6 + 2H_2O = UO_2^{2+} + 6Cl^- + 4H^+$	0.0016	0.0000	0.0022	0.0079	0.0171	0.0268	0.0362	0.0450
UF_3	$UF_3 = U^{3+} + 3F^-$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
UF_4	$UF_4 = U^{4+} + 4F^-$	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	$UF_6 + 2H_2O = UO_2^{2+} + 6F^- + 4H^+$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
UI_3	$UI_3 = U^{3+} + 3I^-$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
UI_4	$UI_4 = U^{4+} + 4I^-$	0.0035	0.0000	0.0046	0.0170	0.0367	0.0575	0.0778	0.0968
UO_2Br_2	$UO_2Br_2 = UO_2^{2+} + 2Br^-$	0.0024	0.0000	0.0031	0.0114	0.0247	0.0387	0.0523	0.0651

Table 6-38. Δlog K (Difference between Incorrect and Corrected Values) for Solid Phases (Continued)

Data0.ymp.R2 Species Name	**Reaction**	**Δlog K 0.01°C**	**Δlog K 25°C**	**Δlog K 60°C**	**Δlog K 100°C**	**Δlog K 150°C**	**Δlog K 200°C**	**Δlog K 250°C**	**Δlog K 300°C**
UO_2Cl_2	$UO_2Cl_2 = UO_2^{2+} + 2Cl^-$	0.0025	0.0000	0.0033	0.0122	0.0263	0.0412	0.0558	0.0694
UO_2F_2	$UO_2F_2 = UO_2^{2+} + 2F^-$	0.0044	0.0000	0.0058	0.0213	0.0459	0.0720	0.0973	0.1211
UO_2SO_4	$UO_2SO_4 = UO_2^{2+} + SO_4^{2-}$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
UO_3 (gamma)	$UO_3 + 2H^+ = UO_2^{2+} + H_2O$	0.0025	0.0000	0.0032	0.0119	0.0256	0.0402	0.0543	0.0676
$UOBr_2$	$UOBr_2 + 2H^+ = U^{4+} + 2Br^- + H_2O$	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
UOCl	$UOCl + 2H^+ = U^{3+} + Cl^- + H_2O$	0.0018	0.0000	0.0024	0.0089	0.0192	0.0300	0.0406	0.0505
$UOCl_2$	$UOCl_2 + 2H^+ = U^{4+} + 2Cl^- + H_2O$	0.0016	0.0000	0.0022	0.0079	0.0171	0.0268	0.0362	0.0450
$UOCl_3$	$UOCl_3 + H_2O = UO_2^+ + 3Cl^- + 2H^+$	0.0026	0.0000	0.0035	0.0127	0.0275	0.0430	0.0582	0.0724
WCl_2 (s)	$WCl_2(s) + 2H_2O + O_2(g) = WO_4^{2-} + 2Cl^- + 4H^+$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
WCl_4 (s)	$WCl_4(s) + 3H_2O + 0.5O_2 = WO_4^{2-} + 4Cl^- + 6H^+$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
WCl_5 (s)	$WCl_5(s) + 3.5H_2O + 0.25O_2 = WO_4^{2-} + 5Cl^- + 7H^+$	0.0003	0.0000	0.0004	0.0015	0.0032	0.0051	0.0068	0.0085
WCl_6 (s)	$WCl_6(s) + 4H_2O = WO_4^{2-} + 6Cl^- + 8H^+$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
WO_2Cl_2 (s)	$WO_2Cl_2(s) + 2H_2O = WO_4^{2-} + 2Cl^- +$ 4H+	0.0006	0.0000	0.0008	0.0031	0.0067	0.0105	0.0142	0.0177
$WOCl_4$ (s)	$WOCl_4(s) + 3H_2O = WO_4^{2-} + 4Cl^- + 6H^+$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
WOF_4 (s)	$WOF_4(s) + 3H_2O = WO_4^{2-} + 4F^- + 6H^+$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Source: Output DTN: SN0410T0510404.001, spreadsheets: *Minerals_j_psd_1_DS_fix.xls* to *Minerals_j_psd_9_DS_fix.xls* and *Minerals_j_psd_10_U_DS_fix.xls*.

* The equation for CoF_3 is corrected from the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), which gives an equation for $CoCl_3$.

Table 6-39. Comparison of ΔH_f° 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/Pla[2]**	**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 $Ca_2Fe_2O_5$	-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
$Ca_3Al_2O_6$	-3,587,800	-3,587,801	1.00	205.9	205.899	0.001	46	445
$CaAl_2O_4$	-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 $CaSiTiO_5$	-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_3O_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
$CoCr_2O_4$	-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
$CoFe_2O_4$	-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
$CoTiO_3$	-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_2O_3	-1,140,600	-1,139,701	-899.00	81.2	81.199	0.001	422	573
$CrCl_3$	-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
CrI_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 $CuFe_2O_4$ (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 $FeAl_2O_4$	-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)

Solid Species	**ΔH_f° (J/mol) 99Bin/Mil[1]**	**ΔH_f° (J/mol) 95Bar/Pla[2]**	**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]**
Molysite $FeCl_3$	-399,200	-399,405	205.00	147.8	142.336	5.464	362	687
Chromite $FeCr_2O_4$	-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 ($CaFe_2O_4$)	-1,479,400	-1,520,340	40940.00	145.2	145.352	-0.152	279	453
Ferrite-Ni ($NiFe_2O_4$)	-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 Mn_2O_3	-959,000	-959,002	2.00	110.5	110.499	0.001	689	1047
Tephroite Mn_2SiO_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_2Cl_2	-725,800	-717,100	-8700.00	120.5	142.256	-21.756	342	1074
Na_2CO_3	-1,130,800	-1,130,768	-32.00	138.8	138.783	0.017	243	1117
Na_2CrO_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_3S_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
$NiCr_2O_4$	-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 $NiFe_2O_4$	-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_2O_3	-1,520,900	-1,520,884	-16.00	77.3	77.237	0.063	772	1694
Ti_3O_5 (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/Pla[2]**	**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
TiI_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
UBr_4	-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
UCl_4	-1,018,800	-1,019,201	401.00	197.2	197.100	0.100	394	1735
UCl_5	-1,041,500	-1,059,000	17500.00	246.9	242.701	4.199	400	1736
UCl_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
UF_5(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_2Br_2	-1,137,600	-1,137,630	30.00	169.5	169.452	0.048	187	1749
UO_2Cl_2	-1,243,500	-1,243,903	403.00	150.6	150.540	0.060	346	1751
UO_2F_2	-1,651,400	-1,648,078	-3322.00	135.6	135.562	0.038	484	1752
UO_2SO_4	-1,845,100	-1,845,102	2.00	154.8	154.808	-0.008	789	1754
UO_3(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
$UOBr_3$	-954,000	-953,952	-48.00	205	205.016	-0.016	202	1749
UOCl	-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
$UOCl_3$	-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
WCl_5(s)	-513,000	-512,958	-42.00	217.6	217.568	0.032	400	1794
WCl_6(s)	-593,700	-593,710	10.00	238.5	238.488	0.012	402	1795
WO_2Cl_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].
2 Barin and Platzki 1995 [DIRS 157865].
Output DTN: This table appears in Output DTN: SN0410T0510404.001.

* The S° values for wollastonite and CoF_2 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.

6.3.4.6 Qualified Equilibrium Constant Data for Solid Phases from Sources Other than Compilations and Handbooks

Data and Calculations Not Documented in Rev. 00 of This Report. Anthony et al. (2000 [DIRS 153209]) performed a study of the solubility of $FeOHCrO_4$. For the reaction $FeOHCrO_4 + H^+ = Fe^{3+} + CrO_4^{2-} + H_2O$ they determined a log K value of -7.1 ± 0.2 (assumed for 25°C). At pH values above 2, they found that $FeOHCrO_4$ is unstable relative to an amorphous product they identified as $Fe_4(OH)_{10}CrO_4$ (here referred to as Cr-ferrihydrite). They determined for the reaction $Fe_4(OH)_{10}CrO_4 + 10\ H^+ = 4\ Fe^{3+} + CrO_4^{2-} + 10\ H_2O$ a log K value of 0.7 ± 0.8. This result (which is the only data known to be available) is directed incorporated into data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) and is retained in data0.ymp.R4 (Output DTN: SN0410T0510404.002) and data0.ymp.R5 (Output DTN: SN0612T0502404.014). The data were obtained in an experiment in which the Cr-ferrihydrite formed spontaneously; hence, these data provide a meaningful bound on aqueous chromate concentrations in the presence of ferric iron. The data for $FeOHCrO_4$ are not used in any of these databases owing to the limited region of stability in pH space.

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], p. 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:

$$HF(aq) = H^+ + F^- \qquad \text{(Eq. 6-34)}$$

Data for dissociation of HF_2^- (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:

$$HF(aq) + F^- = HF_2^- \qquad \text{(Eq. 6-35)}$$

In the current qualification effort it was found that the reaction delineated by Equation 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:

$$HF_2^- = H^+ + 2F^- \qquad \text{(Eq. 6-36)}$$

Moreover, the values given in the source for the reaction delineated by Equation 6-35 are expressed as K, not log K as documented in spreadsheet *HF2- Dissasoc.xls* (DTN: MO0302SPATHDYN.001 [DIRS 161886]). Therefore, the data block needs to be corrected in accord with Equation 6-36 using the retrieved log K data from for reactions given by Equations 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 Equations 6-34 and 6-35 yields the log K value for Equation 6-36 as function of temperature (see spreadsheet *HF2-_Dissoc1_CFJC_fix.xls* in Output DTN: SN0410T0510404.001). The data are compared to the values reported in the qualified database data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]) (Table 6-40).

Table 6-40. Log K Grids for the Aqueous Species HF(aq) and H_2F^- Using Data from Various Sources

T (°C)	0.01	25	60	100	150	200	250	300	Source
HF(aq)[a]	-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^-[b]	4.2705	3.4048	4.2836	4.9121	5.2966	7.9085	-	-	4
HF_2^-[c]	-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^-[d]	-	-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.
3. data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]) for the reaction given by Equation 6-36.
4. Grid for the reaction given by Equation 6-36 as erroneously entered in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) (see text).
5. Wagman et al. 1982 [DIRS 159216], pp. 2-38, 2-45, and 2-46.

[a] This data grid is used in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]), data0.ymp.R4 (Output DTN: SN0410T0510404.002), and data0.ymp.R5 (Output DTN: SN0612T0502404.014).

[b] This data grid is used in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]). It is erroneous (see text).

[c] This data grid is used in data0.ymp.R4 (Output DTN: SN0410T0510404.002) and data0.ymp.R5 (Output DTN: SN0612T0502404.014). Corrected log K grid for the reaction delineated in Equation 6-36 using data from 1 and 2 (see spreadsheet *HF2-_Dissoc1_CFJC_fix.xls* in Output DTN: SN0410T0510404.001).

[d] Calculated using Gibbs energy of formation data from Wagman et al. (1982 [DIRS 159216], pp. 2-38, 2-45, and 2-46) for the species HF_2^-, F^-, and H^+.

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 HF_2^- 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 Equation 6-36 computed using handbook thermodynamic data (Wagman et al. 1982 [DIRS 159216]) is used to evaluate the difference between the corrected values for 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 25ºC 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 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).

Additional errors were subsequently uncovered that affect both data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) and data0.ymp.R4 (Output DTN: SN0410T0510404.002). These were discovered too late to correct in data0.ymp.R4, though they were noted in Rev. 00 of this analysis report and corrected log K grids were presented in that document. These corrections were not implemented in data0.ymp.R5 (Output DTN: SN0612T0502404.014) (see Section 6.8).

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. The corrected log K grids in Table 6-43 should replace the corresponding log K grids from Table 6-41 in data0.ymp.R5 (Output DTN: SN0612T0502404.014).

The combined use of different sets of thermodynamic data could create discrepancies between the retrieved thermodynamic parameters generated by this study (e.g., $\Delta G_f°$ and log K). In this report, two types of thermodynamic data ($\Delta G_f°$ and $\Delta H_f°$; $S°$ and $C_p°$) 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 $\Delta G_f°$ values were obtained from Barin and Platzki (1995 [DIRS 157865]) and the heat capacity data ($C_p°$) used to extrapolate the apparent Gibbs 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 $\Delta G_f°$ (i.e., $\Delta H_f°$ and $S°$) are identical or at least very close within the uncertainty reported in each source. Table 6-45 shows a comparison of $\Delta H_f°$ 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 $\Delta H_f°$ 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 Grids for Gas Species Used in data0.ymp.R2

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
$CoCl_2(g)$	$CoCl_2(g) = Co^{2+} + 2Cl^-$	41.4537	36.7471	31.1543	25.8597	20.4010	15.8084	11.7430	7.8795
$CoF_2(g)$	$CoCl_2(g) = Co^{2+} + 2F^-$	49.3305	43.4386	36.4974	29.9939	23.3714	17.8778	13.0898	8.6294
$CoCl_3(g)$	$CoCl_3(g) = Co^{3+} + 3Cl^-$	22.2966	18.4912	13.8127	9.2301	4.3105	-0.0388	-4.1179	-8.2725
$FeCl_2(g)$	$FeCl_2(g) = Fe^{2+} + 2Cl^-$	39.2745	34.7781	29.4270	24.3536	19.1135	14.6946	10.7712	7.0262
$FeCl_3(g)$	$FeCl_3(g) = Fe^{3+} + 3Cl^-$	33.2539	28.6029	22.9692	17.5297	11.7840	6.7987	2.2182	-2.3408
$FeF_2(g)$	$FeF_2(g) = Fe^{2+} + 2F^-$	50.5720	44.6657	37.7009	31.1680	24.5078	18.9773	14.1542	9.6606
$FeF_3(g)$	$FeF_3(g) = Fe^{3+} + 3F^-$	12.3517	8.7062	4.2443	-0.0944	-4.7214	-8.8021	-12.6442	-16.5964
$H_2O(g)$	$H_2O(g) = H_2O(aq)$	2.2146	1.4999	0.7020	-0.0003	-0.6614	-1.1562	-1.5353	-1.8314
$N_2O(g)$	$N_2O(g) + O_2(g) + H_2O = 2H^+ + 2NO_2^-$	-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
$N_2O_4(g)$	$N_2O_4(g) + H_2O = 2H^+ + NO_3^- + NO_2^-$	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
$NiCl_2(g)$	$NiCl_2(g) = Ni^{2+} + 2Cl^-$	44.3255	39.3145	33.3600	27.7233	21.9152	17.0361	12.7305	8.6624
$NiF_2(g)$	$NiF_2(g) = Ni^{2+} + 2F^-$	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
$TiCl_3(g)$	$TiCl_3(g) + 3.5H_2O + 0.25O_2 = Ti(OH)_4(aq) + 3Cl^- + 3H^+$	70.9080	63.3449	54.2966	45.7197	36.9126	29.5752	23.1791	17.2172

Table 6-41. Log K Grids for Gas Species Used in data0.ymp.R2 (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
$WCl_2(g)$	$WCl_2(g) + 2H_2O + O_2(g) = WO_4^{2-} + 2Cl^- +4H^+$	131.0808	118.0426	102.7000	88.3078	73.6569	61.5713	51.1828	41.7346
$WCl_4(g)$	$WCl_4(g) + 3H_2O + 0.5O_2 = WO_4^{2-} + 4Cl^- + 6H^+$	82.4091	73.8570	63.4710	53.4023	42.7497	33.5415	25.1672	16.9419
$WCl_6(g)$	$WCl_6(g) + 4H_2O = WO_4^{2-} + 6Cl^- + 8H^+$	66.9459	60.2282	51.7525	43.2240	33.8288	25.3346	17.2232	8.7737
$WF(g)$	$WF(g) + 1.5H_2O + 1.25O_2 = WO_4^{2-} + F^- + 3H^+$	446.1868	406.2009	359.7610	316.8493	273.9572	239.3569	210.4069	185.0598
$WF_6(g)$	$WF_6(g) + 4H_2O = WO_4^{2-} + 6F^- + 8H^+$	7.3753	4.1500	-0.2826	-5.0591	-10.6927	-16.1771	-21.8419	-28.2782
$WO_2Cl_2(g)$	$WO_2Cl_2(g) + 2H_2O = WO_4^{2-} + 2Cl^- + 4H^+$	13.4668	10.9926	7.7737	4.4438	0.6700	-2.8458	-6.3093	-10.0460
$WOCl_4(g)$	$WOCl_4(g) + 3H_2O = WO_4^{2-} + 4Cl^- + 6H^+$	42.5106	37.7624	31.7416	25.6554	18.9179	12.7936	6.9105	0.7393
$WOF_4(g)$	$WOF_4(g) + 3H_2O = WO_4^{2-} + 4F^- + 6H^+$	12.8522	9.5474	5.2052	0.6912	-4.4534	-9.2934	-14.1299	-19.4418

Source: DTN: MO0302SPATHDYN.001 [DIRS 161886], spreadsheets: *Minerals_j_psd_1.xls*, *Minerals_j_psd_2.xls*, *Minerals_j_psd_3.xls*, *Minerals_j_psd_4.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)**	**$b \times 10^3$ (J/mol-K^2)**	**$c \times 10^{-6}$ (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
$CrCl_4$(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].
2. Binnewies and Milke 1999 [DIRS 158955].

[a] Heat capacity coefficients a, b, and c defined in Equation 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. Corrected log K Grids for Gas Species in Table 6-41

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**
$CoCl_2(g)$	$CoCl_2(g) = Co^{2+} + 2Cl^-$	41.4541	36.7471	31.1548	25.8615	20.4049	15.8145	11.7513	7.8899
$CoF_2(g)$[b]	$CoF_2(g) = Co^{2+} + 2F^-$	49.3315	43.4386	36.4987	29.9986	23.3815	17.8937	13.1113	8.6562
$CoCl_3(g)$	$CoCl_3(g) = Co^{3+} + 3Cl^-$	22.2987	18.4912	13.8155	9.2403	4.3327	-0.0040	-4.0710	-8.2141
$CrCl_4$ (g)	$CrCl_4(g) + 0.5H_2O = Cr^{3+} + 4Cl^- + 0.25O_2(g) + H^+$	43.5477	38.1077	31.4658	24.9997	18.1084	12.0732	6.4784	0.8564
$FeCl_2(g)$	$FeCl_2(g) = Fe^{2+} + 2Cl^-$	39.2751	34.7781	29.4278	24.3567	19.1202	14.7051	10.7854	7.0438
$FeCl_3(g)$	$FeCl_3(g) = Fe^{3+} + 3Cl^-$	33.2549	28.6029	22.9706	17.5346	11.7946	6.8153	2.2407	-2.3128
$FeF_2(g)$	$FeF_2(g) = Fe^{2+} + 2F^-$	50.5747	44.6657	37.7045	31.1811	24.5361	19.0218	14.2144	9.7355
$FeF_3(g)$	$FeF_3(g) = Fe^{3+} + 3F^-$	12.3544	8.7062	4.2479	-0.0813	-4.6930	-8.7576	-12.5840	-16.5215
$NiCl_2(g)$	$NiCl_2(g) = Ni^{2+} + 2Cl^-$	44.3269	39.3145	33.3619	27.7303	21.9304	17.0599	12.7627	8.7026
$NiF_2(g)$	$NiF_2(g) = Ni^{2+} + 2F^-$	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

Table 6-43. Corrected log K Grids for 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**
$WCl_2(g)$	$WCl_2(g) + 2H_2O + O_2(g) = WO_4^{2-} + 2Cl^- + 4H^+$	131.0810	118.0426	102.7003	88.3089	73.6592	61.5749	51.1877	41.7407
$WCl_4(g)$	$WCl_4(g) + 3H_2O + 0.5O_2 = WO_4^{2-} + 4Cl^- + 6H^+$	82.4109	73.8570	63.4733	53.4106	42.7677	33.5697	25.2054	16.9894
$WCl_6(g)$	$WCl_6(g) + 4H_2O = WO_4^{2-} + 6Cl^- + 8H^+$	66.9486	60.2282	51.7561	43.2371	33.8571	25.3791	17.2833	8.8486
$WF(g)$	$WF(g) + 1.5H_2O + 1.25O_2 = WO_4^{2-} + F^- + 3H^+$	446.1880	406.2009	359.7625	316.8549	273.9692	239.3758	210.4323	185.0915
$WF_6(g)$	$WF_6(g) + 4H_2O = WO_4^{2-} + 6F^- + 8H^+$	7.3823	4.1500	-0.2735	-5.0256	-10.6202	-16.0635	-21.6883	-28.0870
$WO_2Cl_2(g)$	$WO_2Cl_2(g) + 2H_2O = WO_4^{2-} + 2Cl^- + 4H^+$	13.4703	10.9926	7.7783	4.4606	0.7062	-2.7890	-6.2325	-9.9504
$WOCl_4(g)$	$WOCl_4(g) + 3H_2O = WO_4^{2-} + 4Cl^- + 6H^+$	42.5155	37.7624	31.7481	25.6792	18.9694	12.8742	7.0196	0.8751
$WOF_4(g)$	$WOF_4(g) + 3H_2O = WO_4^{2-} + 4F^- + 6H^+$	12.8584	9.5474	5.2133	0.7208	-4.3895	-9.1932	-13.9944	-19.2731

Source: Output DTN: SN0410T0510404.001, spreadsheets: *Minerals_j_psd_1_DS_fix.xls* to *Minerals_j_psd_9_DS_fix.xls* and *Minerals_j_psd_10_U_DS_fix.xls*.

NOTES: These corrections are not implemented in data0.ymp.R5 (Output DTN: SN0612T0502404.014).

The equation for CoF_2 is corrected from the data0.ymp.R2 file (DTN: MO0302SPATHDYN.000 [DIRS 161756]), which gives an equation for $CoCl_2$.

Table 6-44. Δlog K (Difference between Incorrect and Corrected Values) for Gas Species

Data0.ymp.R2 Species Name	Reaction	Δlog K 0.01°C	Δlog K 25°C	Δlog K 60°C	Δlog K 100°C	Δlog K 150°C	Δlog K 200°C	Δlog K 250°C	Δlog K 300°C
$CoCl_2$(g)	$CoCl_2(g) = Co^{2+} + 2Cl^-$	0.0004	0.0000	0.0005	0.0018	0.0039	0.0061	0.0083	0.0103
CoF_2(g)*	$CoF_2(g) = Co^{2+} + 2F^-$	0.0010	0.0000	0.0013	0.0047	0.0102	0.0159	0.0215	0.0268
$CoCl_3$(g)	$CoCl_3(g) = Co^{3+} + 3Cl^-$	0.0021	0.0000	0.0028	0.0103	0.0222	0.0347	0.0470	0.0584
$CrCl_4$ (g)	$CrCl_4(g) + 0.5H_2O = Cr^{3+} + 4Cl^- + 0.25O_2(g) + H^+$	0.0021	0.0000	0.0028	0.0101	0.0219	0.0344	0.0465	0.0578
$FeCl_2$(g)	$FeCl_2(g) = Fe^{2+} + 2Cl^-$	0.0006	0.0000	0.0008	0.0031	0.0067	0.0105	0.0142	0.0177
$FeCl_3$(g)	$FeCl_3(g) = Fe^{3+} + 3Cl^-$	0.0010	0.0000	0.0013	0.0049	0.0106	0.0166	0.0225	0.0280
FeF_2(g)	$FeF_2(g) = Fe^{2+} + 2F^-$	0.0027	0.0000	0.0036	0.0131	0.0284	0.0445	0.0602	0.0749
FeF_3(g)	$FeF_3(g) = Fe^{3+} + 3F^-$	0.0027	0.0000	0.0036	0.0131	0.0284	0.0445	0.0602	0.0749
$NiCl_2$(g)	$NiCl_2(g) = Ni^{2+} + 2Cl^-$	0.0015	0.0000	0.0019	0.0071	0.0152	0.0239	0.0323	0.0402
NiF_2(g)	$NiF_2(g) = Ni^{2+} + 2F^-$	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)	$TiF(g) + 2.5H_2O + 0.75O_2 = Ti(OH)_4(aq) + F^- + H^+$	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. Δlog K (Difference between Incorrect and Corrected Values) for Gas Species (Continued)

Data0.ymp.R2 Species Name	Reaction	Δlog K 0.01°C	Δlog K 25°C	Δlog K 60°C	Δlog K 100°C	Δlog K 150°C	Δlog K 200°C	Δlog K 250°C	Δlog K 300°C
$WCl_2(g)$	$WCl_2(g) + 2H_2O + O_2(g) = WO_4^{2-} + 2Cl^- +4H^+$	0.0002	0.0000	0.0003	0.0011	0.0023	0.0036	0.0049	0.0061
$WCl_4(g)$	$WCl_4(g) + 3H_2O + 0.5O_2 = WO_4^{2-} + 4Cl^- + 6H^+$	0.0017	0.0000	0.0023	0.0083	0.0180	0.0282	0.0382	0.0475
$WCl_6(g)$	$WCl_6(g) + 4H_2O = WO_4^{2-} + 6Cl^- + 8H^+$	0.0027	0.0000	0.0036	0.0131	0.0284	0.0445	0.0602	0.0749
WF(g)	$WF(g) + 1.5H_2O + 1.25O_2 = WO_4^{2-} + F^- + 3H^+$	0.0012	0.0000	0.0015	0.0056	0.0120	0.0188	0.0254	0.0317
$WF_6(g)$	$WF_6(g) + 4H_2O = WO_4^{2-} + 6F^- + 8H^+$	0.0069	0.0000	0.0092	0.0335	0.0725	0.1136	0.1536	0.1911
$WO_2Cl_2(g)$	$WO_2Cl_2(g) + 2H_2O = WO_4^{2-} + 2Cl^- + 4H^+$	0.0035	0.0000	0.0046	0.0168	0.0362	0.0568	0.0768	0.0956
$WOCl_4(g)$	$WOCl_4(g) + 3H_2O = WO_4^{2-} + 4Cl^- + 6H^+$	0.0049	0.0000	0.0065	0.0238	0.0515	0.0807	0.1091	0.1357
$WOF_4(g)$	$WOF_4(g) + 3H_2O = WO_4^{2-} + 4F^- + 6H^+$	0.0061	0.0000	0.0081	0.0296	0.0639	0.1002	0.1355	0.1686

Source: Output DTN: SN0410T0510404.001, spreadsheets: *Minerals_j_psd_1_DS_fix.xls* to *Minerals_j_psd_9_DS_fix.xls* and *Minerals_j_psd_10_U_DS_fix.xls*.

NOTE: The equation for CoF_2 is corrected from the data0.ymp.R2 file (DTN: MO0302SPATHDYN.000 [DIRS 161756]), which gives an equation for $CoCl_2$.

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 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]**
$CoCl_2$(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
$CrCl_4$(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
$TiCl_3$(g)	-539,300	-539,318	18	316.9	316.838	0.062	380	1678
$TiCl_4$(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
TiF_3(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
$WOCl_4$(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:

$$\log \gamma_i = -\frac{A_{\gamma,10} z_i^2 \sqrt{I}}{1 + B_\gamma \mathring{a}_i \sqrt{I}} + \dot{B} I \qquad \text{(Eq. 6-37)}$$

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, $\dot{B}$ is the B-dot parameter, I is the ionic strength, Z_i is the electrical charge number of the species, and $\mathring{a}_i$ 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 to 41) for determining aqueous activity coefficients. Values for the "azero" parameters in a thermochemical database in the data0.ymp.R* series are contained in a 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):

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

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 to 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 and 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 and 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 and 39) is valid for use in the same concentration range as the B-dot equation. Pitzer's equations (Wolery 1992 [DIRS 100836], pp. 44 to 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 are given in spreadsheet *Volume_Q_DS_11-17-04.xls* (Output 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 volume values are compared to those from the data0.ymp.R2 database (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 ($Ni_3(PO_4)_2$), 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 cm^3/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 cm^3/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 cm^3/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 (cm^3/mol)	Calculated Molar Volume (Crystal Parameter) (cm^3/mol)	Calculated Molar Volume (Density) (cm^3/mol)[a]	Density Min. (g/cm^3)	Density Max. (g/cm^3)[b]	Z1[c]	Mineral Volume (cm^3)[d]	Molar Volume (cm^3/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]	-
Beidellite-K	134.15	189.66	164.92	2	2.3	2.00	6.79E-22	204.45	n	Barthelmy 2004 [DIRS 172415]	-
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]	-
$CaUO_4$	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-aluminoceladonite	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

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/cm^3)	Density Max. (g/cm^3)[b]	Z1[c]	Mineral Volume (cm^3)[d]	Molar Volume (cm^3/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	Gaines et al. 1997 [DIRS 172360] Roberts et al. 1990 [DIRS 107105]	1489 (Gaines) 756 (Roberts)
Saponite-H	133.51	180.59	167.06	2.1	2.27	2.00	7.00E-22	210.65	n		
Saponite-K	138.75	186.57	172.60	2.1	2.27	2.00	7.00E-22	210.65	n		

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/cm^3)	Density Max. (g/cm^3)[b]	Z1[c]	Mineral Volume (cm^3)[d]	Molar Volume (cm^3/mol)[e]	Present in R0?	Sources Used for Corroboration	Page Number
Saponite-Mg	132.60	182.34	168.68	2.1	2.27	2.00	7.00E-22	210.65	n		
Saponite-Na	135.32	184.04	170.26	2.1	2.27	2.00	7.00E-22	210.65	n		
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)	251.336	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

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.
[d] Based on crystollographic data as given in source (cm^3).
[e] Based on crystollographic data as given in source (cm^3/mol).
[f] In data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]) but no molar volume or mineral volume data available.
[g] Present in data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]), but there is a slight difference in chemical formula.
[h] Molar volume calculated using density and molecular weight of ferrihydrite (not Cr-ferrihydrite), because no data available for this mineral phase.
[i] Molar volume calculated using density value of the phase $Fe_2(MoO_4)_3{\cdot}8H_2O$, because no data for $Fe_2(MoO_4)_3$ available.
[j] See text for qualification argument.
[k] Density and molecular weight for volume calculation from the mineral Cejkaite, which has the same chemical formula.
[l] Density values are from Montmorillonite, because no data available for this smectite.
[m] Molar volume calculated using the formula for Ripidolite as $Mg_3(Mg_2Al)(Si_3AlO_{10})(OH)_8$. Volume in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) was calculated using the formula $Mg_3Fe_2(Al_2Si_3O_{10})(OH)_8$.
[n] 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.

Volume data and Calculations not Documented in Rev. 00 of This Report. Shoemaker et al. (1977 [DIRS 180793]) performed an x-ray crystallography study of $Cu_3(PO_4)_2$ and determined a density D_x of 4.503 g/cm^3. The database data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576], a qualified source) gives the molecular weight as 380.581 g/mol. Therefore the molar volume would be 380.581 g/mol ÷ 4.503 g/cm^3 = 84.517 cm^3/mol, which exactly matches the datum in data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]).

6.7 CHANGES FOR DATA0.YMP.R5

This section documents the qualification of data changes for data0.ymp.R5 (Output DTN: SN0612T0502404.014). This includes adding data for some new species, updating data for existing species (ones already in data0.ymp.R4, Output DTN: SN0410T0510404.002). In a few instances, species in data0.ymp.R4 (Output DTN: SN0410T0510404.002) are deleted. The methodologies are those previously used in developing data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) and data0.ymp.R4 (Output DTN: SN0410T0510404.002). Section 1.1 presents an overview of these methodologies. Section 6.1 presents more detailed information. Important aspects include the use of SUPCRT92 (see Section 3.1.2) calculations (see Section 6.1.2) and the use of spreadsheets (see Sections 6.1.3 and 6.14), including the use of generic templates for certain kinds of calculations and "library" worksheets containing data commonly used to support spreadsheet calculations.

6.7.1 Update of Data for CrO_3Cl^-, Eskolaite (Cr_2O_3), and CrO_2

The data0 reactions for the aqueous species CrO_3Cl^- and the solids Cr_2O_3 (eskolaite) and CrO_2 are changed for data0.ymp.R5 (Output DTN: SN0612T0502404.014). This is done mainly to preserve (insofar as this is possible) the oxidation state of the Cr in the reaction. This allows greater flexibility in modeling. For example, the mass balance definitions in EQ3/6 in the version 8 series (e.g., EQ3/6 V8.0; see Section 3.1.1) are based on reaction coefficients. This permits separate mass balances for say Cr^{3+} and CrO_4^{2-}, but only if all reactions (save the one linking Cr^{3+} and CrO_4^{2-} to each other) preserve the oxidation state. Also, this practice facilitates suppressing one or the other of the oxidation states. The new inputs for the calculations described in this section are given in Section 4.1.10.

In data0.ymp.R4 (Output DTN: SN0410T0510404.002) the associated reaction for CrO_3Cl^- is:

CrO3Cl- + 3 H+ = Cr+++ + 0.75 O2(g) + Cl- + 1.5 H2O (Eq. 6-39)

(Note: EQ3/6 species names are used here). This is changed to:

CrO3Cl- + H2O = CrO4- + 2 H+ + Cl- (Eq. 6-40)

This preserves Cr(VI) on both sides of the reaction [Cr+++ is Cr(III)]. The input data are those used for the original reaction and processed in DTN: MO0302SPATHDYN.001 [DIRS 161886] (folder: *\CD\Spreadsheets\Aqueous*, spreadsheet: *AqueousSpecies_j_sea.xls*). The original data source was Dellien et al. 1976 [DIRS 151392]). The original data will not be repeated here.

Calculation of the requisite log K values on the EQ3/6 temperature grid (0-25-60-100-150-200-250-300°C) for reaction (6-40) is made in workbook *AqueousSpecies_j_CrO3Cl.xls*, located in folder *\Chromium* in Output DTN: SN0702T0502404.015. The general methodology is the same as that previously employed for reaction (6-39). The isocoulombic/isoelectric method (Lindsay 1980 [DIRS 159038]; Murray and Cobble 1980 [DIRS 159200]) is employed (see Section 6.1.3). The isocoulombic reaction employed in this instance is

$$CrO_3Cl^- + OH^- = HCrO_4^- + Cl^- \qquad \text{(Eq. 6-41)}$$

Here $HCrO_4^-$ conveniently serves as the analogue species for CrO_3Cl^- (the analogue species does not have to be a species appearing in the desired reaction for the data file). The resulting log K grid is given in Table 6-47.

Table 6-47. Log K Temperature Grid for the Reaction $CrO_3Cl^- + H_2O = HCrO_4^- + H^+ + Cl^-$

Temp °C	0.01	25	60	100	150	200	250	300
log K	-6.8731	-6.8964	-7.1882	-7.7066	-8.5214	-9.4874	-10.6333	-12.0844

Source: Output DTN: SN0702T0502404.015, folder: *Chromium*, workbook: *AqueousSpecies_j_CrO3Cl.xls*.

In data0.ymp.R4 (Output DTN: SN0410T0510404.002) the reaction for Cr_2O_3 (*Eskolaite*) is:

Eskolaite + 1.5 O2(g) + 2 H2O = 2 CrO4-- + 4 H+ (Eq. 6-42)

This is changed to:

Eskolaite + 6 H+ = 2 Cr+++ + 3 H2O (Eq. 6-43)

This preserves Cr(III) on both sides of the reaction. The input data used are changed from a combination of Barin and Platzki (1995 [DIRS 157865]) and Binnewies and Milke (1999 [DIRS 158955]) to just Barin and Platzki (1995 [DIRS 157865]). For data0.ymp.R5 (Output DTN: SN0612T0502404.014), the tabulated heat capacities over the 298.15 to 600 K range from Barin and Platzki (1995 [DIRS 157865], p. 573) are used in the calculation in preference to the heat capacity coefficients from Binnewies and Milke (1999 [DIRS 158955]) that were previously used. This requires fitting a new set of heat capacity coefficients to the tabulated data. These fitted coefficients are given in Table 6-48.

Table 6-48. Fitted Heat Capacity (Cp) Coefficients for Eskolaite (Cr_2O_3)

***Cp* Coefficient**	**Value**
a	5.5257×10^{1}
b	9.4582×10^{-2}
c	3.3487×10^{6}

Source: Output DTN: SN0702T0502404.015, folder: *Chromium*, workbook: *Cp_Solids_j_Cr_oxides.xls*.

NOTES: Units are consistent with Cp in Joule/mol-k

$Cp = a + bT + cT^{-2}$.

The log K temperature grid is then calculated in the usual manner for reactions associated with solids and gas species (see Section 6.1.3). These results are given in Table 6-49.

Table 6-49. Log K Temperature Grid for the Reaction $Cr_2O_3 + 6\ H^+ = 2\ Cr^{3+} + 3\ H_2O$

Temp °C	0.01	25	60	100	150	200	250	300
log K	15.0621	11.5662	7.5022	3.7591	0.0033	-3.0908	-5.7941	-8.2945

Source: Output DTN: SN0702T0502404.015, folder: *Chromium*, workbook: *Minerals_j_Cr_Oxides.xls*.

In data0.ymp.R4 (Output DTN: SN0410T0510404.002) the reaction for *CrO2* is:

$$CrO2 = Cr{+}{+} + HCrO4- \qquad \text{(Eq. 6-44)}$$

Here Cr(IV) on the left is converted to a combination of Cr(II) and Cr(VI). This is changed to:

$$CrO2 + 3H+ = Cr{+}{+}{+} + 1.5\ H2O + 0.25\ O2(g) \qquad \text{(Eq. 6-45)}$$

Here Cr(IV) is converted to Cr(III). There is no aqueous basis species for Cr(IV) in any of the data files in the data0.ymp.R* series, nor one for Cr(V). So this reaction is as close as possible with the available basis species. The input data used are changed from those of Dellien et al. (1976 [DIRS 151392]) to those of Barin and Platzki (1995 [DIRS 157865]). The former set of data only permitted a log K to be obtained for 25°C; the latter permits such data to be obtained up to 300°C. For data0.ymp.R5 (Output DTN: SN0612T0502404.014), the new inputs from Barin and Platzki (1995 [DIRS 157865], p. 570) are used to develop the log K data for the CrO_2 dissolution reaction (Equation 6-45) on the EQ3/6 temperature grid. This requires fitting a new set of heat capacity coefficients to the tabulated data. These fitted coefficients are given in Table 6-50. The resulting log K temperature grid is given in Table 6-51.

Table 6-50. Fitted Heat Capacity (Cp) Coefficients for CrO_2

***Cp* Coefficient**	**Value**
a	9.4558×10^{1}
b	1.7155×10^{-2}
c	1.3235×10^{1}

Source: Output DTN: SN0702T0502404.015, folder: *Chromium*, workbook: *Cp_Solids_j_Cr_oxides.xls*.

NOTES: Units are consistent with Cp in Joule/mol-k

$Cp = a + bT + cT^{-2}$.

Table 6-51. Log K Temperature Grid for the Reaction $CrO_2 + 3\ H^+ = Cr^{3+} + 1.5\ H_2O + 0.25\ O_2(g)$

Temp °C	0.01	25	60	100	150	200	250	300
log K	4.2955	3.0034	1.4774	0.0463	-1.4240	-2.6725	-3.8001	-4.8782

Source: Output DTN: SN0702T0502404.015, folder: *Chromium*, workbook: *Minerals_j_Cr_Oxides.xls*.

6.7.2 Addition of $CaSeO_4{:}2H_2O$ and $CaSeO_4(aq)$

Selenium is found as a trace element in many natural environments. Its presence in soils and sediments amounts to ~1 mg/kg where its aqueous form is usually present in even smaller concentrations (Elrashidi et al., 1989 [DIRS 179395]). The toxicity of selenium has been recognized in humans, animals, and certain plants but it is also a necessary nutrient for both humans and animals (Elrashidi et al., 1989 [DIRS 179395]; Sharmasarkar et al. (1998 [DIRS 179396]). ^{79}Se is a long-lived ($t_{1/2}$: 1.1×10^6 years) fission product in radioactive nuclear waste that could contribute to the overall dose (Chen et al. (1999 [DIRS 145440]). Therefore, knowledge of its relative abundance and geochemical controls in repository environments is important for the evaluation of relevant chemical and transport properties effecting limits on Se mobility (Chen et al. (1999 [DIRS 145440]).

Only the oxidized Se(VI) or selenate species are considered due to the relatively oxidized redox conditions adopted for YMP geochemical model environments. Chemical speciation of selenate aqueous species within a wide range of pH is mainly restricted to the selenate (SeO_4^{2-}) species. The aqueous species $HSeO4^-$ only predominates at pH less than ~1.9. Therefore, only SeO_4^{2-} will be considered in the aqueous speciation encompassing pH 2-11. The source of thermodynamic data for $HSeO_4^-$ and SeO_4^{2-} is Shock et al. (1997 [DIRS 127953]).

In general, selenate solid compounds have large solubilities ranging from ~1 to ~6 molal depending on the metal cation. The exception is $CaSeO_4{:}2H_2O$, which has a gypsum-like structure and forms a limited solution with this phase (Fernandez-Gonzalez et al. 2006 [DIRS 179410]). Solid solution with gypsum ($CaSO_4{:}2H_2O$) is conservatively ignored in this solubility analysis.

The aqueous species $CaSeO_4$(aq) and the solid $CaSeO_4{:}2H_2O$ are added to data0.ymp.R5 (Output DTN: SN0612T0502404.014). $CaSeO_4{:}2H_2O$ replaces *CaSeO4* in data0.ymp.R4 (Output DTN: SN0410T0510404.002). *CaSeO4* appears to be a misrepresentation of $CaSeO_4{:}2H_2O$. The inputs for $CaSeO_4$(aq) and the solid $CaSeO_4{:}2H_2O$ are given in Section 4.1.11.

The log K value for $CaSeO_4$(aq) was obtained directly from Olin et al. (2005, Table III-2, p. 60 [DIRS 177640]). The new data for $CaSeO_4{:}2H_2O$ are based on the evaluation by Olin et al. (2005 [DIRS 177640], Equation (A.9), p. 454). They give a tabulated solubility of 0.3557 molal. The software package EQ3/6 (see Section 3.1.1) was used to establish a log K value for the dissolution of $CaSeO_4{:}2H_2O$ that is consistent with this solubility. The *nxmod* alter/suppress option was used in the EQ3NR speciation-solubility code from this package to specify trial values of the desired log K value. Iteration by hand was used until the output saturation index log Q/K (where Q is the activity product and K is the equilibrium constant) was zero to four decimal places. This is the appropriate stopping point, because log K values on an EQ3/6 data file (such as one in the data0.ymp.R* series) are given to four decimal places (note: log Q/K = log Q – log K). The adopted data for $CaSeO_4$(aq) and $CaSeO_4{:}2H_2O$ are given in Table 6-52.

For the solid $CaSeO_4{:}2H_2O$, a log K value of 2.8960 was selected consistent with the solubility value at 298.15 K given by Olin et al. (2005, Table A-16, p. 454 [DIRS 177640]). The difference between this log K value and the 2.68 value given by Olin et al. (2005, Table III-2, p. 60 [DIRS 177640]) is 0.216, which is within the uncertainty (±0.25 log K units) reported by the source. Supporting calculations are in the workbook *Minerals_cal_CaSeO42H2O_CFJC.xls* and the EQ3/6 input and output files *sel_sol.3i* and *sel_sol.3o*, respectively (these are in folder *\Selenium* of Output DTN: SN0612T0502404.015).

Table 6-52. Thermodynamic Data for the Added Selenium Solid and Aqueous Species

Species	Reaction	log K	ΔG_f^0 (cal/mol)	Source
$CaSeO_4{:}2H_2O$	$CaSeO_4{:}2H_2O = Ca^{2+} + SeO_4^{2-} + 2H_2O$	-2.8960	-354946.3	Output DTN: SN0612T0502404.015, folder: *Selenium*, workbook: *Minerals_cal_CaSeO42H2O_CFJC.xls*
$CaSeO_4(aq)$	$CaSeO_4(aq) = Ca^{2+} + SeO_4^{2-}$	2.0	−239.89	Olin et al. (2005, Table III-2, p. 60 [DIRS 177640])

NOTE: Table Table III-2, p. 60 of Olin et al. (2005 [DIRS 177640]) tabulates a ΔG_f^0 for $CaSeO_4(aq)$ of −1003.707 kJ/mol. This value was converted to calories (1 cal = 4.184 J; Weast and Astle 1979 [DIRS 102865]).

6.7.3 Addition of Kogarkoite (Na_3SO_4F)

The phase kogarkoite (Na_3SO_4F) is a potential product of evaporation of seepage waters and is added to data0.ymp.R5 (Output DTN: SN0612T0502404.014). The inputs for the derived data are given in Section 4.1.12. Thermodynamic properties for this phase have been determined by Gurevich et al. (1999 [DIRS 176845]). This source provides standard entropy (Table 6-53) and tabulated heat capacity data (given in Table 4-27; fitted heat capacity coefficients are given in Table 6-54). The Gibbs energy of formation is also needed. Felmy and MacLean (2001 [DIRS 177660]) conducted a solubility evaluation of this solid. These authors provide coefficients for computing the dimensionless standard chemical potential (μ^o/RT, where μ^o is the chemical potential, R is the gas constant, and T is the absolute temperature). This dimensionless chemical potential is converted to the Gibbs energy of formation of the solid (Table 6-53). The data in Tables 6-53 and 6-54 are then used to calculate the log K for kogarkoite dissolution ($Na_3SO_4F = 3\ Na^+ + SO_4^{2-} + F^-$) on the EQ3/6 temperature grid (Table 6-55).

Table 6-53. Standard Thermodynamic Data (298.15 K) for Kogarkoite (Na_3SO_4F)

ΔG_f^o (Joule/mol)	ΔH_f^o (Joule/mol)	S^o (Joule/mol-K)
-1823408.7	-[a]	205.9

Source: ΔG_f^o is from Output DTN: SN0702T0502404.015, folder: *Kogarkoite*, workbook: *Solids_j_Kogarkoite_TJW_Rev1.xls*. The S^o value is direct from Gurevich et al. (1999 [DIRS 176845])

[a] Not calculated (not needed).

Table 6-54. Fitted Heat Capacity (Cp) Coefficients for Kogarkoite (Na_3SO_4F)

***Cp* Coefficient**	**Value**
a	1.0049×10^{2}
b	2.7872×10^{-1}
c	-3.4049×10^{5}

Source: Output DTN: SN0702T0502404.015, folder: *\Kogarkoite*, workbook: *Cp_Solids_j_Kogarkoite_TJW_Rev2.xls*.

NOTE: Units are consistent with Cp in Joule/mol-k.

$Cp = a + bT + cT^{-2}$.

Table 6-55. Log K Temperature Grid for the Reaction $Na_3SO_4F = 3\ Na^+ + SO_4^{2-} + F^-$

Temp °C	0.01	25	60	100	150	200	250	300
log K	-2.2018	-2.0247	-2.0694	-2.3260	-2.8603	-3.6269	-4.6979	-6.2783

Source: Output DTN: SN0702T0502404.015, folder: *\Kogarkoite*, workbook: *Solids_j_Kogarkoite_TJW_Rev1.xls*.

6.7.4 Addition of SnO_2(am) and Some Sn(IV) Aqueous Species

The solid SnO_2(am) along with some Sn(IV) aqueous complexes is added to data0.ymp.R5 (Output DTN: SN0612T0502404.014). The requisite inputs are given in Section 4.1.13. Most of the thermodynamic data for solids and aqueous species in data0.ymp.R4 (Output DTN: SN0410T0510404.002) are from the comprehensive work of Jackson and Helgeson (1985 [DIRS 151264]). This work encompassed the comprehensive retrieval of thermodynamic data for a large suite of Sn(IV) aqueous species as well as the Sn(IV) solid cassiterite. Tin (Sn) has been identified as an important fission product in nuclear waste with a half-life of 10^5 years (Séby et al. 2001 [DIRS 177245]. The stable aqueous species under oxidized conditions are the stannic or Sn(IV). Among the most common solubility controlling solids for Sn(IV) is SnO_2 which occurs naturally as the mineral cassiterite. However, a low temperature and amorphous form of this phase (SnO_2(am)) has been identified in laboratory experiments (Amaya et al. 1997 [DIRS 176843]).

The changes addressed here are focused on SnO_2(am) since it forms at low temperatures and the available solubility data extends to the alkaline pH range. The selected thermodynamic data for Sn(IV) solids and aqueous species selected to represent SnO_2(am) solubility in data0.ymp.R5 (Output DTN: SN0612T0502404.014) are in part from Jackson and Helgeson (1985 [DIRS 151264]), with additional data taken from Amaya et al. (1997 [DIRS 176843]), and one corrected input datum as determined in this analysis report, based on the solubility data of Amaya et al. (1997 [DIRS 176843]). All of the new data here are restricted to 25°C. Other recent studies on the thermodynamic and solubility properties of Sn(IV) species include those by Lothenbach et al. (2000 [DIRS 177244]) and the review of Séby et al. (2001 DIRS 177245). However, no new data from those studies are used as direct inputs to this analysis report.

As noted above, Jackson and Helgeson (1985 [DIRS 151264]) is the source of data for various Sn chemical species adopted in data0.ymp.R4 (Output DTN: SN0410T0510404.002). A minor transcription error in the standard Gibbs energy of formation for $Sn(OH)_4$(aq) was noted in the spreadsheet calculation of the corresponding log K grid for this species (Output

DTN: SN0410T0510404.001, folder: *\CD\Spreadsheets,* spreadsheet: *AqueousAqueousSpecies_j_SRA_1.xls*; here the value -227310 cal/mol should have been -227360 cal/mol). The corrected data for $Sn(OH)_4(aq)$ are used to transform the data for new Sn(IV) species in Table 4-29 to correspond to reactions that are written in terms of Sn^{4+}, not $Sn(OH)_4(aq)$. That is necessary because Sn^{4+} is used as the basis species for Sn(IV) in the data0.ymp.R* databases. The corrected log K grid for Sn(OH)4(aq) is given in Table 6-56. Only the 25°C value is required in processing the data for the new Sn(IV) species, as those data are restricted to that temperature. That value, -0.8863, replaces the uncorrected value of -0.8497.

Table 6-56. Log K Temperature Grid for the Reaction $Sn(OH)_4(aq) + 4\ H^+ = Sn^{4+} + 4\ H_2O$

Temp °C	0.01	25	60	100	150	200	250	300
log K	-1.0516	-0.8863	-0.6586	-0.4108	-0.1540	0.0100	0.0468	-0.0723

Source: Output DTN: SN0702T0502404.015, folder: *\Tin*, workbook: *AqueousSpecies_cal_Sn_CFJC.xls*.

NOTE: These results correct a small transcription error that affected the corresponding grid in data0.ymp.R4 (Output DTN: SN0410T0510404.002); see text.

Amaya et al. (1997 [DIRS 176843]) studied the solubilities of crystalline and amorphous SnO_2 in 0.1 molal $NaClO_4$ at 25°C. The solubility data generated in this study comprise a range in pH from 2 to 7.8 for crystalline SnO_2 (undersaturation) and 2 to ~12 for SnO_2(am) (oversaturation). Evaluation of SnO_2(am) at pH>8 requires the addition of the aqueous species $Sn(OH)_5^-$ and $Sn(OH)_6^{2-}$. Table 4-29 lists the log K values for the reactions given by Amaya et al. (1997 [DIRS 176843]), which are used here as inputs. Conversion of these log K values for the solubility reactions on the basis of Sn^{4+} instead of $Sn(OH)_4(aq)$ is necessary for inclusion in the EQ3/6 database file. This conversion is described in Output DTN: SN0702T0502404.015 (folder: *\Tin*, workbook: *AqueousSpecies_cal_Sn_CFJC.xls*).

As noted in Section 4.1.13, the log K value of 17.31 for the aqueous species $Sn(OH)_6^{2-}$ given by Amaya et al. (1997 [DIRS 176843]) appears to suffer from a transcription error, and should be 18.31. The log K values from Amaya et al. (1997 [DIRS 176843]) were tested against the solubility data (Table 4-30) of those authors for SnO_2(am) (oversaturation) using the computer code EQ3/6 (see Section 3.1.1). An excellent agreement was obtained between solubility data and code predictions except for a deviation from the solubility trend at high pH where the aqueous species $Sn(OH)_6^{2-}$ is predominant. Further evaluation of the log K value of 17.31 for the complexation reaction $Sn(OH)_4(aq) + 2H_2O = Sn(OH)_6^{2-} + 2H^+$ as given by Amaya et al. (1997 [DIRS 176843]) indicates that changing it to 18.31 results in a very good representation of the data in the alkaline pH range. In addition, the value of 18.31 is in good agreement with that given by Lothenbach et al. (2000 [DIRS 177244]) of 18.4 for the same reaction. The value of 18.31 is adopted as the correct one for the reaction as given by Amaya et al. (1997 [DIRS 176843]).

Table 6-57 gives the log K data for the new solid and the two new aqueous species, after the reactions have been converted to be written in terms of Sn^{4+} (the basis species for Sn[IV]). These data are used in data0.ymp.R5 (Output DTN: SN0612T0502404.014).

Table 6-57. Log K Data at 25°C for the Added Sn(IV) Solid and Aqueous Species

Species	Reaction	log K
SnO_2(am)	SnO_2(am) + $4H^+$ = Sn^{4+} $2H_2O$	-8.3463
$Sn(OH)_5^-$	$Sn(OH)_5^-$ + $5H^+$ = Sn^{4+} $5H_2O$	6.7637
$Sn(OH)_6^{2-}$	$Sn(OH)_6^{2-}$+ $6H^+$ = Sn^{4+} $6H_2O$	17.4237

Source: Output DTN: SN0702T0502404.015, folder: *\Tin*, workbooks: *Minerals_cal_SnO2(am)_CFJC.xls* and *AqueousSpecies_cal_Sn_CFJC.xls*.

6.7.5 Addition of $NiMoO_4$ Solid

The solid $NiMoO_4$ is a potential product of the long-term corrosion of stainless steels containing nickel and molybdenum; it is added to data0.ymp.R5 (Output DTN: SN0612T0502404.014). The inputs for this solid are given in Section 4.1.14. Thermodynamic properties for $NiMoO_4$ have been determined by Morishita and Navrotsky (2003) [DIRS 176846]). This source provides standard Gibbs energy of formation, enthalpy of formation, and entropy (Table 4-31) and heat capacity coefficients (Table 4-32) for this phase. No other source of data is known for this phase in the temperature range of interest (25°C to 300°C). The input data are used to calculate the log K for $NiMoO_4$ dissolution ($NiMoO_4$ = Ni^{2+} + MoO_4^{2-}) on the EQ3/6 temperature grid. The results are given in Table 6-58.

After the data were entered into data0.ymp.R5 (Output DTN: SN0612T0502404.014), a transcription error in the calculation was discovered. The heat capacity coefficient e from Table 4-37, which has a value of -15.788×10^6, was entered as -1.5788×10^8, equivalent to -15.788×10^7. This error had a significant effect on the calculated temperature dependence of the log K data. Table 6-58 gives log K grid used in data0.ymp.R5, the corrected log K grid, and the differences. The effect of the error is to make NiMoO4 seem more soluble than it should be at grid temperatures other than 25°C.

Table 6-58. Log K Temperature Grid for the Reaction $NiMoO_4$ = Ni^{2+} + MoO_4^{2-}

Temp °C	0.01	25	60	100	150	200	250	300
data0.ymp.R5	-5.8328	-6.5033	-6.6098	-6.1013	-5.1146	-4.1164	-3.3380	-2.9911
Corrected	-6.1822	-6.5033	-7.0706	-7.7878	-8.7575	-9.8273	-11.0601	-12.6017
Difference	0.3494	0.0000	0.4608	1.6865	3.6430	5.7109	7.7221	9.6106

Source: Output DTN: SN0702T0502404.015, folder: *\Nickel*, workbook: *Solids_j_NiMoO4_CFJC.xls*.

6.7.6 Additions and Changes for Thorium Species

Some changes are made regarding the thorium species in data0.ymp.R5 (Output DTN: SN0612T0502404.014). The inputs for these changes are given in Section 4.1.15. The changes are based on results reported by Altmaier et al. (2005 [DIRS 173048]). They determined the solubility of amorphous Th(IV) hydrated thorium oxide in carbonate solutions using phase separation to remove colloidal particles. They concluded that Th(IV) concentrations reported by Österhols et al. (1994 [DIRS 150834]) and Neck et al. (2002 [DIRS 168259]) for –log [H^+] values between approximately 4 and 7 were too large because of the added contribution of Th(IV) colloids. From their own data for -log [H+] > ~ 4 and from other data reported by

Östhols et al. (1994 [DIRS 150834]) and Neck et al. (2002 [DIRS 168259]) for -log [H+] < ~ 4, Altmaier et al. (2005 [DIRS 173048]) were able to determine the identities of species that contribute significantly to the Th(IV) solubilities and the values of the equilibrium constants for the formation reactions of those species. The essential data for their model are summarized in Table 4-33. These data are restricted to 25°C.

Simultaneous evaluation by Altmaier et al. (2005 [DIRS 173048]) of different sets of experimental data (for ionic strength equal to 0.5 Molar) showed that $Th(OH)(CO_3)^{(-5)}$ and $Th(OH)_2(CO_3)_2^{2-}$ are the dominant ternary Th(IV) complexes, and that $Th(OH)_2(CO_3)(aq)$, $Th(OH)_3(CO_3)^-$, and $Th(OH)_4(CO_3)^{2-}$ also contribute significantly to $ThO_2{:}2H_2O(am)$ solubility in carbonate-bearing solutions. Four dissolved Th(IV) hydroxide complexes, $ThOH^{3+}$, $Th(OH)_2^{2+}$, $Th(OH)_3^+$, and $Th(OH)_4(aq)$, also contribute to a lesser degree; however, no other ternary Th complexes or pure Th-carbonate complexes contribute significantly to $ThO_2{:}2H_2O(am)$ solubility under these conditions, and Altmaier et al. (2005 [DIRS 173048]) derived only upper limits for these latter species. Altmaier et al. (2005 [DIRS 173048]) also determined that $ThO_2{:}2H_2O(am)$ is the appropriate solid phase controlling dissolved Th(IV) concentrations in their experiments and reports the corresponding solubility product for this solid which is used to determine the values of formation constants for the five ternary aqueous complexes and four hydroxide complexes. These values are tabulated in Table 1 of Altmaier et al. (2005 [DIRS 173048]) and constitute their solubility model. The resulting set of equilibrium constants is considered here to be the best currently available for inclusion in the data0.ymp.R5.

Altmaier et al. (2005 [DIRS 173048]) derived their solubility model for Th(IV) in two steps. In a first step, an upper limit was calculated for each complex $Th(OH)_y(CO3)_z^{4-y-2z}$ by increasing log $K_{s,1yz}$ until the calculated species concentration exceeded one of the five sets of experimental data for any value of -log $[H^+]$. In that way, $Th(OH)CO_3)_4^{5-}$ [complex (114)] and $Th(OH)_2(CO_3)_2^{2-}$ [complex (122)] were identified as contributing most significantly to Th concentrations in the range of -log $[H^+]$ values considered. The type of complexes *1yz* within brackets [] follows the notation of Altmaier et al. (2005 [DIRS 173048]).

In a second step, a least-squares fit was used to consider simultaneously all experimental data for ionic strength of 0.5 Molar. An approximation that included only the complexes (114) and (122) was extended step by step by adding successively other complexes *(1yz)* and repeating the optimization procedure. This sensitivity analysis clearly showed whether a complex contributed significantly to at least some of the Th concentration data, and no significant contributions were found for either the pure Th-carbonate complexes *(10z)* or the eight ternary complexes, (111), (112), (113), (123), (124), (132), (133) and (142). Therefore, only upper limits were derived for the formation constants of these species.

These data (from Table 4-33) are used to make changes in data0.ymp.R5 (Output DTN: SN0612T0502404.014). Some species are added, data for a few are updated, and some species are deleted. The reactions in Table 4-33 are changed for consistency with the basis species used in the data0.ymp.R* series. In particular, OH^- and CO_3^{2-} are not used as basis species. Instead, the respective corresponding basis species are H^+ and HCO_3^-. These conversions require the following data for linking reactions, here taken from data0.ymp.R4 (Output DTN: SN0410T0510404.002): $CO_3^{2-} + H^+ = HCO_3^-$, log K = 10.3288; and $OH^- + H^+ = H_2O$, log K = 13.9951. The results of these conversions are given in Table 6-59.

Table 6-59. Equilibrium Constants (298.15 K) for Some Thorium Species

Species	Chemical Reaction	log K
$Th(OH)^{3+}$	$Th(OH)^{3+} + H^+ = Th^{4+} + H_2O$	2.1951
$Th(OH)_2^{2+}$	$Th(OH)_2^{2+} + 2\ H^+ = Th^{4+} + 2\ H_2O$	6.5902
$Th(OH)_3^+$	$Th(OH)_3^+ + 3\ H^+ = Th^{4+} + 3\ H_2O$	11.3853
$Th(OH)_4(aq)$	$Th(OH)_4(aq) + 4\ H^+ = Th^{4+} + 4\ H_2O$	16.9804
$Th(OH)(CO_3)_4^{(5-)}$	$Th(OH)(CO_3)_4^{(5-)} + 5\ H^+ = Th^{4+} + H_2O + 4\ HCO_3^-$	19.5103
$Th(OH)_2CO_3(aq)$	$Th(OH)_2CO_3(aq) + 3\ H^+ = Th^{4+} + 2\ H_2O + HCO_3^-$	7.6190
$Th(OH)_2(CO_3)_2^{2-}$	$Th(OH)_2(CO_3)_2^{2-} + 4\ H^+ = Th^{4+} + 2\ H_2O + 2\ HCO_3^-$	11.6478
$Th(OH)_3CO_3^-$	$Th(OH)_3CO_3^- + 4\ H^+ = Th^{4+} + 3\ H_2O + HCO_3^-$	13.8141
$Th(OH)_4CO_3^{2-}$	$Th(OH)_4CO_3^{2-} + 5\ H^+ = Th^{4+} + 4\ H_2O + HCO_3^-$	25.7092
$ThO_2.2H_2O(am)$	$ThO_2 \cdot 2H_2O(am) + 4H^+ = Th^{4+} + 4\ H_2O$	8.1804

Source: Output DTN: SN0702T0502404.015, folder: *\Thorium*, workbook: *Th(IV)_H2O_CO3_System.xls*. Altmaier et al. (2005 [DIRS 173048]) also refer to the solid in this table as $Th(OH)_4(am)$.

Consistent with these inputs, the species *ThO2(am)* and *Th(CO3)5(6-)* that appear in data0.ymp.R4 (Output DTN: SN0410T0510404.002) are deleted. *ThO2(am)* is an anhydrous representation of the "new" solid *ThO2.2H2O(am)*. The formula of the new representation is merely more explicit regarding water content. The species *Th(CO3)5(6-)* is not consistent with the newly added thorium hydroxy-carbonate species (see Altmaier et al. 2005 [DIRS 173048]), Section 3.3.3, pp. 88 and 89).

The species *Th(OH)3+*, *Th(OH)4(aq)*, and *Th(OH)3(CO3)-* already appear in data0.ymp.R4 (Output DTN: SN0410T0510404.002). The data for these species are changed by the results given in Table 6-59.

Table 6-60 compares the equilibrium constants in Table 6-59 (which are incorporated into data0.ymp.R5, Output DTN: SN0612T0502404.014) with those from data0.ymp.R4 (Output DTN: SN0410T0510404.002).

Table 6-60. Comparison of Equilibrium Constants (298.15 K) for Some Thorium Species Common to data0.ymp.R5 and data0.ymp.R4

Species	data0.ymp.R5 log K values	data0.ymp.R4 log K values	Comments
$Th(OH)_4(aq)$	16.9804 ± 0.5	17.5	Difference is within uncertainty assigned in Altmaier et al. (2005 [DIRS 173048]) = ±0.5
$Th(OH)_3^+$	11.3853 ± 1.0	11.3	Difference is within uncertainty assigned in Altmaier et al. (2005 [DIRS 173048]) = ±1.0
$Th(OH)_3CO_3^-$	13.8141 ± 0.6	10.8588	$Th(OH)_3CO_3^-$ is a major contributor to solubility in the -log $[H^+]$ range of approximately 4 to 5. This is the range where Altmaier et al. (2005 [DIRS 173048]) found evidence that Th(IV) solubilities reported by Östhols et al. (1994 [DIRS 150834]) and Neck et al. (2002 [DIRS 168259]) (at –log $[H^+]$ in the range 4–7) are anomalously large due to contributions by colloidal particles.
ThO_2:$2H_2O$(am)	8.1804 ± 0.3	7.31	The data0.ymp.R4 value is for "$ThO_2(am)$".

NOTE: data0.ymp.R5 log K values are from Table 6-59. The associated uncertainties are those assigned by Altmaier et al. (2005 [DIRS 173048]) to the unconverted (original) reactions. Additional uncertainty associated with conversion should be negligible in comparison as the thermodynamics of the linking reactions (see text above) are well known to significantly higher precision. The data0.ymp.R4 values are from Output DTN: SN0410T0510404.002.

6.7.7 Update of Data for $NiCO_3$ Aqueous and Solid Species

The thermochemical data for $NiCO_3$ (nickel carbonate) are corrected in data0.ymp.R5 (Output DTN: SN0612T0502404.014). Data are added for two new species, $NiCO_3(aq)$ and $NiCO_3$:$5.5H_2O$. The input data for the three species are described in Section 4.1.16. The need to correct the data for the solid $NiCO_3$ (nickel carbonate) was identified in CR 7542 (see Section 1.2 of this analysis report). The data0.ymp.R4 (Output DTN: SN0410T0510404.002) data (for 25°C only) leads to a very high nickel solubility that is realized in the in-package chemistry calculations (BSC 2005 [DIRS 174583]). A recent NAGRA/PSI 2002 report (Hummel et al 2002 [DIRS 161904]) states how previous databases commonly contained this incorrect solubility product. The species $NiCO_3(aq)$ and $NiCO_3$:$5.5H_2O$ are not included in data0.ymp.R4 (Output DTN: SN0410T0510404.002). The data for $NiCO_3(aq)$ are also taken from Hummel et al 2002 [DIRS 161904]). The data for $NiCO_3$:$5.5H_2O$ are taken from the OECD/NEA volume *Chemical Thermodynamics of Nickel* (Gamsjäger et al. 2005 [DIRS 178266]). The results for the anhydrous $NiCO_3$ solid are compared with the recent recommendations of Gamsjäger et al. (2005 DIRS [178266]).

The input data in Table 4-34 are for reactions written in terms of CO_3^{2-} or $CO_2(g)$. These reactions are here converted to be written in terms of HCO_3^- (the usual EQ3/6 basis species) instead of CO_3^{2-} or $CO_2(g)$. The results are given in Table 6-61. These conversions require the following data for linking reactions, here taken from data0.ymp.R4 (Output DTN: SN0410T0510404.002): $CO_3^{2-} + H^+ = HCO_3^-$, log K = 10.3288; and $CO_2(g) + H_2O = HCO_3^- + H^+$, log K = -7.8136. The desired reaction for the anyhydrous solid is $NiCO_3$ + H+ = $Ni^{2+} + HCO_3^-$. This is simply obtained by combining the source reaction $NiCO_3$= $Ni^{2+} + CO_3^{2-}$ (Table 4-34) with the carbonate protonation reaction $CO_3^{2-} + H^+ = HCO_3^-$. The resulting log K is the sum of the log K values of the reactions combined. Hence, log K for $NiCO_3$ + H+ = Ni^{2+} + HCO_3^- = -11.2 + 10.3288 = -0.8712. Analogously, log K for $NiCO_3$ + H+ = Ni^{2+} + HCO_3^- = -

4.0 + 10.3288 = 6.3288. For the hydrate solid, the source reaction $NiCO_3$:5.5H_2O + 2 H^+ = Ni^{2+} + CO_2(g) + 6.5 H_2O must be combined with the reaction CO_2(g) + H_2O = HCO_3^- + H^+. The combination of these reactions is the desired $NiCO_3$:5.5H_2O + H^+ = Ni^{2+} + HCO3- + 5.5 H_2O. Gamsjäger et al. (2005 [DIRS 178266], p. 70) give log K = 1.472 ± 0.020 for CO_2(aq) = CO_2(g) and log K = 6.354 ± 0.020 for H^+ + HCO_3^- = CO_2(aq) + H_2O. Combining these data, one obtains log K = -(1.472) - (6.354) = -7.826 for CO_2(g) + H_2O = HCO_3^- + H^+. This varies slightly from -7.8136 value from data0.ymp.R4 (Output DTN: SN0410T0510404.002), and will be used instead for consistency within the source data. The log K for $NiCO_3$:5.5H_2O + H^+ = Ni^{2+} + HCO3- + 5.5 H_2O is therefore calculated to be 10.63 + (-7.826) = 2.8040.

Table 6-61. Thermodynamic Data (25°C) for $NiCO_3$ Aqueous and Solid Species in data0.ymp.R5

Species	Reaction	log K	Source
$NiCO_3$	$NiCO_3$ + H+ = Ni^{2+} + HCO_3^-	-0.8712	This section, based on Hummel et al 2002 [DIRS 161904]
$NiCO_3$(aq)	$NiCO_3$(aq) + H+ = Ni^{2+} + HCO_3^-	6.3288	This section, Hummel et al 2002 [DIRS 161904]
$NiCO_3$:5.5H_2O	$NiCO_3$:5.5H_2O + H^+ = Ni^{2+} + HCO_3^- + 5.5H_2O	2.8040	This section, based on Gamsjäger et al. 2005 [DIRS 178266]

Gamsjäger et al. (2005 [DIRS 178266], p. 50) give log K = -7.16 ± 0.18 for the reaction CO_2(g) + H_2O + Ni^{2+} = 2 H^+ + $NiCO_3$. Above it was shown that other data they give (p. 70) are equivalent to log K = -7.826 for CO_2(g) + H_2O = HCO_3^- + H^+. Therefore, for the reaction $NiCO_3$ + H^+ = Ni^{2+} + HCO_3^-, log K = -(-7.16) + (-7.826) = -0.666. This compares well with the value of -0.8712 given in Table 6-61 for this reaction.

6.7.8 Phosphate Corrections

This section implements changes made to the data for phosphate (P[V]) species. The main purpose is correct the phosphate data to resolve problems noted in CR 6731 (see Section 1.2). Most of the requisite inputs have been used previously in the development of data0.ymp.R4 (Output DTN: SN0410T0510404.002). New inputs, and inputs to resolve CR 6731, are given in Section 4.1.17. Some of the new inputs represent opportunities for improvement, mainly in regard to the addition of a few new species. The changes associated with these factors are incorporated into data0.ymp.R5 (Output DTN: SN0702T0502404.015).

The larger problem identified by CR 6731 is a significant inconsistency (~6800 J/mol per P) in the Gibbs energies (and enthalpies) of formation for key phosphate species. Particularly affected are the data for HPO_4^{2-} (which is the strict basis species for P[V] in the data0.ymp.R* databases) and $H_2PO_4^-$. The discrepancy is discussed in Section 1.2, Section 4.1.17, and Appendices A and B. It essentially traces to the recommendations of *CODATA Key Values for Thermodynamics* (Cox et al. 1989 [DIRS 150874]) on the one hand and *The NBS Tables of Chemical Thermodynamic Properties, Selected Values for Inorganic and C_1 and C_2 Organic Substances in SI Units* (Wagman et al. 1982 [DIRS 159216]; Wagman et al. 1989 [DIRS 179315]) on the other. Historically, the discrepancy has earlier roots (see Appendix B), which go back as far as 1962.

The second problem identified by CR 6731 is incorrect compositions for rare earth element (REE) phosphates. Data were previously taken for a large set of such compounds from the compilation of Spahiu and Bruno (1995 [DIRS 103804]). A number of the phosphate compounds (whose thermochemical properties were determined by solubility) had an unknown degree of water of hydration. In these instances, "X" was used to denote the unknown number of waters. When these data were originally processed, the "X" was misinterpreted as the roman numeral for ten. The actual numbers (by reference to other REE phosphates for which the degree of hydration was known) should have been about one or two. This causes no significant errors in calculated solubilities as long as solutions remain very dilute and the activity of water is very close to unity. In more concentrated solutions, however, the solubilities could be substantially overpredicted.

The phosphate key data inconsistency will be addressed first. The thermochemical databases in the data0.ymp.R* series are founded on a core of data from two sources. One is the *SUPCRT92* database based on the work of H.C. Helgeson and various students and coworkers (e.g., Helgeson et al. 1978 [DIRS 101596]; Shock and Helgeson 1988 [DIRS 144817]; Shock et al. 1997 [DIRS 150770]). This database is represented in the SUPCRT92 data files *sprons98.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886] and *speq02.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886]) used previously in this analysis report. The other is the data in the *Chemical Thermodynamics* series sponsored by OECD/NEA (e.g.,volume 1, *Chemical Thermodynamics of Uranium*, Grenthe et al. 1992 [DIRS 101671]; volume 2, *Chemical Thermodynamics of Americium*, Silva et al. 1995 [DIRS 102087]). The OECD/NEA sponsored data are based on explicit acceptance of the *CODATA* key values (Cox et al. 1989 [DIRS 150874]). The *SUPCRT92* data (based on an internal reference in *sprons98.dat* to Wagman et al. 1982 [DIRS 159216]) appear to be tied to the *NBS Tables* (Wagman et al. 1982 [DIRS 159216]; Wagman et al. 1989 [DIRS 179315]).

It is thus clear that the data0.ymp.R* databases up to and including data0.ymp.R4 (Output DTN: SN0410T0510404.002) have used (and mixed) data from two sources with highly discrepant phosphate key data. The problem is actually more complex than that, because the literature on phosphate thermodynamic data has until now failed to recognize this discrepancy. Some literature explicitly follows *CODATA*, some explicitly follows the *NBS Tables*, and some only refers to key data as "the standard values" without citation. Furthermore, data tied to both sets of key values have doubtless been mixed in the literature. It should also be pointed out that a source such as the *NBS Tables* Wagman et al. 1982 [DIRS 159216]; Wagman et al. 1989 [DIRS 179315]), which gives specific values for the key data, offers no guarantee that other phosphate data given actually are consistent with those key data.

EQ3/6 (see Section 3.1.1) requires that a set of basis species be defined. Generally speaking, basis species are used as universal "building blocks" in writing chemical reactions. For aqueous systems, these are usually the solvent, liquid H_2O, and fundamental solute species such as Na^+, H^+, Ca^{2+}, UO_2^{2+}, SO_4^{2-}, HCO_3^-, and $SiO_2(aq)$. At a minimum, there must be one basis species for each chemical element (e.g., H_2O for O, H^+ for H, Na^+ for Na, UO_2^{2+} for U, HCO_3^- for C). In general, a basis species may be composed of (at most), the associated chemical element, O, and H. Assuming that redox reactions are to be considered, an additional basis species is required. This is referred to as the redox basis species. On EQ3/6 data files, this is normally $O_2(g)$, but a species such as e^- (the fictive aqueous electron) will also suffice. Basis species in the minimum set are referred to as “strict” basis species. Such a basis species does not have an associated linking reaction. Additional basis species (usually representing an associated chemical element in an alternate oxidation state) may also be defined. For example, if SO_4^{2-} is the strict basis species for S, then HS^- may be defined as an “auxiliary” basis species. Each auxiliary basis species has an associated reaction linking it to a corresponding strict basis species (e.g., HS^- to SO_4^{2-}). Once a species has been defined as an auxiliary basis species, it may then be used as a building block in writing reactions. In some software (e.g., EQ3/6 V8.0; see Section 3.1.1), it is then possible to define a separate mass balance for an auxiliary basis species as a component, and thus model disequilibrium between that basis species and the corresponding strict basis species. That is not normally done, however.

In the thermochemical databases in the data0.ymp.R* series, HPO_4^{2-} is the strict basis species corresponding to the element phosphorus. $H_2PO_4^-$ is not treated as a basis species. It is linked to HPO_4^{2-} through a rapid deprotonation reaction that does not allow sensible disequilibrium. It could be defined as an auxiliary basis species for convenience, but there is no compelling reaction to do so. The species HPO_4^{2-} is a form of P(V). Phosphorus occurs in several other oxidation states. For example, HPO_3^{2-} is a P(III) species. This is defined as an auxiliary basis species in data0.ymp.R4 (Output DTN: SN0410T0510404.002). The species $H_2PO_2^-$ is a P(I) species that is also in data0.ymp.R4 (Output DTN: SN0410T0510404.002). However, it is not defined as an auxiliary basis species, primarily because it would be insignificant under oxidizing conditions and there is only one other P(I) aqueous species, $H_2PO_2^-$, in data0.ymp.R4 (Output DTN: SN0410T0510404.002).

In the data0.ymp.R* series of databases up to and including data0.ymp.R4 (Output DTN: SN0410T0510404.002), log K data for phosphate aqueous species and minerals have been largely constructed using standard Gibbs energies of formation at 25°C (where data are available only at that temperature) or apparent standard Gibbs energies of formation on the EQ3/6 temperature grid (0-25-60-100-150-200-250-300°C) for the species appearing in the associated reactions. Gibbs energy temperature grids for the basis species are largely derived from SUPCRT92 (see Section 3.1.2) calculations. See Section 6.1.2 for details on the usage of SUPCRT92. In some instances, SUPCRT92 is used to directly calculate log K values; attention here will focus on calculated Gibbs energies. The Gibbs energy grids are incorporated into library worksheets in a library workbook, and these are then used in other workbooks following generic template formats (see Section 6.1.3) to make spreadsheet calculations in which a Gibbs energy grid for a non-basis aqueous species or a solid (or gas species) is first derived using the methods described in Sections 6.1.1 and 6.1.4. A corresponding log K grid is then derived from that Gibbs energy grid and the Gibbs energy grids for the basis species obtained from the library worksheets.

For the data0.ymp.R* series of databases up to and including data0.ymp.R4 (Output DTN: SN0410T0510404.002), these SUPCRT92 calculations were based on the use of the *sprons98.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886]) and *speq02.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886]) databases. As noted above, the key phosphate data in these databases appear consistent with the *NBS Tables* (Wagman et al. 1982 [DIRS 159216]; Wagman et al. 1989 [DIRS 179315]). Mixing of data from SUPCRT92 and the above-cited databases (as for the basis species HPO_4^{2-}) with phosphate data consistent with the *CODATA* recommendations (Cox et al. 1989 [DIRS 150874]), such as the data in the *Chemical*

Thermodynamics series sponsored by OECD/NEA (e.g.,volume 1, *Chemical Thermodynamics of Uranium*, Grenthe et al. 1992 [DIRS 101671]; volume 2, *Chemical Thermodynamics of Americium*, Silva et al. 1995 [DIRS 102087]) will result in a significant inconsistency error. As shown in Appendix B, this can result in errors in calculated log K values of ~1.2 units per phosphorus appearing in the associated reaction. That is substantial, especially considering that some phosphate aqueous species and minerals have multiple units of phosphorus in their molecular formulas and associated reactions (e.g., from Grenthe et al. 1992 [DIRS 101671], p. 44-45: $(UO_2)_3(PO_4)_2(cr)$, $U(HPO_4)_2{\cdot}4H_2O(cr)$, and $UO_2(HPO_4)_2(aq)$).

This inconsistency error is here addressed for data0.ymp.R5 (Output DTN: SN0612T0502404.014). Appendix A of this analysis report compares the *CODATA* (Cox et al. 1989 [DIRS 150874]) key values for aqueous ions with the corresponding values from both the *NBS Tables* (Wagman et al. 1982 [DIRS 159216]; Wagman et al. 1989 [DIRS 179315]) and the *SUPCRT92* database as represented by *sprons98.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886]) or *speq02.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886]). While numerous differences were found (see Appendix A), substantial discrepancies were found in the case of the two key phosphate ions HPO_4^{2-} and $H_2PO_4^-$. These results are summarized in Table 6-62.

Table 6-62. Standard Thermodynamic Functions (298.15 K) for HPO_4^{2-} and $H_2PO_4^-$: *CODATA* vs. *NBS Tables* vs. *SUPCRT92*

CODATA[a]			
Species	**ΔG_f^o J/mol**	**ΔH_f^o J/mol**	**S^o J/mol-K**
HPO_4^{2-}	-1095985.0[b]	-1299000.0	-33.500
$H_2PO_4^-$	-1137152.0[b]	-1302600.0	92.500
NBS Tables[c]			
Species	**ΔG_f^o J/mol**	**ΔH_f^o J/mol**	**S^o J/mol-K**
HPO_4^{2-}	-1089150.0	-1292140.0	-33.500
$H_2PO_4^-$	-1130280.0	-1296290.0	90.400
SUPCRT92[d]			
Species	**ΔG_f^o J/mol**	**ΔH_f^o J/mol**	**S^o J/mol-K**
HPO_4^{2-}	-1089137.0	-1292082.0	-33.5
$H_2PO_4^-$	-1130265.8	-1296286.9	90.4

[a] Cox et al. 1989 [DIRS 150874].

[b] *CODATA* does not give values of Gibbs energies. The values shown are those given by Grenthe et al. (1992 [DIRS 101671], p. 70). To the nearest J/mol, these values are consistent with those from Table A-1 of Appendix A, which are calculated from the CODATA enthalpies and entropies of formation, along with the CODATA values for the entropies of the elements in their reference states.

[c] Wagman et al. 1982 [DIRS 159216]; Wagman et al. 1989 [DIRS 179315].

[d] As represented by sprons98.dat (DTN: MO0302SPATHDYN.001 [DIRS 161886]) or speq02.dat (DTN: MO0302SPATHDYN.001 [DIRS 161886]). Values from those files are in calorie units. Values shown here are from Table A-4 of Appendix A.

NOTE: This table repeats Table 4-35.

The numbers from *SUPCRT92* and the *NBS Tables* are quite close. Such differences are likely due to unit conversion and (in instances excessive) rounding (see Output DTN: SN0702T0502404.015, folder: *\SUPCRT Work*, workbook: *Revised_P_data_for_Speq06_db.xls*, worksheet: "Wagman"). However, the *CODATA* numbers for Gibbs energies of formation differ from the *SUPCRT92* and *NBS Tables* numbers by ~ 6800-6900 J/mol for both HPO_4^{2-} and $H_2PO_4^-$. The entropy values are very nearly the same for all three sources. The discrepancy in the Gibbs energies is essentially associated with a discrepancy in the enthalpies of formation. The differences in the corresponding thermodynamic properties of the species HPO_4^{2-} and $H_2PO_4^-$ are essentially negligible. Thus, any of the above source sets would produce very nearly the same results for the reaction $H_2PO_4^- = H^+ + HPO_4^{2-}$.

Before the issue of inconsistencies can be further addressed, it must be determined which set of values (*CODATA* or *NBS Tables*/*SUPCRT92*) should be used for the thermochemical properties of HPO_4^{2-} (and $H_2PO_4^-$). Appendix B presents an evaluation that favors the *CODATA* values. The *SUPCRT92* values trace to the *NBS Tables* (Wagman et al. 1982 [DIRS 159216]; Wagman et al. 1989 [DIRS 179315]). The *NBS Tables* give only recommended values; they include no information as to sources or alternative values considered. Nevertheless, it appears (see Appendix B) that the *NBS Tables* values are based on a now-discredited study (Holmes (1962 [DIRS 178649]) of the enthalpy of formation of the solid P_4O_{10}(cr) (this solid is the acid anhydride of phosphoric acid). Therefore, the *CODATA* values (Cox et al. 1989 [DIRS 150874]) adopted by OECD/NEA (e.g.,volume 1, *Chemical Thermodynamics of Uranium*, Grenthe et al. 1992 [DIRS 101671]) are adopted as the correct key phosphate data set for use in data0.ymp.R5 (Output DTN: SN0612T0502404.014).

In making these corrections, the original input data for most of the phosphate solids and aqueous species in data0.ymp.R4 (Output DTN: SN0410T0510404.002) remain the same. Depending on the nature of these inputs, the resulting log K data to be put in data0.ymp.R5 (Output DTN: SN0612T0502404.014) may be changed or remain unchanged by the shift to the *CODATA* key values (Cox et al. 1989 [DIRS 150874]), and which will depend on whether or not they are already consistent with those key values. While most of the original inputs for phosphate species are unchanged, the inputs will be changed for some solids and aqueous species in order (a) to make use of improved data and/or (b) to use data whose origin (and consistency with the *CODATA* key values or the lack thereof) is better documented.

In general, the following expectations apply as to whether or not corrections need to be applied to the data for a given aqueous or solid species. If the input data are in the form of equilibrium constants and have been obtained directly from experimental measurements of equilibrium involving aqueous species, the data should remain unchanged. The data compiled in Smith and Martell (1976 [DIRS 127382]) fall into this category. If the input data are in the form of equilibrium constants but the associated experimental data are based on other types of measurements such as calorimetry or solid-solid phase equilibrium relations (that is, the equilibrium constants are "synthetic"), correction may be necessary, depending on the assumptions made in deriving the input equilibrium constants. There are few inputs of this type in this analysis report. Many of the outputs, however, would be examples. If the input data are in the form of Gibbs energies (which are commonly tabulated, as in Barin and Platzki 1995 [DIRS 157865], Wagman et al. 1982 [DIRS 159216], and Robie and Hemingway 1995 [DIRS 153683]), correction may be necessary regardless of the nature of the associated experimental measurements. Whether correction is necessary or not depends on the assumptions made in deriving the Gibbs energies. In cases where assumptions made in deriving data are required to determine whether or not corrections are required, the necessary information may not be explicitly available and may have to be inferred. It is better to choose sources that provide the necessary information explicitly or for which it can be inferred with reasonable certainty.

In addition to HPO_4^{2-} and $H_2PO_4^-$, there are other simple P(V) species (PO_4^{3-} and H_3PO_4(aq)). There are also the closely related diphosphate (or pyrophosphate) species that form in equilibrium with the simple phosphate species. Table 4-36 in Section 4.1.17 contains the recommendations of OCED/NEA (e.g., Grenthe et al. 1992 [DIRS 101671]) for both simple phosphate and diphosphate species. These data are used as direct inputs to data0.ymp.R5 (Output DTN: SN0612T0502404.014). The enthalpy of formation and entropy data are not included for four of the five diphosphate species in Table 4-36. To fill in the missing data, entropy data from the *NBS Tables* (Wagman et al. 1982 [DIRS 159216]) are used. These data are summarized in Table 4-37. The use of these data is discussed in Section 4.1.17. The values in Table 4-37 are corrected for consistency with the data in Table 4-36 by calculating an entropy of reaction for a reaction linking each diphosphate species other than $H_4P_2O_7$(aq) with $H_4P_2O_7$(aq). For example, for $P_2O_7^{4-}$, the reaction is $P_2O_7^{4-} + 4\ H^+ = H_4P_2O_7$(aq). Only the NBS data are used in this calculation (the entropy of H^+ is zero by convention). The assumption is that the NBS entropy values were obtained from such entropies of reaction in the first place, in conjunction with a calorimetrically derived entropy for one diphosphate species (possibly $H_4P_2O_7$(aq)). Wagman et al. (1982 [DIRS 159216]) do not document how they obtained their entropy values for diphosphate species, but it would seem that they must have used entropy of reaction data for all but one of the species. The NEA data for $H_4P_2O_7$(aq) are then used to extract the desired ("NEA-consistent") entropy of the species of interest from that entropy of reaction. Corresponding enthalpies of formation data are then calculated from the Gibbs energies of formation and the entropies. For that purpose, data for the entropies of the relevant chemical elements in their standard reference states (Table 4-38; from Cox et al. (1989 [DIRS 150874]) are employed. For further details of these calculations, see Output DTN: SN0702T0502404.015 (folder: *\SUPCRT Work*, workbook: *Revised_P_data_for_Speq06_db.xls*, worksheet: "Wagman"). Here data are calculated for reactions involving these diphosphate species that use $H_2P_2O_7^{2-}$ as an auxiliary basis species. Only the species $H_2P_2O_7^{2-}$ among these is linked to HPO_4^{2-} (the strict basis species for P(V) in data0.ymp.R5; Output DTN: SN0612T0502404.014). The results are given in Table 6-63.

All of the phosphate and diphosphate species in Table 6-63 are included in the SUPCRT92 databases *sprons98.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886]) and *speq02.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886]). Because of the equation of state treatment afforded there that permits accurate temperature extrapolation (and because the HPO_4^{2-} basis species is included in this set), the data in Table 6-63 are incorporated into a revised SUPCRT92 data file called *speq06.dat* (Output DTN: SN0702T0502404.015, folder: *\Speq06_db*). This is done in a manner similar to that for updating the SiO_2(aq) data in *speq02.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886]) for consistency with the "Rimstidt" paradigm of silica solubility (See Section 6.1.5). To use these data in *speq06.dat*, the data in Table 6-63 must first be converted to calorie units, and the Gibbs energies and the enthalpies must be rounded to the nearest cal/mol (this is a SUPCRT92 quirk; see Johnson et al. 1992 [DIRS 101632]). The requisite data are given in Table 6-64.

Table 6-63. Standard Thermodynamic Functions (298.15 K) for Phosphate and Diphosphate Species (OECD/NEA Recommendations from Grenthe et al. 1992 [DIRS 101671])

Species	ΔG_f^o kJ/mol	ΔH_f^o kJ/mol	S^o J/mol-K
PO_4^{3-}	-1025.491	-1284.400	-220.970
$P_2O_7^{4-}$	-1935.503	-2284.831[a]	-110.081[a]
HPO_4^{2-}	-1095.985	-1299.000	-33.500
$H_2PO_4^-$	-1137.152	-1302.600	92.500
H_3PO_4(aq)	-1149.367	-1294.120	161.912
$HP_2O_7^{3-}$	-1989.158	-2289.887[a]	52.919[a]
$H_2P_2O_7^{2-}$	-2027.117	-2292.963[a]	169.919[a]
$H_3P_2O_7^-$	-2039.960	-2290.898[a]	219.919[a]
$H_4P_2O_7$(aq)	-2045.668	-2280.210	274.919

Source: Output DTN: SN0702T0502404.015, folder: *\SUPCRT Work*, workbook: *Revised_P_data_for_Speq06_db.xls.*

[a] Data from Wagman et al. 1982 [DIRS 159216], adjusted for consistency with corresponding OECD/NEA data for $H_4P_2O_7$(aq) (see text).

Table 6-64. Standard Thermodynamic Functions (298.15 K) for Phosphate and Diphosphate Species in the SUPCRT92 Database *speq06.dat*

Species	ΔG_f^o cal/mol	ΔH_f^o cal/mol	S^o cal/mol-K
PO_4^{3-}	-245098	-306979	-52.813
$P_2O_7^{4-}$	-462596	-546088	-26.310
HPO_4^{2-}	-261947	-310468	-8.007
$H_2PO_4^-$	-271786	-311329	22.108
H_3PO_4(aq)	-274705	-309302	38.698
$HP_2O_7^{3-}$	-475420	-547296	12.648
$H_2P_2O_7^{2-}$	-484493	-548031	40.612
$H_3P_2O_7^-$	-487562	-547538	52.562
$H_4P_2O_7$(aq)	-488926	-544983	65.707

Source: Output DTN: SN0702T0502404.015, folder: *\SUPCRT Work*, workbook: *Revised_P_data_for_Speq06_db.xls.*

SUPCRT92 (SUPCRT92 V1.0; see Section 3.1.2) is then used with *speq06.dat* (Output DTN: SN0702T0502404.015, folder: *\Speq06_db*) to obtain Gibbs energy grids for basis species and log K grids for reactions associated with all species except the strict basis species HPO_4^{2-}. In so doing, the species $H_2P_2O_7^{2-}$ and $H_2PO_2^-$ are added as auxiliary basis species for data0.ymp.R5 (Output DTN: SN0612T0502404.014), joining HPO_3^{2-}. $H_2PO_2^-$ is added to the auxiliary basis set because it represents a different oxidation state, P(I). $H_2P_2O_7^{2-}$ is added mainly for convenience. Like HPO_4^{2-}, it is a P(V) species. In geologic systems, mutual equilibrium among simple phosphate and diphosphate is probably quite rapid. However, the formation of diphosphate from simple phosphate is a type of condensation reaction that might not always equilibrate so rapidly in the laboratory. Therefore, there is some value in putting it in the auxiliary basis set besides convenience.

Table 6-65 gives the calculated Gibbs energy grids for the four phosphorus basis species. Here the SUPCRT92 outputs (in calorie units) are converted to Joule units (1 cal = 4.184 J; Weast and

Astle 1979 [DIRS 102865]). It will be noted that the 25°C values here do not precisely match those in Table 6-63. For example, the 25°C Gibbs energy for HPO_4^{2-} is changed from -1095985 J/mol to -1095986.2 J/mol. The difference is a consequence of converting the former value to calorie units and rounding to the nearest calorie. The maximum possible difference is 0.5 cal or $0.5 \times 4.184 = 2.092$ J/mol. A difference at this level is inconsequential (compare uncertainties for the Gibbs energies of aqueous ions in Table A-1 of Appendix A) and is acceptable. These Gibbs energy grids are incorporated into the library workbooks *BasisSpeciesLib_j_TJW_2p0.xls* (reproduced in Appendix C) and *ReferenceSpecies_j_TJW_2p0.xls* (Output DTN: SN0702T0502404.015, folder: *\Library Workbooks*). They are then used to calculate reaction data for other phosphate species in other workbooks, in the manner used previously (the workbook methodology is described in Sections 6.1.3 and 6.1.4).

Table 6-66 gives the calculated log K grids for the reactions associated with the auxiliary basis species and the non-basis species. These results are used directly in data0.ymp.R5 (Output DTN: SN0612T0502404.014). The calculations for the reaction $H_2PO_3^- = HPO_3^{2-} + H^+$ correct a significant error in earlier members of the data0.ymp.R* series. The erroneous data come from the data0.ymp.R0 database (DTN: MO0009THRMODYN.001 [DIRS 152576]) and appear to be associated with a major typographical error in the Gibbs energy for HPO_3^{2-} ("-20.235 kcal/mol" should have been "-202.35 kcal/mol). The 25°C value of the log K in data0.ymp.R4 (Output DTN: SN0410T0510404.002) is 127.3709, whereas the corresponding value in Table 6-66 is a much more reasonable -6.1206. The effect of the erroneous log K data would have been to destabilize the $H_2PO_3^-$ to such an extent that it would effectively not appear in the model under any realistic conditions.

Table 6-65. Apparent Gibbs Energy Grids (J/mol) for Phosphate Basis Species for data0.ymp.R5

Species	**0.01°C**	**25 °C**	**60 °C**	**100 °C**	**150 °C**	**200 °C**	**250 °C**	**300 °C**
HPO_4^{2-}	-1096515.9	-1095986.2	-1094383.8	-1091655.8	-1086913.2	-1080381.6	-1071298.6	-1057863.7
$H_2P_2O_7^{2-}$	-2022954.0	-2027118.7	-2033203.5	-2040394.1	-2049429.1	-2058041.8	-2065396.9	-2069692.2
HPO_3^{2-}	-811063.0	-811696.0	-811987.2	-811693.9	-810329.9	-807513.3	-802468.6	-793390.6
$H_2PO_2^-$	-509556.8	-512121.6	-515608.1	-519511.8	-524210.0	-528525.4	-532081.4	-534014.4

Source: Output DTN: SN0702T0502404.015, folder: *\SUPCRT Work*, workbook: *Revised_SUPCRT_P_outputs.xls.*

Table 6-66. SUPCRT92-Computed log K Grids for Phosphate Aqueous Species for data0.ymp.R5

Reaction	**0.01°C**	**25 °C**	**60 °C**	**100 °C**	**150 °C**	**200 °C**	**250 °C**	**300 °C**
$H_2PO_4^- = HPO_4^{2-} + H^+$	-7.3200	-7.2120	-7.2065	-7.3155	-7.5638	-7.9129	-8.3711	-8.9931
$H_3PO_4(aq) = HPO_4^{2-} + 2\ H^+$	-9.3536	-9.3517	-9.5386	-9.8927	-10.4715	-11.1851	-12.0698	-13.2546
$PO_4^{3-} + H^+ = HPO_4^{2-}$	12.6494	12.3504	12.1600	12.1319	12.2803	12.5821	13.0271	13.6515
$H_2P_2O_7^{2-} + H_2O = 2\ HPO_4^{2-} + 2\ H^+$	-12.5130	-12.6713	-13.2037	-14.0214	-15.2162	-16.5560	-18.0631	-19.8540
$H_4P_2O_7(aq) = H_2P_2O_7^{2-} + 2\ H^+$	-3.0852	-3.2494	-3.5335	-3.8917	-4.3852	-4.9566	-5.6718	-6.6952
$H_3P_2O_7^- = H_2P_2O_7^{2-} + H^+$	-2.2358	-2.2496	-2.3114	-2.4162	-2.5903	-2.8207	-3.1356	-3.6092
$HP_2O_7^{3-} + H^+ = H_2P_2O_7^{2-}$	6.7452	6.6506	6.6488	6.7509	6.9824	7.3108	7.7482	8.3537
$P_2O_7^{4-} + 2\ H^+ = H_2P_2O_7^{2-}$	16.3346	16.0506	16.0856	16.4575	17.2247	18.2395	19.4980	21.0983
$HPO_3^{2-} + 0.5\ O_2(g) = HPO_4^{2-}$	55.0715	49.8056	43.7088	38.0942	32.5162	28.0698	24.4329	21.3946
$H_2PO_3^- = HPO_3^{2-} + H^+$	-6.1715	-6.1206	-6.1677	-6.3132	-6.5858	-6.9450	-7.4062	-8.0318
$H_3PO_3(aq) = HPO_3^{2-} + 2\ H^+$	-7.9129	-7.9165	-8.0716	-8.3623	-8.8436	-9.4520	-10.2323	-11.3242
$H_2PO_2^- + O_2(g) = HPO_4^{2-} + H^+$	113.2127	102.2889	89.6099	77.8991	66.2095	56.8152	49.0212	42.3246
$H_3PO_2(aq) = H_2PO_2^- + H^+$	-1.9249	-1.9791	-2.0903	-2.2415	-2.4592	-2.7171	-3.0429	-3.5096

Source: Output DTN: SN0702T0502404.015, folder: *\SUPCRT Work*, spreadsheet: *Revised_SUPCRT_P_outputs.xls*, worksheet: “Reactions.”

The SUPCRT92 databases *speq02.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886]) *speq06.dat* (Output DTN: SN0702T0502404.015, folder: *\Speq06_db*) contain data for other phosphate species. These are all 1:1 complexes of trivalent rare earth element (REE) cations with $H_2PO_4^-$ ($CeH_2PO_4^{2+}$, $DyH_2PO_4^{2+}$, $ErH_2PO_4^{2+}$, $EuH_2PO_4^{2+}$, etc.). These data were necessarily derived from equilibrium constants. The Gibbs energies for these species must have been chosen to be consistent with the Gibbs energy of HPO_4^{2-} in *speq02.dat* (DTN: MO0302SPATHDYN.001 [DIRS 161886]) that was inherited from the earlier sprons98.dat (DTN: MO0302SPATHDYN.001 [DIRS 161886]). While the Gibbs energies for those species could have been updated for consistency with the revised Gibbs energy of HPO_4^{2-} that that was added to *speq06.dat* (Output DTN: SN0702T0502404.015, folder: *\Speq06_db*) and the log K grids for the reactions associated with these complexes recalculated with the revised data for incorporation in data0.ymp.R5 (Output DTN: SN0612T0502404.014), this path was not taken. The equivalent log K values could be obtained by using the uncorrected data for HPO_4^{2-} retained in *speq06.dat* (Output DTN: SN0702T0502404.015). However, none of the existing data0.ymp.R* databases employ log K grids for these particular species generated by SUPCRT92. Instead, they use 25°C-only data based on data from Spahiu and Bruno (1995 [DIRS 103804]). These data entered the series through the data0.ymp.R0 database (DTN: MO0009THRMODYN.001 [DIRS 152576]). There is an opportunity for possible future improvement to use full log K grids generated by SUPCRT92 for this particular set of REE phosphate complexes. However, it is noted that data for other REE phosphate complexes not in this set, such as $Ce(HPO_4)_2^-$, $CeHPO_4^+$, $CePO_4(aq)$, $Ce(PO_4)_2^{3-}$, $Dy(HPO_4)_2^-$, $DyHPO_4^+$, $DyPO_4(aq)$, and $DyHPO_4^+$ (which are also from Spahiu and Bruno 1995 [DIRS 103804] and similarly limited to 25°C) could not be similarly improved as the corresponding SUPCRT92 data are lacking and the entropy data needed to utilize the isocoulombic/isoelectric method are also lacking.

Another set of P(V) aqueous species of special interest are the mono- and diflurophosphate species. The thermochemical database data0.ymp.R4 (Output DTN: SN0410T0510404.002) has data for the two monofluorophosphate species HPO_3F^- and PO_3F^{2-} (taken from Wagman et al. 1982 [DIRS 159216]). Because of potential uncertainties in using data from that source, and to take the opportunity to expand the number of fluorophosphates species, the relevant data for data0.ymp.R5 (Output DTN: SN0612T0502404.014) are taken from another source.

The thermochemical properties of the fundamental mono- and di-flurophosphate species have been studied by Larson and Su (1994 [DIRS 179362]) and Larson and Su (1994 [DIRS 179363]). The actual inputs are from Larson and Su (1994 [DIRS 179363]). Although the methodology is an equilibrium study (including equilibrium between simple phosphate and fluorophosphates species) that inherently gives log K data and temperature derivative data directly, Larson and Su (1994 [DIRS 179363]) tabulate their data in terms of standard thermodynamic functions that are constant with the key phosphate data of Wagman et al. 1982 [DIRS 159216]. Those data were given in Table 4-39 in Section 4.1.17. Here Gibbs energies and entropies are first converted to be consistent with the CODATA recommendations (Cox et al. 1989 [DIRS 150874]) for key phosphate data. The enthalpy data are not needed for subsequent calculations and are not converted here.

Table 6-67. Gibbs Energies and Entropies (298.15 K) for Mono- and Di-fluorophosphate Species

Species	**ΔG_f^o J/mol**	**S^o J/mol-K**
$H_2PO_3F(aq)$	-1196433.9	180.320
HPO_3F^-	-1193333.9	113.320
PO_3F^{2-}	-1165933.9	-4.680
$HPO_2F_2(aq)$	-1236842.1	172.927
$PO_2F_2^-$	-1235142.1	140.927

Source: Output DTN: SN0702T0502404.015, folder: *Phosphate*, workbook: *AqueousSpecies_j_PO3F_species.xls.*

NOTE: These data have been recalculated to be consistent with the key phosphate data recommended by Cox et al. 1989 [DIRS 150874].

The data in Table 6-67 are then used to calculate log K temperature grids for these species, treating them all as non-basis species. Here the isocoulombic/isoelectric method (see Section 6.1.4) is used in spreadsheet calculations. These log K grids are given in Table 6-68.

Better data than that from previous sources were available for the species $KP_2O_7^{3-}$, $MgP_2O_7^{2-}$, and $NiP_2O_7^{2-}$. These newer data permit temperature extrapolation (the previous data were restricted to 25°C). Data for the first two complexes are taken from Smith and Martell 1976 [DIRS 127382]) and are given in Table 4-40. Additional data (from the same source) for reactions involving the first two protonations of $P_2O_7^{4-}$ are included and are used here to rewrite the reactions involving these complexes to be in terms of $H_2P_2O_7^{2-}$. Data for $NiP_2O_7^{2-}$ are taken from Wagman et al. (1982 [DIRS 159216]) and are given in Table 4-41. These are converted for consistency with the key phosphate data of Cox et al. (1989 [DIRS 150874]). Table 6-69 gives the calculated log K grids for these three diphosphate complexes.

Table 6-68. Calculated log K Grids for Mono- and Difluorophosphate Aqueous Species for data0.ymp.R5

Reaction	0.01°C	25°C	60°C	100°C	150°C	200°C	250°C	300°C
$H_2PO_3F(aq) + H_2O = HPO_4^{2-} + 3H^+ + F^-$	-9.3961	-9.7896	-10.5474	-11.5346	-12.8721	-14.3292	-15.9798	-18.0257
$HPO_3F^- + H_2O = HPO_4^{2-} + 2H^+ + F^-$	-9.0936	-9.2465	-9.6574	-10.2584	-11.1265	-12.1096	-13.2452	-14.6552
$PO_3F^- + H_2O = HPO_4^{2-} + H^+ + F^-$	-4.3678	-4.4461	-4.6532	-4.9539	-5.3855	-5.8710	-6.4283	-7.1171
$HPO_2F_2(aq) + 2H_2O = HPO_4^{2-} + 4\ H^+ + 2F^-$	-8.2884	-9.0606	-10.3705	-11.9734	-14.0524	-16.2396	-18.6453	-21.5432
$PO_2F_2^- + 2H_2O = HPO_4^{2-} + H^+ + 2F^-$	-8.0863	-8.7627	-9.8920	-11.2606	-13.0197	-14.8506	-16.8366	-19.1774

Source: Output DTN: SN0702T0502404.015, folder: *Phosphate*, workbook: *AqueousSpecies_j_PO3F_species.xls*.

Table 6-69. Calculated log K Grids for Three Aqueous Diphosphate Complexes for data0.ymp.R5

Reaction	0.01°C	25°C	60°C	100°C	150°C	200°C	250°C	300°C
$KP_2O_7^{3-} + 2H^+ = K^+ + H_2P_2O_7^{2-}$	14.5840	13.9506	13.3301	12.8671	12.5426	12.4325	12.5151	12.8279
$MgP_2O_7^{2-} + 2H^+ = Mg^{2+} + H_2P_2O_7^{2-}$	9.5756	8.9000	8.1241	7.4156	6.7184	6.1685	5.7237	5.3565
$NiP_2O_7^{2-} + 2H^+ = Ni^{2+} + H_2P_2O_7^{2-}$	8.8363	9.0050	9.1987	9.3756	9.5497	9.6870	9.7981	9.8897

Source: Output DTN: SN0702T0502404.015, folder: *Phosphate*, workbook: *AqueousSpecies_j_P2O7_complexes.xls*.

NOTE: $H_2P_2O_7^{2-}$ is used as an auxiliary basis species in data0.ymp.R5 (Output DTN: SN0612T0502404.014).

The input data were also revised for the aqueous complex $UO_2PO_4^-$. Rai et al. (2005 [DIRS 181002]) recently conducted a solubility study of the solid $(UO_2)_3(PO_4)_2$:$4H_2O$ at 25°C. They found that the previously used data (from Grenthe et al. 1992 [DIRS 101671], reiterated by Guillaumont et al. 2003 [DIRS 168382]) lead to significant overpredictions of solubility above about pH 6. This is clearly illustrated in their Figures 5 and 6. They recommend a bounding value: $\Delta G_f^o/RT \geq -823.3$ (Table 4-41a). This is used to obtain a bounding log K value of -0.8689 for the reaction $UO_2PO_4^- + H^+ = UO_2^{2+} + HPO_4^{2-}$ (Table 6-69a). Although this is a bounding value, its usage is conservative in regard to predicting dissolved uranium concentrations. Calculated solubility behavior is expected to be accurate up to pH 9, the maximum value in the source study. It should be recognized that at higher pH values, overprediction of dissolved uranium might occur.

Table 6-69a. Thermodynamic Data (25°C) for $UO_2PO_4^-$ in data0.ymp.R5

Species	Reaction	log K
$UO_2PO_4^-$	$UO_2PO_4^- + H^+ = UO_2^{2+} + HPO_4^{2-}$	-0.8689

Source: Output DTN: SN0702T0502404.015, folder: *\Phosphate*, spreadsheet: *AqueousSpecies_j_PO4_KBH.xls*, worksheet: "UO2PO4-."

The species $PbH_2PO_4^+$ is added to data0.ymp.R5 (Output DTN: SN0612T0502404.014). Nriagu (1972 [DIRS 151244]) measured the solubility of $PbHPO_4$ in dilute phosphoric acid solutions at 25°C. He interpreted the solubility behavior in terms of the formation of two aqueous complexes, $PbH_2PO_4^+$ and $PbHPO_4$(aq). His equilibrium constant data are given in Table 4-41b. The reactions given there must be reversed for consistency with EQ3/6 reaction formats. Reversing the reaction for the first species gives $PbH_2PO_4^+ = Pb^{2+} + H_2PO_4^-$ and log K = -1.5. From Table 6-66 we have $H_2PO_4^- = HPO_4^{2-} + H^+$ and log K = -7.2120. Adding these reactions gives $PbH_2PO_4^+ = Pb^{2+} + HPO_4^{2-} + H^+$ and log K = -8.7120. The second reaction is simply reversed (and log K sign changed). The results are shown in Table 6-69b. The datum for $PbHPO_4$(aq) was in data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]), was carried forward into subsequent members of the data0.ymp.R* series, and thus is not new.

Table 6-69b. Equilibrium Constants (298.15 K) for Two Lead Phosphate Complexes

Species	Chemical Reaction	log K
$PbH_2PO_4^+$	$PbH_2PO_4^+ = Pb^{2+} + HPO_4^{2-} + H^+$	-8.7120
$PbHPO_4$(aq)	$PbHPO_4(aq) = Pb^{2+} + HPO_4^{2-}$	-3.1

Source: See text.

Data for the mineral berlinite ($AlPO_4$) were previously taken from two sources. The standard 298.15 K properties (Gibbs energy of formation, enthalpy of formation, and entropy) were taken from the *NBS Tables* (Wagman et al. 1982 [DIRS 159216]). The heat capacity coefficients were taken from Robie et al. (1979 [DIRS 107109]). These are replaced by data taken from a single source (Barin and Platzki 1995 [DIRS 157865]). These data are given in Tables 4-42 and 4-43. Data for the mineral strengite ($FePO_4 \cdot 2H_2O$) were previously taken from the *NBS Tables* (Wagman et al. 1982 [DIRS 159216]), including both the standard 298.15 K properties (Gibbs energy of formation, enthalpy of formation, and entropy) and a single heat capacity value. These data will be replaced by data taken from Barin and Platzki (1995 [DIRS 157865]). These data are given in Tables 4-44 and 4-45. Data for the mineral Whitlockite ($Ca_3(PO_4)_2$) were previously taken from Robie et al. (1979 [DIRS 107109]), including both the standard 298.15 K properties (Gibbs energy of formation, enthalpy of formation, and entropy) and heat capacity coefficients. These data will be replaced by data taken from (Barin and Platzki 1995 [DIRS 157865]). These data are given in Tables 4-46 and 4-47. The heat capacities tabulated as functions of temperature over the range 298.15 to 600 K were first fit to the Maier-Kelley equation. The results are given in Table 6-70. The calculated log K grids are shown in Table 6-71.

Table 6-70. Fitted Heat Capacity (Cp) Coefficients for Whitlockite, Strengite, and Berlinite

Solid	***a***	***b***	***c***
Whitlockite	1.8366E+02	1.4805E-01	-6.8539E+01
Strengite[a]	1.0299E+02	3.7582E-01	-3.9034E+06
Berlinite	5.1460E+01	1.3933E-01	1.1634E+02

Source: Output DTN: SN0702T0502404.015, folder: *\Phosphate*, workbook: *Cp_Solids_j_Phosphates_Set1.xls*.

[a] The data shown here for Strengite (FePO4:$2H_2O$) were erroneously fit to entropy data from the source. See Section 6.8 for a correction.

NOTE: Data are consistent with Cp in units of Joule/mol-K. for the equation: $Cp = a + bT + cT^{-2}$.

Table 6-72 shows calculated log K grids for another group of phosphate solids that were recalculated in the same set as the three solids noted above. Except as noted here, the input data for the associated species (but not the phosphate and diphosphate basis species) are the same as for data0.ymp.R4 (Output DTN: SN0410T0510404.002).

In reviewing the thermodynamic properties of some apatite phases present in this database, it was noted that the source Robie et al. (1979 [DIRS 107109]) tabulates thermodynamic data for the solids whitlockite ($Ca_3(PO_4)_2$), hydroxyapatite ($Ca_5(PO_4)_3(OH)$), and fluorapatite ($Ca_5(PO_4)_3F$) that are significantly different from the previous version of this compilation (Robie et al. 1978 [DIRS 179157]). Robie et al. (1979 [DIRS 107109]) is used as a source of thermodynamic data for these three phosphate-bearing phases and other solids in previous versions of data0.ymp.R*. Robie et al. (1979 [DIRS 107109]) is a corrected version of Robie et al. (1978 [DIRS 179157]) but the former does not give details on any of the corrections to the affected data nor the specific solids involved in these corrections. Clearly, the differences in tabulated values for standard enthalpy and Gibbs energies of formation in these two compilations indicate that these phosphate-bearing phases were indeed affected. Interestingly, the more recent update of these two compilations (Robie and Hemingway (1995 [DIRS 153683]) has values for standard enthalpy and Gibbs energies of formation that are significantly different from those in Robie et al. (1979 [DIRS 107109]). However, the standard enthalpies of formation are somewhat consistent with those given in Robie et al. (1978 [DIRS 179157]). These discrepancies in thermodynamic data between compilations is cause for concern as for the retrieval of standard thermodynamic properties of these phases and their consistency when used with other phosphate data in YMP thermodynamic databases. Furthermore, it was also noted that the standard state thermodynamic properties for elemental phosphorus (P) adopted in Robie et al. (1978 [DIRS 179157]) and Robie et al. (1979 [DIRS 107109]) are for P(red) whereas in Robie and Hemingway (1995 [DIRS 153683]) is for P(white). According to the NIST-JANAF (Chase 1998 [DIRS 157874]) compilation of thermochemical tables, the adopted reference-state form chosen for the tabulation of standard-state thermodynamic properties of this element is P(white). This choice of elemental P corresponds to the adopted convention in recent compilations of thermodynamic data including Robie and Hemingway (1995 [DIRS 153683]). Since the standard entropy value of elemental P is needed in the determination of Gibbs energies of formation for these phosphate-bearing phases, then the values for this thermodynamic parameter given in Robie et al. (1978 [DIRS 179157]) and Robie et al. (1979 [DIRS 107109]) need to be revisited for consistency with thermodynamic data of phosphate solids obtained from other thermodynamic data compilations such as Barin and Platzki (1995 [DIRS 157865]).

Data for fluorapatite was obtained from the study by Westrich and Navrotsky (1981 [DIRS 178567]). This study encompass thermochemical determinations of the minerals fluorapatite, fluorpargasite, and fluorphlogopite. Fluorapatite enthalpy of formation for the oxides was recalculated using heat of solution and heat content data given in Tables 3 and 5 of Westrich and Navrotsky (1981 [DIRS 178567]). The spreadsheet *Apatite_Thermo_Calcs_CFJC.xls* (Output DTN: SN0702T0502404.015) provide details of these calculations. The data from Westrich and Navrotsky (1981 [DIRS 178567]) are considered in this revision given the reported lower uncertainties when using a SiO_2 diluent in their calorimetric determinations and the more comprehensive nature of their sample characterization. Note that the recalculated heat of solution at 985 K in the spreadsheet *Apatite_Thermo_Calcs_CFJC.xls* (Output DTN: SN0702T0502404.015) is slightly less negative (~1.3 kJ/mol) than that given by Westrich and Navrotsky (1981, p. 1096 1995 [DIRS 178567]) for measurements involving a SiO_2 diluent. The source of this discrepancy cannot be resolved at this time but it is well within the uncertainty given by the authors (±6 kJ/mol). In this revision, the enthalpy of formation from the oxides was calculated using the enthalpy of solution and heat content data for CaF_2, $Ca_3(PO_4)_2$, and $Ca_5(PO_4)_3F$ given by Westrich and Navrotsky (1981 [DIRS 178567]). This calculation is done by combining the heat of solution and heat content data in the appropriate stoichiometric molar proportions for the fluorapatite formation reaction in the thermodynamic cycle (see spreadsheet *Apatite_Thermo_Calcs_CFJC.xls* in Output DTN: SN0702T0502404.015). The standard enthalpy of formation (from the elements) of fluorapatite was calculated using standard enthalpy of formation data for CaF_2 by Robie and Hemingway (1995 [DIRS 153683]) and for $Ca_3(PO_4)_2$ from Barin and Platzki (1995 [DIRS 157865]) yielding a value of -6857.42 kJ/mol. This value is about 2 kJ/mol less negative than that given by Westrich and Navrotsky (1981 [DIRS 178567], p. 1097) but still well within the uncertainty (±7.42 kJ/mol) given by the authors. The Gibbs energy of formation for fluorapatite was calculated using a $\Delta_f S°$ value obtained using the standard entropy for this phase given by Egan et al. (1951 [DIRS 178570]) (Table 4-50) (converted to Joule units and modified for consistency with the chemical formula used in this analysis report) and that of the elements adopted in data0.ymp.R5 (Output DTN: SN0612T0502404.014). The standard entropy value considered here for elemental phosphorus is for P(white); consistent with the adopted reference-state of this element in recent thermodynamic data compilations. The calculated Gibbs energy of formation is -6477.16 kJ/mol is 18 kJ/mol less negative than that tabulated by Westrich and Navrotsky (1981 [DIRS 178567], p. 1097) of -6495.31 kJ/mol. The difference in these values could be attributed to the choice of standard entropy data for P from Robie et al. (1978 [DIRS 179157]) which is consistent with P(red) reference state instead of P(white). If the value for enthalpy of formation from the elements given by Westrich and Navrotsky (1981 [DIRS 178567]) is used with the standard entropy of formation consistent with P(white), the difference in the obtained Gibbs energy of formation is about 2 kJ/mol. This is consistent with the difference in the enthalpy of formation from the elements calculated in the spreadsheet *Apatite_Thermo_Calcs_CFJC.xls* (Output DTN: SN0702T0502404.015) and that given by Westrich and Navrotsky (1981 [DIRS 178567]) as explained above. The calculated value for Gibbs energy of formation from the elements is about 12.5 kJ/mol less negative than that tabulated in Robie and Hemingway (1995 [DIRS 153683]). This difference is slightly less than that between the enthalpy of formation from the elements from this source which is about 14.6 kJ/mol. These differences cannot be resolved at this point given the information present in Robie and Hemingway (1995 [DIRS 153683]). Note that the current convention in tabulations of thermodynamic data adopts P(white) as the reference state for this element even when it's believed to be less stable than P(red) at reference-state conditions (1 bar and 298.15 K) (Schlesinger (2002, [DIRS 178844]). The spreadsheet *Apatite_Thermo_Calcs_CFJC.xls* (Output DTN: SN0702T0502404.015) also compares heat content data as a function of temperature from Robie and Hemingway (1995 [DIRS 153683]), and Egan et al. (1951 [DIRS 178570]) since the former refers to Wagman et al. (1982 [DIRS 159216]). The Wagman et al. (1982 [DIRS 159216]) compilation doesn't gives a source for the tabulated thermodynamic data. The strong correspondence in fluorapatite heat content to high temperatures from the two sources (see the heat content plots in spreadsheet *Apatite_Thermo_Calcs_CFJC.xls* of Output DTN: SN0702T0502404.015) indicates that Egan et al. (1951 [DIRS 178570]) is the likely source used by Robie and Hemingway (1995 [DIRS 153683]). Therefore, given this strong agreement in heat content data up to high temperatures, the heat capacity coefficients (Table 4-51) were retrieved from data reported by Robie and Hemingway (1995 [DIRS 153683]) and used for the extrapolation of fluorapatite Gibbs energies of formation to elevated temperatures.

Data for hydroxyapatite ($Ca_5(PO_4)_3OH$) were previously taken from Robie et al. (1979 [DIRS 107109]), including both the standard 298.15 K properties (Gibbs energy of formation, enthalpy of formation, and entropy) and heat capacity coefficients. These data are replaced by data taken from Robie and Hemingway (1995 [DIRS 153683]) for the reasons explained above. The new input data are given in Tables 4-48 and 4-49. There are several thermodynamic studies for hydroxyapatite that indicate a wide range of values for standard enthalpies of formation. Suggested reasons for such large ranges include factors such as experimental methodology, and composition and crystallinity of the hydroxyapatite phase suggesting that further thermochemical work needs to be done. The study by Jacques (1963 [DIRS 178846]) reports a relatively close value to that reported by Robie and Hemingway (1995 [DIRS 153683]) for high purity material derived from calcined human teeth roots. The estimated standard enthalpy of formation reported in this study is -6755.07 ± 21 kJ/mol which is ~16.6 kJ/mol more negative than that tabulated in Robie and Hemingway (1995 [DIRS 153683]). Although this difference may seem important, notice that it is still within the uncertainty range (± ~21 kJ/mol) given by Jacques(1963 [DIRS 178846]). It should be noted that heat content data tabulated in Robie and Hemingway (1995 [DIRS 153683]) as a function of temperature is in excellent agreement with that given by Egan et al. (1950 [DIRS 178568]). Robie and Hemingway (1995 [DIRS 153683]) points to Wagman et al. (1982 [DIRS 159216]) as the source of heat content data but since the latter does not provide one, this strong agreement in data indicates that Egan et al. (1950 [DIRS 178568]) is the most likely source. This is similar to the case of fluorapatite described above.

Molar volume data for the phases UP_2O_7, $(UO_2)_3(PO_4)_2{:}4H_2O$, $(UO_2)_3(PO_4)_2{:}6H_2O$, and $UO2HPO_4{:}4H_2O$ [and an entropy for $(UO_2)_3(PO_4)_2{:}6H_2O$] are estimated on worksheet "Cp of Phosphates" in workbook *Minerals_j_YC_U_phosphates.xls* of

DTN: MO0302SPATHDYN.001 [DIRS 161886]. These data were used in developing the log K grids for these four solids used in data0.ymp.R2 Database (DTN: MO0302SPATHDYN.000 [DIRS 161756]). As noted above, the single estimated entropy is now replaced by an Established Fact value. These estimated molar volumes are in part based on a molar volume of 34.460 cm^3/mol for $UO_{3(beta)}$, which was taken from data0.ymp.R0 (DTN: MO0009THRMODYN.001 [DIRS 152576]). Weast and Astle (1982 [DIRS 100833], p. B-161; Established Fact) give a density of 7.92 g/cc for $UO_{3(beta)}$. Combined with a molecular weight of 286.03 g/mol (same source) for that solid, this yields a molar volume of 39.236 cm^3/mol. This new value is used in workbook *Estim_Cp_solids_j_phosphates_Set1.xls* in folder *\Phosphate* of Output DTN: SN0702T0502404.015 and notably changes the estimated molar volumes of $(UO_2)_3(PO_4)_2$:$4H_2O$, $(UO_2)_3(PO_4)_2$:$6H_2O$, and UO2HPO_4:$4H_2O$. The molar volume of $(UO_2)_3(PO_4)_2$:$4H_2O$ changes from 182.708 cm^3/mol to 197.036 cm^3/mol; that for $(UO_2)_3(PO_4)_2$:$6H_2O$ changes from 198.708 cm^3/mol to 213.036 cm^3/mol; and that for UO2HPO_4:$4H_2O$ changes from 96.974 cm^3/mol to 101.750 cm^3/mol. These molar volumes are only used in the estimation of the corresponding log K grids in workbook *Minerals_j_Phosphates_Set1.xls* in folder *\Phosphate* of Output DTN: SN0702T0502404.015. The effect of these molar volume changes is small, less than 0.1 log K unit, and zero for temperatures at 100°C or less (because the pressure here is taken to be equal to the reference pressure).

A molar volume is estimated for $AmPO_4$(am) on worksheet "CpofSolids" in spreadsheet *Solids_j_YC_Am.xls* of DTN: MO0302SPATHDYN.001 [DIRS 161886]. This was used in developing the log K grid used in data0.ymp.R2 Database (DTN: MO0302SPATHDYN.000 [DIRS 161756]). The molar volume calculation depends on an input for the volume of the phase Am_2O_3. The value used is 11.68 g/cc Weast and Astle 1982 [DIRS 100833], p. B-74; Established Fact). Unfortunately, this value is for the density of the related solid AmO_2. Lide (2006 [DIRS 178081], p. 4-46) gives a density of 11.77 g/cc for Am_2O_3, and repeats the previously cited value for Am_2O_3. The incorrect value is used again on worksheet "Americium Phosphate" of workbook *Estim_Cp_solids_j_phosphates_Set1.xls* of Output DTN: SN0702T0502404.015. This error (less than 1% difference) would have little effect on the calculated molar volume of 52.571 cm^3/mol. Furthermore, this molar volume is only used in calculating the log K grid, which is relatively insensitive to it. The 1% error in the density of Am_2O_3 translates into a 1% error in the corresponding molar volume, which in turn translates to a roughly half-percent error in the calculated molar volume for $AmPO_4$(am). Using zero for the molar volume of $AmPO_4$(am) induces a maximum change in the calculated log K of only 0.0406 unit (which is for 300°C). A half-percent perturbation leads to a maximum change of 0.0002 unit (again at the same temperature). The effect of this molar volume error is zero for temperatures at 100°C or less (because the pressure here is taken to be equal to the reference pressure).

It is noted that other calculations in workbook *Estim_Cp_solids_j_phosphates_Set1.xls* in folder *\Phosphate* of Output DTN: SN0702T0502404.015 merely repeat calculations previously made in elements of DTN: MO0302SPATHDYN.001 [DIRS 161886]. In particular, the estimated heat capacity coefficients are unchanged.

Table 6-71. Calculated log K Grids for Berlinite, Strengite, and Whitlockite for data0.ymp.R5

Reaction	0.01°C	25°C	60°C	100°C	150°C	200°C	250°C	300°C
$AlPO_4 + H^+ = HPO_4^{2-} + Al^{3+}$	-5.1902	-6.6228	-8.5260	-10.5218	-12.8272	-15.0379	-17.2880	-19.7663
$FePO_4{:}2H_2O + H^+ = HPO_4^{2-} + Fe^{3+}$ $+ 2\ H_2O$ (a)	-11.8075	-12.2416	-12.9308	-13.7531	-14.8382	-16.0358	-17.4293	-19.1736
$Ca_3(PO_4)_2 + 2H^+ = 2HPO_4^{2-} + 3\ Ca^{2+}$	-4.5510	-6.0658	-8.2529	-10.7018	-13.7096	-16.7712	-20.0744	-23.9669

Source: Output DTN: SN0702T0502404.015, folder: *Phosphate*, workbook: *Minerals_j_Phosphates_Set1.xls*.

[a] The data shown for the $FePO_4{:}2H_2O$ (Strengite) reaction were based on heat capacity coefficients erroneously fit to entropy data from the source. See Section 6.8 for a correction. Corrected data are given in Table 6-96.

Table 6-72. Calculated log K Grids for Some Other Phosphorus-Containing Solids in "Set 1" for data0.ymp.R5

Reaction	0.01°C	25°C	60°C	100°C	150°C	200°C	250°C	300°C
$SrHPO_4 = Sr^{2+} + HPO_4^{2-}$ (a)	-4.6845	-5.0417	-5.6104	---	---	---	---	---
$Ni_3(PO_4)_2 + 2\ H^+ = 3Ni^{2+} + 2HPO_4^{2-}$	---	-4.2415	---	---	---	---	---	---
$Ni_2P_2O_7 + 2H^+ = 2Ni^{2+} + H_2P_2O_7^{2-}$	---	6.1721	---	---	---	---	---	---
$Ca_5(PO_4)_3OH + 4H^+ = 3HPO_4^{2-} + 5Ca^{2+} + H_2O$	-6.0753	-8.4110	-11.6996	-15.3187	-19.7242	-24.2039	-29.0620	-34.8365
$Ca_5(PO_4)_3F + 3H^+ = 3HPO_4^{2-} + F^- + 5Ca^{2+}$	-24.0888	-25.1410	-27.3075	-30.2732	-34.4609	-39.1564	-44.5401	-51.1241
$PuPO_4$ (s, hyd) + $H^+ = Pu^{3+} + HPO_4^{2-}$	---	-12.2500	---	---	---	---	---	---
$PuP + H^+ + 2O_2(g) = Pu^{3+} + HPO_4^{2-}$ (a)	263.5911	238.4760	209.4201	---	---	---	---	---
$Pu(HPO_4)_2$(am,hyd) = $2HPO_4^{2-} + Pu^{4+}$	---	-30.4500	---	---	---	---	---	---
$AmPO_4$(am) + $H^+ = Am^{3+} + HPO_4^{2-}$ (b)	-11.9105	-12.4399	-13.2919	-14.3128	-15.6390	-17.0571	-18.6454	-20.5555
$UO_2HPO_4{:}4H_2O = 4H2O + HPO_4^{2-} + UO_2^{2+}$	-12.0044	-11.8123	-11.7278	-11.7885	-12.0459	-12.4980	-13.1868	-14.2419
$U(HPO_4)_2{:}4H_2O = 4H_2O + 2HPO_4^{2-} + U^{4+}$ (a)	-30.5483	-30.4577	-30.4594	---	---	---	---	---
$(UO2)_3(PO_4)_2{:}6H_2O(c) + 2H+ = 3UO_2^{2+} + 2HPO_4^{2-} + 6H_2O$	-24.0012	-24.5489	-25.4829	-26.6570	-28.2782	-30.1400	-32.3899	-35.3388
$(UO_2)_3(PO_4)_2{:}4H_2O + H+ = 4H_2O + 2HPO_4^{2-} + 3UO_2^{2+}$	-23.7849	-24.6023	-25.8763	-27.3957	-29.3976	-31.5968	-34.1504	-37.3763
$(UO_2)_3(PO_4)_2 + 2H^+ = 2HPO_4^{2-} + 3UO_2^{2+}$	-9.1253	-11.5914	-14.8191	-18.1923	-22.1081	-25.9038	-29.8323	-34.2790
$(UO_2)_2P_2O_7(c) + 2H^+ = 2UO_2^{2+} + H_2P_2O_7^{2-}$	1.9694	0.4105	-1.4420	-3.2388	-5.2068	-7.0394	-8.9016	-11.0099
$UP_2O_7 + 2H^+ = H_2P_2O_7^{2-} + U^{4+}$ (c)	-17.4200	-17.9135	-18.5384	-19.1979	-20.0200	-20.9256	-22.0167	-23.4534

Source: Output DTN: SN0702T0502404.015, folder: *Phosphate*, workbook: *Minerals_j_Phosphates_Set1.xls*.

[a] Extrapolated from 25°C to 0.01°C and to 60°C in the absence of heat capacity data for the solid that appears in the reaction. See Appendix D for justification.

[b] In the calculation of the log K grid for $AmPO_4$(am),a heat capacity coefficient for a term in T^2 was omitted. The log K values for temperatures other than 25°C are affected. This is discussed in Section 6.8. See Table 6-98 for a corrected grid.

[c] In the calculation of the log K grid for UP_2O_7, the c heat capacity coefficient was incorrectly entered as -1.7827×10^{-5} instead of -17.827×10^{-5} (values consistent with heat capacity in units of J/mol-K). The log K values for temperatures other than 25°C are affected. This is discussed in Section 6.8. See Table 6-97 for a corrected grid.

Data for the species $AmPO_4$(am) and $AmH_2PO_4^{2+}$ were previously taken from the OECD/NEA volume *Chemical Thermodynamics of Americium* (Silva et al. 1995 [DIRS 102087]. Also, data for the species UP_2, UPO_5, $UO_2P_2O_7$, $U(HPO_4)_2{\cdot}4H_2O$, $(UO_2)_3(PO_4)_2$, and $(UO_2)_3(PO_4)_2{\cdot}6H_2O$ were previously taken from the OECD/NEA volume *Chemical Thermodynamics of Uranium* (Grenthe et al. 1992 [DIRS 101671]). The data for these species were checked against those in the newer OECD/NEA volume *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium* (Guillaumont et al. 2003 [DIRS 168382]). The only change of note is that a standard molar entropy is now given for $(UO_2)_3(PO_4)_2{\cdot}6H_2O$: 669.00 J/mol-K (Guillaumont et al. 2003 [DIRS 168382], p. 57). An insignificant difference was found for the leading heat capacity coefficient (a) for UPO_5: Grenthe et al. (1992 [DIRS 101671], p. 62 give $a = 1.10427 \times 10^2$ J/mol-K, whereas Guillaumont et al. (2003 [DIRS 168382], p. 77) give $a = 1.10430 \times 10^2$ J/mol-K. As the other coefficients for this solid are unaffected, the slight difference appears to be due to some minor data processing inconsistency.

Other recalculated phosphate data do not involve the use of new inputs for the associated species. Data for the phosphate and diphosphate basis species are now the ones adopted here in Section 6.7.8. Also the one diphosphate species ($H_2P_2O_7^{2-}$) is now an auxiliary basis species. Depending on circumstances, the log K data may or may not change from those in data0.ymp.R4 (Output DTN: SN0410T0510404.002). The recalculated log K grids for reactions associated with one additional set of solids are given in Table 6-73. The recalculated log K grids for reactions associated with additional diphosphate aqueous species are given in Table 6-74. The recalculated log K grids for reactions associated with additional simple phosphate aqueous species are given in Table 6-75.

Table 6-73. Calculated log K Grids for Phosphorus-Containing Solids in "Set 2" for data0.ymp.R5

Reaction	**0.01°C**	**25°C**	**60°C**	**100°C**	**150°C**	**200°C**	**250°C**	**300°C**
$YbPO_4{:}2H_2O + H^+ = HPO_4^{2-} + Yb^{3+} + 2H_2O$	-	-11.7495	-	-	-	-	-	-
$(VO)_3(PO_4)_2 + 2\ H^+ = 2HPO_4^{2-} + 3VO^{2+}$	-	51.1865	-	-	-	-	-	-
$UPO_5 + H_2O = HPO_4^{2-} + UO_2^+ + H^+$	-18.9104	-18.3752	-18.0559	-18.0580	-18.4231	-19.0939	-20.0568	-21.4062
$UP_2 + 3.25O_2(g) + 1.5H_2O = 2HPO_4^{2-} + U^{3+} + H^{+}$ [(a)]	390.8556	353.3199	309.7469	-	-	-	-	-
$UP + 2O_2(g) + H^+ = HPO_4^{2-} + U^{3+}$ [(a)]	252.8822	228.6555	200.5830	-	-	-	-	-
$U_3P_4 + 7.25O_2(g) + 1.5H_2O + H^+ = 4HPO_4^{2-} + 3U^{3+}$ [(a)]	896.6230	810.6242	710.8952	-	-	-	-	-
$TmPO_4{:}2H_2O + H^+ = HPO_4^{2-} + Tm^{3+} + 2H_2O$	-	-11.8495	-	-	-	-	-	-
$Th_{0.75}PO_4 + H^+ = HPO_4^{2-} + 0.75Th^{4+}$	-	-15.6495	-	-	-	-	-	-
$TbPO_4{:}2H_2O + H^+ = HPO_4^{2-} + Tb^{3+} + 2H_2O$	-	-11.9495	-	-	-	-	-	-
$SmPO_4{:}H_2O + H^+ = HPO_4^{2-} + Sm^{3+} + H_2O$	-	-12.1495	-	-	-	-	-	-
$Pb_5(PO_4)_3OH + 4H^+ = 3HPO_4^{2-} + 5Pb^{2+} + Cl^- + H_2O$	-	-25.7534	-	-	-	-	-	-
$Pb_5(PO_4)_3Cl + 3H^+ = 3HPO_4^{2-} + 5Pb^{2+} + Cl^-$	-	-47.3485	-	-	-	-	-	-
$PrPO_4{:}H_2O + H^+ = HPO_4^{2-} + Pr^{3+} + H_2O$	-	-12.2495	-	-	-	-	-	-
$PmPO_4{:}1.5H_2O + H^+ = HPO_4^{2-} + Pm^{3+} + 1.5H_2O$	-	-12.1495	-	-	-	-	-	-
$PbHPO_4 = HPO_4^{2-} + Pb^{2+}$	-	-15.6308	-	-	-	-	-	-
$Pb_4O(PO_4)_2 + 4H^+ = 2HPO_4^{2-} + 4Pb^{2+} + H_2O$	-	-12.1753	-	-	-	-	-	-
$Pb_3(PO_4)_2 + 2H^+ = 2HPO_4^{2-} + 3Pb^{2+}$	-	-19.5780	-	-	-	-	-	-
$NdPO_4{:}H_2O + H^+ = HPO_4^{2-} + Nd^{3+} + H_2O$	-	-12.1495	-	-	-	-	-	-
$LuPO_4{:}0.5H_2O + H^+ = HPO_4^{2-} + Lu^{3+} + 0.5H_2O$	-	-11.6495	-	-	-	-	-	-
$LaPO_4{:}H_2O + H^+ = HPO_4^{2-} + La^{3+} + H_2O$	-	-12.3495	-	-	-	-	-	-
$Zn_3(PO_4)_2{:}4H_2O + 2H^+ = 2HPO_4^{2-} + 3Zn^{2+} + 4\ H_2O$	-	-10.5990	-	-	-	-	-	-
$HoPO_4{:}2H_2O + H^+ = HPO_4^{2-} + Ho^{3+} + 2H_2O$	-	-11.8495	-	-	-	-	-	-

Table 6-73. Calculated log K Grids for Phosphorus-Containing Solids in “Set 2” for data0.ymp.R5 (Continued)

Reaction	0.01°C	25°C	60°C	100°C	150°C	200°C	250°C	300°C
$GdPO_4{:}2H_2O + H^+ = HPO_4^{2-} + Gd^{3+} + 2H_2O$	-	-11.9495	-	-	-	-	-	-
$EuPO_4{:}H_2O + H^+ = HPO_4^{2-} + Eu^{3+} + H_2O$	-	-12.0495	-	-	-	-	-	-
$ErPO_4{:}2H_2O + H^+ = HPO_4^{2-} + Er^{3+} + 2H_2O$	-	-11.8495	-	-	-	-	-	-
$DyPO_4{:}2H_2O + H^+ = HPO_4^{2-} + Dy^{3+} + 2H_2O$	-	-11.9495	-	-	-	-	-	-
$Cu_3(PO_4)_2 + 2H^+ = 2HPO_4^{2-} + 3Cu^{2+}$	-	-12.1707	-	-	-	-	-	-
$CoHPO_4 = HPO_4^{2-} + Co^{2+}$	-	-6.7187	-	-	-	-	-	-
$Co_3(PO_4)_2 + 2H^+ = 2HPO_4^{2-} + 3Co^{2+}$	-	-10.0036	-	-	-	-	-	-
$CePO_4{:}H_2O + H^+ = HPO_4^{2-} + Ce^{3+} + H_2O$	-	-12.2495	-	-	-	-	-	-
$Ce_3(PO_4)_4 + 4H^+ = 4HPO_4^{2-} + 3Ce^{4+}$	-	-40.6980	-	-	-	-	-	-
$Cd_3(PO_4)_2 + 2H^+ = 2HPO_4^{2-} + 3Cd^{2+}$	-	-7.9124	-	-	-	-	-	-
$Ag_3PO_4 + H^+ = HPO_4^{2-} + 3Ag^+$	-	-5.1995	-	-	-	-	-	-

Source: Output DTN: SN0702T0502404.015, folder: *\Phosphate*, workbook: *Minerals_j_Phosphates_Set2.xls*.

[a] Extrapolated from 25°C to 0.01°C and to 60°C in the absence of heat capacity data for the solid that appears in the reaction. See Appendix D for justification.

Table 6-74. Calculated log K Grids for Some Other Diphosphate Aqueous Species for data0.ymp.R5

Reaction	0.01°C	25°C	60°C	100°C	150°C	200°C	250°C	300°C
$CaP_2O_7^{2-} + 2H^+ = Ca^{2+} + H_2P_2O_7^{2-}$	-	9.3000	-	-	-	-	-	-
$CdP_2O_7^{2-} + 2H^+ = Cd^{2+} + H_2P_2O_7^{2-}$	-	7.4000	-	-	-	-	-	-
$Na_2P_2O_7^{2-} + 2H^+ = 2Na^+ + H_2P_2O_7^{2-}$	-	12.8	-	-	-	-	-	-
$NaHP_2O_7^{2-} + H^+ = Na^+ + H_2P_2O_7^{2-}$	-	5.3	-	-	-	-	-	-
$NaP_2O_7^{3-} + 2H^+ = Na^+ + H_2P_2O_7^{2-}$	-	13.81	-	-	-	-	-	-
$NiHP_2O_7^- + H^+ = Ni^{2+} + H_2P_2O_7^{2-}$	-	2.8029	-	-	-	-	-	-
$PbP_2O_7^{2-} + 2H^+ = Pb^{2+} + H_2P_2O_7^{2-}$	-	4.6573	-	-	-	-	-	-
$SrP_2O_7^{2-} + 2H^+ = Sr^{2+} + H_2P_2O_7^{2-}$	-	10.700	-	-	-	-	-	-

Source: Output DTN: SN0702T0502404.015, folder: *\Phosphate*, workbook: *Revised_P2O7_complex_25C_data.xls*.

Table 6-75. Calculated log K Grids for Some Other Phosphate Aqueous Species for data0.ymp.R5

Reaction	**0.01°C**	**25°C**	**60°C**	**100°C**	**150°C**	**200°C**	**250°C**	**300°C**
$AmH_2PO_4^{2+} = HPO_4^{2-} + Am^{3+} + H^+$	-	-10.2120	-	-	-	-	-	-
$CaPO_4^- + H^+ = Ca^{2+} + HPO_4^{2-}$	-	5.8905	-	-	-	-	-	-
$Ce(PO_4)_2^{3-} + 2H^+ = Ce^{3+} + 2HPO_4^{2-}$	-	6.2010	-	-	-	-	-	-
$CeH_2PO_4^{2+} = H^+ + Ce^{3+} + HPO_4^{2-}$	-	-9.7121	-	-	-	-	-	-
$CePO_4(aq) + H^+ = Ce^{3+} + HPO_4^{2-}$	-	1.0005	-	-	-	-	-	-
$Dy(PO_4)_2^{3-} + 2H^+ = Dy^{3+} + 2HPO_4^{2-}$	-	3.5010	-	-	-	-	-	-
$DyH_2PO_4^{2+} = H^+ + Dy^{3+} + HPO_4^{2-}$	-	-9.6121	-	-	-	-	-	-
$DyPO_4(aq) + H^+ = Dy^{3+} + HPO_4^{2-}$	-	-0.1495	-	-	-	-	-	-
$Er(PO_4)_2^{3-} + 2H^+ = Er^{3+} + 2HPO_4^{2-}$	-	3.3010	-	-	-	-	-	-
$ErH_2PO_4^{2+} = H^+ + Er^{3+} + HPO_4^{2-}$	-	-9.6121	-	-	-	-	-	-
$ErPO_4(aq) + H^+ = Er^{3+} + HPO_4^{2-}$	-	-0.3495	-	-	-	-	-	-
$Eu(PO_4)_2^{3-} + 2H^+ = Eu^{3+} + 2HPO_4^{2-}$	-	4.0410	-	-	-	-	-	-
$EuH_2PO_4^{2+} = H^+ + Eu^{3+} + HPO_4^{2-}$	-	-9.6121	-	-	-	-	-	-
$EuPO_4(aq) + H^+ = Eu^{3+} + HPO_4^{2-}$	-	0.1505	-	-	-	-	-	-
$Gd(PO_4)_2^{3-} + 2H^+ = Gd^{3+} + 2HPO_4^{2-}$	-	4.0012	-	-	-	-	-	-
$GdH_2PO_4^{2+} = Gd^{3+} + 2HPO_4^{2-} + H^+$	-	-9.6120	-	-	-	-	-	-
$GdPO_4(aq) + H^+ = Gd^{3+} + HPO_4^{2-}$	-	0.1505	-	-	-	-	-	-
$Ho(PO_4)_2^{3-} + 2H^+ = Ho^{3+} + 2HPO_4^{2-}$	-	3.4010	-	-	-	-	-	-
$HoH_2PO_4^{2+} = H^+ + Ho^{3+} + HPO_4^{2-}$	-	-9.5121	-	-	-	-	-	-
$HoPO_4(aq) + H^+ = Ho^{3+} + HPO_4^{2-}$	-	-0.2495	-	-	-	-	-	-
$La(PO_4)_2^{3-} + 2H^+ = La^{3+} + 2HPO_4^{2-}$	-	7.1010	-	-	-	-	-	-
$LaH_2PO_4^{2+} = H^+ + La^{3+} + HPO_4^{2-}$	-	-9.7121	-	-	-	-	-	-
$LaPO_4(aq) + H^+ = La^{3+} + HPO_4^{2-}$	-	1.3905	-	-	-	-	-	-
$Lu(PO_4)_2^{3-} + 2H^+ = Lu^{3+} + 2HPO_4^{2-}$	-	2.8010	-	-	-	-	-	-
$LuH_2PO_4^{2+} = H^+ + Lu^{3+} + HPO_4^{2-}$	-	-9.7121	-	-	-	-	-	-
$LuPO_4(aq) + H^+ = Lu^{3+} + HPO_4^{2-}$	-	-0.6495	-	-	-	-	-	-
$Nd(PO_4)_2^{3-} + 2H^+ = Nd^{3+} + 2HPO_4^{2-}$	-	5.2010	-	-	-	-	-	-

Table 6-75. Calculated log K Grids for Some Other Phosphate Aqueous Species for data0.ymp.R5 (Continued)

Reaction	0.01°C	25°C	60°C	100°C	150°C	200°C	250°C	300°C
$NdH_2PO_4^{2+} = H^+ + Nd^{3+} + HPO_4^{2-}$	-	-9.6121	-	-	-	-	-	-
$NdPO_4(aq) + H^+ = Nd^{3+} + HPO_4^{2-}$	-	0.5505	-	-	-	-	-	-
$Pm(PO_4)_2^{3-} + 2H^+ = Pm^{3+} + 2HPO_4^{2-}$	-	4.7410	-	-	-	-	-	-
$PmH_2PO_4^{2+} = H^+ + Pm^{3+} + HPO_4^{2-}$	-	-9.6121	-	-	-	-	-	-
$PmPO_4(aq) + H^+ = Pm^{3+} + HPO_4^{2-}$	-	0.4005	-	-	-	-	-	-
$Pr(PO_4)_2^{3-} + 2H^+ = Pm^{3+} + 2HPO_4^{2-}$	-	5.6210	-	-	-	-	-	-
$PrH_2PO_4^{2+} = H^+ + Pm^{3+} + HPO_4^{2-}$	-	-9.6621	-	-	-	-	-	-
$PrPO_4(aq) + H^+ = Pm^{3+} + HPO_4^{2-}$	-	0.7505	-	-	-	-	-	-
$Sm(PO_4)_2^{3-} + 2H^+ = Sm^{3+} + 2HPO_4^{2-}$	-	4.3010	-	-	-	-	-	-
$SmH_2PO_4^{2+} = H^+ + Sm^{3+} + HPO_4^{2-}$	-	-9.5621	-	-	-	-	-	-
$SmPO_4(aq) + H^+ = Sm^{3+} + HPO_4^{2-}$	-	0.2505	-	-	-	-	-	-
$Tb(PO_4)_2^{3-} + 2H^+ = Tb^{3+} + 2HPO_4^{2-}$	-	3.7010	-	-	-	-	-	-
$TbH_2PO_4^{2+} = H^+ + Tb^{3+} + HPO_4^{2-}$	-	-9.6121	-	-	-	-	-	-
$TbPO_4(aq) + H^+ = Tb^{3+} + HPO_4^{2-}$	-	-0.0495	-	-	-	-	-	-
$Tm(PO_4)_2^{3-} + 2H^+ = Tm^{3+} + 2HPO_4^{2-}$	-	3.1010	-	-	-	-	-	-
$TmH_2PO_4^{2+} = H^+ + Tm^{3+} + HPO_4^{2-}$	-	-9.7121	-	-	-	-	-	-
$TmPO_4(aq) + H^+ = Tm^{3+} + HPO_4^{2-}$ (a)	-	-0.0495	-	-	-	-	-	-
$Y(PO_4)_2^{3-} + 2H^+ = Y^{3+} + 2HPO_4^{2-}$	-	3.3010	-	-	-	-	-	-
$YH_2PO_4^{2+} = H^+ + Y^{3+} + HPO_4^{2-}$	-	-9.6121	-	-	-	-	-	-
$YPO_4(aq) + H^+ = Y^{3+} + HPO_4^{2-}$	-	-0.2495	-	-	-	-	-	-
$Yb(PO_4)_2^{3-} + 2H^+ = Yb^{3+} + 2HPO_4^{2-}$	-	2.8010	-	-	-	-	-	-
$YbH_2PO_4^{2+} = H^+ + Yb^{3+} + HPO_4^{2-}$	-	-9.6121	-	-	-	-	-	-
$YbPO_4(aq) + H^+ = Yb^{3+} + HPO_4^{2-}$	-	-0.5495	-	-	-	-	-	-
$UO_2PO_4^- + H^+ = UO_2^{2+} + HPO_4^{2-}$	-	-0.8689	-	-	-	-	-	-
$UO_2HPO_4(aq) = UO_2^{2+} + HPO_4^{2-}$	-	-7.2290	-	-	-	-	-	-
$UO_2H_3PO_4^{2+} = UO_2^{2+} + HPO_4^{2-} + 2H^+$	-	-10.1011	-	-	-	-	-	-
$UO_2H_2PO_4^+ = UO_2^{2+} + HPO_4^{2-} + H^+$	-	-10.4611	-	-	-	-	-	-

Table 6-75. Calculated log K Grids for Some Other Phosphate Aqueous Species for data0.ymp.R5 (Continued)

Reaction	**0.01°C**	**25°C**	**60°C**	**100°C**	**150°C**	**200°C**	**250°C**	**300°C**
$UO_2(H_2PO_4)_2(aq) = UO_2^{2+} + 2HPO_4^{2-} + 2H^+$	-	-19.3331	-	-	-	-	-	-
$UO_2(H_2PO_4)(H_3PO_4)^+ = UO_2^{2+} + 2HPO_4^{2-} + 3H^+$	-	-20.3430	-	-	-	-	-	-
$NpO_2H_2PO_4^+ = NpO_2^{2+} + HPO_4^{2-} + H^+$	-	-10.5247	-	-	-	-	-	-

Source: Output DTN: SN0702T0502404.015, folder: *\Phosphate*, workbooks: *AqueousSpecies_j_Phosphates_CFJC.xls* (top through $YbPO_4(aq)$) and *AqueousSpecies_j_PO4_KBH.xls* ($UO_2PO_4^-$ to bottom).

[a] A data entry error (-12.4 instead of -12.8) was made in calculating the log K value for $TmPO_4(aq)$. See Section 6.8, which gives a corrected value.

CR 6731 (Section 1.2) in addition to addressing the problem in data for key phosphate species also addresses a problem regarding the compositions of rare earth phosphates. Data (25°C only) were previously taken for a large set of such compounds from the compilation of Spahiu and Bruno (1995 [DIRS 103804]). In this set, a number of the phosphate compounds (whose thermochemical properties were determined by solubility) were indeterminate in regard to water of hydration. Europium phosphate was for example represented in this compilation as "EuPO4.XH_2O", where X was intended to represent an unknown number whose value was probably close to one or two (and probably also varying according to the exact phase). When these data were originally processed, the "X" was misinterpreted as the roman numeral for ten. This causes no significant errors in calculated solubilities as long as solutions remain very dilute and the activity of water is very close to unity. In more concentrated solutions, however, the solubilities could be substantially overpredicted.

Structural studies on REE (Rare Earth Element) phosphates (Hezel and Ross 1966 [DIRS 177990]; Hezel and Ross 1967 [DIRS 178227]; Assaaoudi et al. 1997 [DIRS 177936]); Assaaoudi et al. 2000 [DIRS 177992]); and Assaaoudi et al. 2001 [DIRS 179602]) are used here to assign values for waters of hydration to REE phosphates for which Spahiu and Bruno (1995 [DIRS 103804]) had indicated "XH2O". It is assumed that hydrous REE phosphate phases of Gd, Tb, Dy, Ho, Er, Tm, Pm, and Yb correspond to those of the weinschenkite structural type having two waters of hydration (Assaaoudi et al. 2001 [DIRS 179602]); thus having the formula REE_PO_4:2H_2O. The hydrous REE phosphates of La, Ce, Pr, Nd, Sm, and Eu correspond to those of the rhabdophane structural type having only one water of hydration; thus having the stoichiometry REE_PO_4:H_2O. For hydrous phosphate phases containing Pm (xenotime) and Lu (rhabdophane), 1.5 and 0.5 waters of hydration were assigned to these phases, respectively. In general, phases of the weinschenkite and rhabdophane structural types can be related to low temperature regimes which correspond to the log K values at 25°C in the thermodynamic database. The updated chemical formulas are listed in Table 6-76. These formulas are used in the recalculations given above in this section.

Table 6-76. Updated Stoichiometry of Some Hydrous REE Phosphate Solids

Old H_2O Stoichiometry	New H_2O Stoichiometry
$CePO_4$:10H_2O	$CePO_4$:H_2O
$DyPO_4$:10H_2O	$DyPO_4$:2H_2O
$ErPO_4$:10H_2O	$ErPO_4$:2H_2O
$EuPO_4$:10H_2O	$EuPO_4$: H_2O
$GdPO_4$:10H_2O	$GdPO_4$:2H_2O
$HoPO_4$:10H_2O	$HoPO_4$:2H_2O
$LaPO_4$:10H_2O	$LaPO_4$: H_2O
$LuPO_4$:10H_2O	$LuPO_4$:0.5H_2O
$NdPO_4$:10H_2O	$NdPO_4$:H_2O
$PmPO_4$:10H_2O	$PmPO_4$:1.5H_2O
$PrPO_4$:10H_2O	$PrPO_4$: H_2O
$SmPO_4$:10H_2O	$SmPO_4$: H_2O

Table 6-76. Updated Stoichiometry of Some Hydrous REE Phosphate Solids (Continued)

Old H_2O Stoichiometry	New H_2O Stoichiometry
$TbPO_4$:10H_2O	$TbPO_4$:2H_2O
$TmPO_4$:10H_2O	$TmPO_4$:2H_2O
$YbPO_4$:10H_2O	$YbPO_4$:2H_2O

Source: This section (see text above).

6.7.9 Addition of Some Magnesium Silicates

The data blocks for Mg silicates considered for inclusion in data0.ymp.R5 (Output DTN: SN0612T0502404.014) were initially developed for data0.ypf.R2 (output SN0504T0502205.008 [DIRS 179388]) and described in the In-Drift Precipitates/Salts Model report (SNL 2007 [DIRS 177411]). For completeness, these descriptions are also included in this section. The relevant inputs are given in Section 4.1.18. The solubility constant for the added phase amorphous sepiolite (sepiolite(am), $Mg_4Si_6O_{15}(OH)_2$:6H_2O) is based on the solubility study of Wollast et al. (1968 [DIRS 162340]). The source only provides a log K value at 25°C. However, log K values other than 25°C are given in the data block up to a temperature of 100°C. These values are added for a validation analysis in the In-Drift Precipitates/Salts Model report (SNL 2007 [DIRS 177411]). It must be emphasized that the log K values other than that at 25°C are fictive in the sense that these represent a constant increment in log K relative to that of crystalline sepiolite. That is, the increment in log K applied to sepiolite(am) values other than 25°C is defined by the difference between the log K value for "Sepiolite(am)" and "Sepiolite" at 25°C. This Δlog K at 25°C is 7.1161 and the affected log K values "Sepiolite(am)" at temperatures other than 25°C are estimated as the sum of the log K value for "Sepiolite" at the temperature of interest plus the Δlog K value of 7.1161. It should be also emphasized that use of these data above 25°C requires explicit justification for YMP applications since these "extrapolated" values were not obtained with the thermodynamic parameter extrapolation technique described in this report. The IDPS model report explains the purpose and use of "Sepiolite(am)".

Table 6-77. Estimated log K Values for "Sepiolite(am)" at Temperatures up to 100°C

T(°C)	log K
0	39.5037
25	37.5600[a]
60	34.2871
100	31.0129

Source: This section (see above text).

[a] This value is not estimated and was obtained from Wollast et al. (1968 [DIRS 162340]).

The phase palygorskite was also added to data0.ymp.R5 (Output DTN: SN0612T0502404.014). The log K value is computed using the estimated Gibbs energy of formation (ΔG_f^o, for 298.15 K) for a palygorskite composition of $Mg_{2.84}Al_{1.8}Si_{7.73}O_{20}(OH)_2$:4$H_2O$ reported in the work of Birsoy (2002 [DIRS 178220]), who adopted the method of Nriagu (1975 [DIRS 178321]) to estimate the ΔG_f^o of the solid. For the calculation of ΔG_f^o, the reaction delineating the formation of palygorskite from its constituents is given by: (Birsoy 2002 [DIRS 178220]):

$$\begin{aligned}&Mg_{2.84}Al_{1.8}Si_{7.73}O_{20}(OH)_2(OH_2)_4:4H_2O \;+\; 12\,H_2O \;=\; 2.84\,Mg(OH)_2\\&+\,1.8\,Al(OH)_3 \;+\; 7.73\,Si(OH)_4\end{aligned}$$

(Eq. 6-46)

ΔG_f^o is estimated using the method of Nriagu (1975 [DIRS 178321]) which requires the following formulation to represent the formation of palygorskite as given by Birsoy (2002 [DIRS 178220]):

$$\Delta G^{\circ}_{f,298,paly} = \sum n_i \Delta G^{\circ}_{f,298,(hydroxide)} - \left(\sum n_i z_i - 30\right)\Delta G^{\circ}_{f,298,(H_2O)} - \left[0.39(n_i z_i - 30)\right]$$

(Eq. 6-47)

where n_i represents the stoichiometric coefficient of the i^{th} hydroxide phase in the mass balance reaction and z_i refers to the charge on the cation of the i^{th} hydroxide phase. The term $[0.39(n_i z_i - 30)]$ is an empirical parameter based on the number of water of hydration molecules captured or released during the reaction derived by Nriagu (1975 [DIRS 178321]) including a 0.39 regression coefficient.

The calculation and reaction established by Nriagu (1975 [DIRS 178321]) also employs amorphous $Si(OH)_4$, rather than one of the anhydrous silica polymorphs (e.g. SiO_2(quartz) and SiO_2(am)) appearing in data0.ymp.R5 (Output DTN: SN0612T0502404.014). A representative value for this constituent that would be consistent with data0.ymp.R5 (Output DTN: SN0612T0502404.014) was obtained by summing the standard free energy of quartz plus twice that of water (Output DTN: SN0702T0502404.015), to give: (2*237181.4) + 856280.7 = 1330643.5 j/mol (318.03 kcal/mol). This value is close to the value of 318.6 kcal/mol appearing in Nriagu (1975 [DIRS 178321]), suggesting that the choice was a reasonable one. This result also supports simply carrying forward the 0.39 regression coefficient in the empirical calculation evaluated by Nriagu (1975 [DIRS 178321]) to account for loss of water of hydration without modifying its value. It should be noted that the free energies are somewhat different from those used in the literature (Nriagu, 1975 [DIRS 178321]) to evaluate the clay free energy values on which the value of the regression coefficient was initially evaluated. Furthermore, the 0.39 regression-coefficient in equation 6-47 (see also Birsoy 2002 [DIRS 178220]) is scaled in accordance with the unit conversion between kcal/mol and J/mol.

The expression adopted in this report for the formation of palygorskite is similar to that by Birsoy (2002 [DIRS 178220]) but consistent with the use of SiO_2(quartz) instead of $Si(OH)_4$ (Equation 6-48). The reaction expression is thus given as:

$$\begin{aligned}&Mg_{2.84}Al_{1.8}Si_{7.73}O_{20}(OH)_2(OH_2)_4:4H_2O + 11.08\,H^+ = 2.84\,Mg^{2+} +\\&1.8\,Al^{3+} + 7.73\,SiO_2(aq) + 14.54\,H_2O\end{aligned}$$

(Eq. 6-48)

This difference in silica species does not affect the results since both Si constituents are equivalent based on the thermodynamic conventions in the data0.ymp.R5 database (Output DTN: SN0612T0502404.014). The Gibbs energies for $Mg(OH)_2$ [-835318.86 J/mol], $Si(OH)_4$ [1330643.5 J/mol] and $H_2O(aq)$ [-238181.38 J/mol] used in this calculation were taken directly from workbook *Solids_j_Mg_Silicates_CFJC.xls* within folder *\Mg Silicates* of Output DTN: SN0702T0502404.015, while the Gibbs energy for $Al(OH)_3$ (-1155486.91 J/mol) was taken from data0.ymp.R4 (DTN: SN0410T0510404.002]; see table 6-78).

The value for ΔG_f^o estimated from Equations 6-46 and 6-47 is calculated in Output DTN: SN0702T0502404.015 as follows:

$$\begin{aligned}\Delta G^{\mathrm{o}}_{f,298,\mathrm{paly}} &= 2.84(-835318.9) + 1.8(-1155486.9) + 7.73(-318.03\times 1000\times 4.184)\\ &-12(-237181.4) - (0.39\times 12\times 1000\times 4.184) = 11911460.55 \ \ \mathrm{J/mol}\end{aligned}$$

(Eq. 6-49)

This ΔG_f^o value of 11911.46 kJ/mol yields a log K value of 26.41 when computed in spreadsheet *Solids_j_Mg_Silicates_CFJC.xls* (Output DTN: SN0702T0502404.015). In fact, when Birsoy (2002 [DIRS 178220]) employed Nriagu's (1975 [DIRS 178321]) thermodynamic data as a basis for evaluating the standard free energy of polygorskite he calculated a value of -11944.32 kcal/mol, which when carried through the rest of the computation process using Birsoy's (2002 [DIRS 178220]) value results in a log K of 20.65.

The estimated ΔG_f^o value using the thermodynamic data from workbook *Solids_j_Mg_Silicates_CFJC.xls* (Output DTN: SN0702T0502404.015) differs from that given by Birsoy (2002 [DIRS 178220]) by 32855.45 J/mol and is not unreasonable given the different source of thermodynamic data for some constituents in the formation reaction required for consistency with the data0.ymp.R5 database (Output DTN: SN0612T0502404.014; see Table 6-78). By comparison, Birsoy (2002 [DIRS 178220]) uses thermodynamic data for constituents in Equation 6-46 from Helgeson et al. (1978 [DIRS 101596]). Also note that the numerical expression associated with Birsoy's (2002 [DIRS 178220]) chemical equation in the printed text has a typographic error: "-12(56.69)" should read "-12(-56.69)". Table 6-79 gives the adopted 25°C log K value.

Table 6-78. Thermodynamic Data of Components Used in the Estimation of Palygorskite Standard Gibbs Energy of Formation

Component	**ΔG_f^o (J/mol)**	**Source Spreadsheets[a]**
$Mg(OH)_2$	-835318.9	*Solids_j_Mg_Silicates_CFJC.xls*, worksheet: "Misc. Solids"
$Al(OH)_3$	-1155486.9	data0.ymp.R4 (Output DTN: SN0410T0510404.002)
SiO_2(quartz)	-856280.7	*Solids_j_Mg_Silicates_CFJC.xls*, worksheet: "Misc. Solids"
H_2O	-237181.4	*Solids_j_Mg_Silicates_CFJC.xls*, worksheet: "Basis Species 1"
$Mg_{2.84}Al_{1.8}Si_{7.73}O_{20}(OH)_2(OH_2):4H_2O$	-11911460.55	*Solids_j_Mg_Silicates_CFJC.xls*, worksheet: "Palygorskite"

[a] Spreadsheet *Solids_j_Mg_Silicates_CFJC.xls* is in Output DTN: SN0702T0502404.015 (folder: *\Mg Silicates*).

Log K values for the phase "Antigorite(am)" or "poorly crystalline antigorite" in the source reference were obtained from the work by Gunnarsson et al. (2005 [DIRS 176844]). In this study, the composition of this phase has the designated chemical stoichiometry of $Mg_3Si_2O_5(OH)_4$ instead of that of the mineral antigorite ($Mg_{48}Si_{34}O_{85}(OH)_{62}$). This stoichiometry corresponds to that of the serpentine mineral chrysotile. This stoichiometry was designated for this phase in their study based on the Mg/Si ratio (i.e., 3/2) of sampled solutions and the infrared spectra obtained for this poorly crystalline solid (Gunnarsson et al. 2005 [DIRS 176844]). The Mg/Si ratio for antigorite is slightly smaller relative to that of a serpentine mineral. The ΔG_f^o (298.15 K) for "Antigorite(am)" was computed in spreadsheet *Solids_j_Mg_Silicates_CFJC.xls* based on the log K value obtained from Equation 3 of Gunnarsson et al. (2005 [DIRS 176844]). Table 6-79 lists the log K values for the reaction $Mg_3Si_2O_5(OH)_4 + 6\ H^+ = Mg^{2+} + 2\ SiO_2(aq) + 5\ H_2O$ and adopted in data0.ymp.R5 (Output DTN: SN0612T0502404.014).

Table 6-79. Calculated log K Temperature Grids for Palygorskite and Poorly Crystalline Antigorite

data0.ymp.R5 Species Designation	**Reaction**	**0.01°C**	**25°C**	**60°C**	**100°C**	**150°C**	**200°C**	**250°C**	**300°C**
Palygorskite	$Mg_{2.84}Al_{1.8}Si_{7.73}O_{20}(OH)_2(OH_2)4{:}4H_2O + 11.08H^+ = 2.84Mg^{2+} + 1.8Al^{3+} + 7.73SiO_2(aq) + 14.54H_2O$	-	26.4078	-	-	-	-	-	-
Poorly Crystalline Antigorite	$Mg_3Si_2O_5(OH)_4$ + 6H+ = $3Mg^{2+} + 2SiO_2(aq) + 5H_2O$	37.3589	34.5025	31.2224	28.2271	25.2793	22.9545	21.0741	19.5218

Source: Output DTN: SN0702T0502404.015, folder: *\Mg Silicates*, workbook: *Solids_j_Mg_Silicates_CFJC.xls.*

6.7.10 Addition of Some Uranyl Oxy-Hydrates and Silicates

Uranyl oxy-hydrates and silicates have been reported as alteration products of spent nuclear fuel in oxidizing environments, several of which were observed to form during corrosion tests on both unirradiated UO_2 and spent fuel (Wronkiewicz et al. 1996 [DIRS 102047], Chen et al. 1999 [DIRS 123270]); however, many of these uranyl compounds were not included in the development of the data0.ymp.R4 (Output DTN: SN0410T0510404.002) thermodynamic database (see CR7756 description in Section 1.2). Recent studies have focused on directly determining thermodynamic properties for many potentially YMP-relevant uranyl compounds (Perez et al. 2000 [DIRS 157910], Guillaumont et al. 2003 [DIRS 168382], McKenzie et al. 2001 [DIRS 172346] , Perez et al. 1997 [DIRS 100812], Möll et al. 1996 [DIRS 106349], Sandino and Grambow 1994 [DIRS 113360], Rai et al. 2002 [DIRS 168155], Vochten and Van Haverbeke 1990 [DIRS 113433], Casas et al. 1997 [DIRS 102432], Kubatko et al. 2003 [DIRS 173070]) and efforts have been made to estimate thermodynamic properties of additional uranyl solids by using high-quality structural data (Finch 1997 [DIRS 106347], Chen et al. 1999 [DIRS 123270]).

Inputs for the present analysis are given in Section 4.1.19. This section discusses and qualifies additional and recalculated data for a number of uranium minerals, and these are used in data0.ymp.R5 (Output DTN: SN0612T0502404.014). The requisite spreadsheet calculations are contained in workbooks in Output DTN: SN0702T0502404.015, in folder *\Uranyl_Minerals_KBH*. This section also recommends some data to include in a future update. These data were developed near the end of the development of this analysis report and were not available in time to include in data0.ymp.R5 (Output DTN: SN0612T0502404.014). These data reflect an improved understanding of structures and stoichiometries, factors which affect the calculation of thermodynamic properties using estimation methods employed here (e.g., Chen et al. 1999 [DIRS 123270]). The spreadsheet calculations for these data are contained in workbooks in Output DTN: SN0702T0502404.015, in folder *\Uranyl_Minerals_KBH_RJF*.

Data have previously been derived in this analysis report for some of these uranium minerals (soddyite, Section 6.3.4.1; uranophane, Section 6.3.4.2; sodium weeksite, Section 6.3.4.3; and sodium boltwoodite, Section 6.3.4.4). The methodologies employed here are the same. A standard molar Gibbs energy of formation at 25°C is obtained as a direct input, calculated using a predictive correlation algorithm, or is calculated from a log K value obtained from a solubility measurement. A standard molar volume is obtained as a direct input or calculated from a density value and the molecular weight of the solid. The other thermodynamic parameters for these solids generally need to be estimated using correlation algorithms, due to a lack of experimental data. In general, the calculations involving this particular set of solids are carried out mostly in calorie units (1 cal = 4.184 Joule; Weast and Astle 1979 [DIRS 102865]).

The standard molar entropy at 25°C is estimated using the method described in Section 6.1.4.2 (see also equation 6-18). This method requires entropy values for constituent oxides components and the molar volume of the solid. Heat capacity coefficients (generally the a, b, and c coefficients that appear in the Maier-Kelley equation (equation 6-2) are estimated using a correlation algorithm described in Section 6.1.4.1 (equations 6-14, 6-15, and 6-16). This method involves summing contributions from constituent oxide components. The methods used to estimate the entropy and heat capacity coefficients are the same as those used for a number of clay minerals (see Section 6.3.1). The Gibbs energy at 25°C, the entropy at 25°C, the heat capacity coefficients, and the molar volume are used to calculated the apparent Gibbs energy of formation on the EQ3/6 temperature grid (0-25-60-100-150-200-250-300°C) using the retrieval equation (equation 6-3). A corresponding log K grid for reaction for dissolution of the solid is then calculated from this Gibbs energy grid and Gibbs energy grids for the other species appearing in the reaction (see Section 6.1.3).

The constituent oxide data (volumes, entropies, and heat capacity coefficients) required to estimate the entropy and the heat capacity coefficients are largely taken from Helgeson et al. (1978 [DIRS 101596], Table 2, p. 48). These same data are used to estimate the entropies and heat capacity coefficients of some clay minerals in Section 6.3.1. In addition, data are required for the UO_3 component. These are taken to be equivalent to the corresponding data for the phase β-UO_3. The entropy and heat capacity coefficient data are taken from Grenthe et al. (1992 [DIRS 101671]) in Joule units and are converted to calorie units using 4.184 J/cal (Weast and Astle 1981 [DIRS 100833], p. F-304). The entropy is from Table III.1, p. 31: 96.320 J/mol = (96.320 J/mol)/(4.184 J/cal) = 23.02 cal/mol. The heat capacity coefficients are from Table III.3, p. 61: a = 8.61700×10^{1}, b = 2.49840×10^{-2}, and “e” (here c) = -1.09150×10^{6} (in units consistent with the heat capacity in units of J/mol-K). Division by 4.184 J/cal then gives: a = 20.60, b = 5.97×10^{-3}, c = -26.1×10^{5}, or, using traditional Maier-Kelley coefficient scaling, a = 20.60, $b \times 10^{3} = 5.97$, $c \times 10^{-5} = -2.61$ (all in units consistent with the heat capacity in cal/mol-K). The volume of 34.46 cm^3/mol is from Hemingway et al. (1982 [DIRS 157905]).

The molar volumes, entropies, and heat capacity coefficients are treated in the workbooks *Usilicates_HC_S_KBH.xls* and *Usilicates_yc_tls_ch_CFJC.xls* in folder *\Uranyl_minerals_KBH* of Output DTN: SN0702T0502404.015. The data from these spreadsheets are used in workbooks *Minerals_cal_KBH_Usilicates.xls* and *Minerals_cal_YC_Usilicates_CFJC.xls*, respectively, in the same folder of this output DTN, to calculate the requisite log K grids. In the cases of the minerals in this group treated previously in this analysis report (soddyite, Section 6.3.4.1; uranophane, Section 6.3.4.2; sodium weeksite, Section 6.3.4.3; and sodium boltwoodite, Section 6.3.4.4), the values for the molar volumes, entropies, and heat capacity coefficients remain unchanged in many instances. However, they are all recalculated for the sake of completeness and transparency. The spreadsheets noted above are the source of the data for the affected species in the data0.ymp.R5 database (Output DTN: SN0612T0502404.014).

Late in the production of this analysis report, certain small errors and opportunities for improvement became apparent. These were analyzed in an updated set of the above worksheets that are present in folder *\Uranyl_minerals_KBH_RJF* of Output DTN: SN0702T0502404.015. These updated spreadsheets have “_rjf” appended to the root names. For each of the uranium minerals addressed in this section, the development of the data in data0.ymp.R5 (Output DTN: SN0612T0502404.014) is discussed first, followed by the development of data for “post-data0.ymp.R5 corrections.” In most instances, the magnitude of the corrections is no greater than the actual uncertainty. Nevertheless, it is recommended that the corrected values be utilized in future updates.

Uranophane: $Ca[(UO_2)(SiO_3OH)]_2{:}5H_2O$

There are two naturally occurring polymorphs of uranophane (alpha and beta). The crystal structures for both are well defined, although, to the best of our knowledge, there are no studies on the solubility of uranophane-beta. On the other hand, several studies report thermodynamic data for uranophane-alpha (Langmuir 1978 [DIRS 101703], Hemingway et al. 1982 [DIRS 157905], McKenzie et al. 2001 [DIRS 172346], Nguyen et al. 1992 [DIRS 100809], Finch 1997 [DIRS 106347], Chen et al. 1999 [DIRS 123270], Perez et al. 2000 [DIRS 157910], Casas et al. 1997 [DIRS 102432], Casas et al. 1994 [DIRS 100714]); however, only four of these report solubility products derived from measured data (Nguyen et al. 1992 [DIRS 100809], Perez et al. 2000 [DIRS 157910]), Casas et al. 1997 [DIRS 102432], Casas et al. 1994 [DIRS 100714]).

Nguyen et al (1992 [DIRS 100809]) measured the solubility of synthetic uranophane-alpha in water at pH = 3.5(±0.5), T=303 K, under an inert atmosphere. They studied the reaction:

$$\text{Uranophane} + 6\ H^+ = Ca^{2+} + 2\ UO_2^{2+} + 2\ Si(OH)_4(aq) + 5\ H_2O \qquad \text{(Eq. 6-50)}$$

The authors assumed that silicic acid was the only dissolved Si species in their solutions at the experimental pH of 3.5. They used total measured U and Si concentrations in the equilibrated solution to calculate the remaining solution species by taking relevant thermodynamic data for dissolved species from Grenthe et al. (1992 [DIRS 101671]), including the U(VI) hydrolysis data. Applying guidelines used by the NEA's Thermochemical Database Project (see Guillaumont et al. 2003 [DIRS 168382]), Nguyen et al (1992 [DIRS 100809]) derived log K = 9.42 (±0.48) for the reaction (6-50).

A critical analysis of this study can be found in Guillaumont et al. (2003 [DIRS 168382], Vol 5., pp. 256 and 440 to 443). Citing problems with phase impurity and super-saturation with respect to silica, Guillaumont et al. (2003 [DIRS 168382]) did not select this value of log K for uranophane.

Perez et al. (2000 [DIRS 157910]) conducted a similar study of uranophane by using dilute bicarbonate solutions ($10^{-3} < [HCO_3^-] < 2 \times 10^{-2}$ Molar), pH between 8 and 9, and 25°C. A critical analysis of Perez et al. (2000 [DIRS 157910]) can be found in Guillaumont et al. (2003 [DIRS 168382], Vol. 5., pp. 677 and 678 and 440 to 443). Perez et al. (2000 [DIRS 157910]) employed several techniques to characterize their solids, and Guillaumont et al. (2003 [DIRS 168382], Vol. 5) noted that the composition of the uranophane sample studied by Perez et al. (2000 [DIRS 157910]) was deficient in Ca (only 80% of the expected value in the formula) and that no charge-compensating cation was determined (e.g., Na^+). Thus the uncertain composition of the sample studied by Perez et al. (2000 [DIRS 157910]) led Guillaumont et al. (2003 [DIRS 168382]) to reject the log K value of 11.7 (±0.6) reported by Perez et al. (2000 [DIRS 157910]).

Casas et al. (1997 [DIRS 102432]), which is essentially a preliminary report upon which the paper by Perez et al. (2000 [DIRS 157910]) is based, report the same value for log K (1) = 11.7 (±0.6), which, as for Perez et al. (2000 [DIRS 157910]), is based on the average of a range of log K values between 10.75 and 12.94: log K = 11.7 (±0.6).

However, the x-ray diffraction patterns reported by Casas et al. (1997 [DIRS 102432]) for starting materials used by both Casas et al. (1997 [DIRS 102432]) and Perez et al. (2000 [DIRS 157910]) indicate a considerable amount of becquerelite in at least one uranophane sample used by them (batch B, see Casas et al. 1997 [DIRS 102432], Figure 2-4, p. 6).

Several years before the evaluation by Guillaumont et al. (2003 [DIRS 168382]), Chen et al. (1999 [DIRS 123270]) had evaluated solubility data available at that time and chose to use the solubility product reported by Casas et al. (1997 [DIRS 102432]) in their paper (Chen et al. 1999 [DIRS 123270]; p. 664), from which they derive $\Delta G_f°$ (uranophane-alpha) = -6192.3 (±3.4) kJ/mol.

There is a wide range of values for the Gibbs energy of formation of uranophane derived from various thermodynamic modeling techniques (Langmuir 1978 [DIRS 101703]; Hemingway et al. 1982 [DIRS 157905]; McKenzie e al. 2001 [DIRS 172346]; Finch 1997 [DIRS 106347]; Chen et al. (1999 [DIRS 123270]). Guillaumont et al. (2003 [DIRS 168382], pp. 442 to 443) do not recommend any specific value, but do point to the $\Delta G_f°$ value of 6192.3 (±3.4) derived by Chen et al. (1999 [DIRS 123270], p. 654). We believe this selection is justified for the reasons already discussed on page 664 of Chen et al. (1999 [DIRS 123270]). By using the $\Delta G_f°$ value reported by Chen et al. (1999 [DIRS 123270]), we derive a log K of 12.2810 for reaction (6-50). This is close to the upper end of the range (10.75-12.94) reported by Casas et al. 1997 [DIRS 102432] and Perez et al. (2000 [DIRS 157910]). We retain this value of log K in data0.ymp.R5 (Output DTN: SN0612T0502404.014). However, we note that the value of $\Delta G_f°$ that corresponds to a log K of 11.7 is -6195.6 kJ/mol, which is within the uncertainty estimated by Chen et al. (1999 [DIRS 123270]).

This Gibbs energy value was used with values of other thermodynamic parameters (molar volume, standard molar entropy, and Maier-Kelley heat capacity coefficients a, b, and c, to obtain the apparent Gibbs energy of formation on the EQ3/6 temperature grid (0-25-60-100-150-200-250-300°C), and thence to obtain log K values on the same temperature grid (see results for “data0.ymp.R5” in Table 6-80). The values for these other parameters are the same as in the previous analysis given in Section 6.3.4.2. The molar volume of 251.336 cm^3/mol is given in Table 4-21. The standard molar entropy (S^o), and heat capacity values were estimated from the predictive correlation algorithms discussed above (at the beginning of Section 6.7.10). For calculational details, see spreadsheet *Minerals_cal_KBH_Usilicates.xls* from folder *\Uranyl_minerals_KBH* of Output DTN: SN0702T0502404.015. The entropy value obtained is 155.402 cal/mol-K; the heat capacity coefficients obtained are: a = 139.41, $b \times 10^3 = 37.66$, $c \times 10^{-5} = -12.18$ (all in units consistent with the heat capacity in cal/mol-K).

It is noted that the molar volume of 251.336 cm^3/mol given in Table 4-21 is not the true input from the cited source (Hemingway 1982 [DIRS 157905]), which actually gives a value of 224.9 cm^3/mol. The actual source value was “corrected” to be consistent with a stoichiometry of $Ca(UO_2)_2(SiO_3OH)_2{:}5H_2O$ based on an understanding that the source value was consistent with a stoichiometry of $Ca(UO_2)_2(SiO_3OH)_2$. That understanding was not correct. The stoichiometry given by the source is $Ca(UO_2)_2(SiO_3OH)_2{:}3H_2O$. The original “correction” assumed that the density calculated from the source’s molar volume and stoichiometry was correct and that a corrected molar volume could be obtained from that density. That is the source of the 251.366 cm^3/mol value. Using the correct source stoichiometry (3 waters of hydration instead of zero) results in a molar volume of 234.778 cm^3/mol and hence an estimated standard molar entropy of 176.437 cal/mol-K (see noted corrections in workbook *Usilicates_yc_tls_ch_CFJC.xls*, which is in folder *\Uranyl_minerals_KBH* of Output DTN: SN0702T0502404.015). The error in the original “correction” for both molar volume and entropy may well be within the actual uncertainties, especially considering that uranophane is not an especially well-characterized mineral that exhibit a certain degree of natural variation. However, a better molar volume value is discussed below.

Post-data0.ymp.R5 Corrections. The following corrections are made. First, the log K value of 11.7 was more or less expected in the above calculation, as the Gibbs energy of formation value that was used was obtained from this log K value. The inconsistency is apparently associated with the values of the Gibbs energies of water and the aqueous ions appearing in the reaction. Appendix A points out that recommended values do vary among commonly used sources. Chen et al. (1999 [DIRS 123270]) do not define their source. However, most of the discrepancy here seems to be associated with the Gibbs energy of formation of aqueous silica and the shift to the Rimstidt paradigm discussed in Section 6.1.5. Also, the molar volume was changed from the 251.336 cm^3/mol given in Table 4-21 to 221.6 cm^3/mol (Ginderow 1988 [DIRS 180758]). This increases the estimated entropy from the previously obtained 155.402 cal/mol-K to 170.895 cal/mol-K (see workbook *Usilicates_yc_tls_ch_CFJC_RJF.xls* in folder *\Uranyl_minerals_KBH_RJF* of Output DTN: SN0612T0502404.015). On the basis of these corrections, we have recalculated the log K grid for uranophane-alpha ("Corrected" in Table 6-80). The differences shown in Table 6-80 are relatively small and essentially within the uncertainty of the available data. No change was made to the existing data0.ymp.R5 (Output DTN: SN0612T0502404.014) data block for uranophane-alpha; however, it is suggested that the corrected data be used in a future update.

Table 6-80. The data0.ymp.R5 and Corrected log K Values for Uranophane-alpha

Temp. °C	0.01	25	60	100	150	200	250	300
data0.ymp.R5[a]	14.7917	12.2810	9.3729	6.8112	4.4178	2.5963	1.0843	-0.3513
Corrected[b]	13.9074	11.7000	9.1400	6.8962	4.8145	3.2363	1.9172	0.6348
Difference	0.8842	0.5810	0.2329	-0.0851	-0.3966	-0.6400	-0.8329	-0.9862

[a] Output DTN: SN0702T0502404.015, folder: *\Uranyl_minerals_KBH*, workbook: *Minerals_cal_YC_Usilicates_CFJC.xls*.

[b] Output DTN: SN0702T0502404.015, folder: *\Uranyl_minerals_KBH_RJF*, workbook: *Minerals_cal_YC_Usilicates_CFJC_rjf.xls*.

Soddyite: $(UO_2)_2(SiO_4)$:$2H_2O$

Several authors report thermodynamic data for soddyite (Hemingway et al. 1982 [DIRS 157905], Nguyen et al. 1992 [DIRS 100809], Perez et al. 1997 [DIRS 100812], Moll et al. 1996 [DIRS 106349]). A more comprehensive critical review of these reports can be found in the work by Guillaumont et al. (2003 [DIRS 168382], Vol.5, p. 254). A brief summary of their findings is presented here.

Moll et al (1996 [DIRS 106349]) measured the solubility of a well characterized, coarsely crystalline sample of soddyite in 0.1 M $NaClO_4$ at 298.15 K over a wide range of pH. Guillaumont et al. (2003 [DIRS 168382]) noted problems with how Moll et al. (1996 [DIRS 106349]) reported their data and recalculated the solubility constant in light of that fact for the following reaction:

$$\text{Soddyite} + 4\ H^+ = 2\ UO_2^{2+} + Si(OH)_4(aq) + 2\ H_2O \qquad \text{(Eq. 6-51)}$$

Guillaumont et al. (2003 [DIRS 168382]) obtained log K = 6.7 (±0.5) for the recalculated reaction. Perez et al. (1997 [DIRS 100812]) conducted a solubility study of synthetic soddyite under experimental conditions similar to those used by Perez et al (2000 [DIRS 157910]) for uranophane-alpha, reporting log K = 3.9 (±0.7). However, Guillaumont et al. (2003 [DIRS 168382]) note a "systematic variation" (i.e., a monotonic trend in log K) in the solubility product reported by Perez et al. (1997 [DIRS 100812]; Table II, p. 569) and do not select their value.

Nguyen et al. (1992 [DIRS 100809]) used a similar experimental methodology to determine the solubility of uranophane-alpha (water, inert atmosphere, pH = 3.00 (±0.05), T=303 K) and derived log K = 5.74 (±0.21) for reaction (6-51). The lack of concurrence among the available data prevented Guillaumont et al. (2003 [DIRS 168382]) from selecting a value for the solubility constant of soddyite. However, they recommend as a reasonable approximation averaging data from Moll et al. (1996 [DIRS 106349]) and Nguyen et al. (1992 [DIRS 100809]). This leads to a log K value of 6.2 (±1.0). We believe use of this value is justified because (1) it is based on the latest available measured data, (2) does not dismiss measured data with no obvious flaws, and (3) is consistent with the Guillaumont et al. (2003 [DIRS 168382]) recommendation.

By using the Gibbs energy of formation for soddyite of -3653.0 kJ/mol derived by Chen et al. (1999 [DIRS 123270]; p. 664), we calculate log K = 6.2767, which is within error of the contingent value recommended by Guillaumont et al. (2003 [DIRS 168382]). This value is used in the data block for soddyite in data0.ymp.R5 (Output DTN: SN0612T0502404.014).

This Gibbs energy value was used with values of other thermodynamic parameters (molar volume, standard molar entropy, and Maier-Kelley heat capacity coefficients a, b, and c, to obtain the apparent Gibbs energy of formation on the EQ3/6 temperature grid (0-25-60-100-150-200-250-300°C), and thence to obtain log K values on the same temperature grid (see results for "data0.ymp.R5" in Table 6-81). The values for these other parameters are the same as in the previous analysis given in Section 6.3.4.1. The molar volume of 131.27 cm^3/mol is as given by the International Centre for Diffraction Data (1986 [DIRS 180858]). The standard molar entropy (S^o), and heat capacities were estimated from the predictive correlation algorithms discussed above (at the beginning of Section 6.7.10). For calculational details, see spreadsheets *Minerals_cal_YC_Usilicates.xls* and *Usilicates_yc_tls_ch_CFJC.xls* in folder *\Uranyl_minerals_KBH* of Output DTN: SN0702T0502404.015. The entropy value obtained is 78.9922 cal/mol-K, and the heat capacity coefficients obtained are: a = 66.63, $b \times 10^3 = 36.62$, $c \times 10^{-5} = -7.92$ (all in units consistent with the heat capacity in cal/mol-K).

Post-data0.ymp.R5 Corrections. The following corrections are made. A unit cell volume was derived from Demartin et al. (1992 [DIRS 180859], $V° = 131.35$ cm^3/mol. Additionally, because of a small discrepancy in the value of the gas constant used in the workbook *Usilicates_YC_tls_ch_CFJC.xls* in folder *\Uranyl_minerals_KBH* of Output DTN: SN0612T0502404.015, (8.331403 instead of the 8.314510 used by Guillaumont et al. 2003 [DIRS 168382]), we recalculated values for log K and compare these with those in data0.ymp.R5 (Output DTN: SN0612T0502404.014) in the following table, which shows that the differences are insignificant. Therefore, we have made no change to the current entries in data0.ymp.R5 (Output DTN: SN0612T0502404.014).

Table 6-81. The data0.ymp.R5 and Corrected log K Values for Soddyite

Temp. °C	0.01	25	60	100	150	200	250	300
data0.ymp.R5[a]	7.7967	6.2767	4.5264	2.9733	1.4919	0.3254	-0.6815	-1.6652
Corrected[b]	7.7965	6.2766	4.5264	2.9734	1.4921	0.3256	-0.6813	-1.6650
Difference	0.0002	0.0001	--	-0.0001	-0.0002	-0.0002	-0.0002	-0.0002

[a] Output DTN: SN0702T0502404.015, folder: *\Uranyl_minerals_KBH*, workbook: *Minerals_cal_YC_Usilicates_CFJC.xls*.

[b] Output DTN: SN0702T0502404.015, folder: *\Uranyl_minerals_KBH_RJF*, workbook: *Minerals_cal_YC_Usilicates_CFJC_rjf.xls*.

Dehydrated Schoepite: $(UO_2)O_{0.25-x}(OH)_{1.5+2x}$ ($0 \leq x \leq 0.25$)

Dehydrated schoepite forms a solid solution described by the formula $UO_2O_{0.25-x}(OH)_{1.5+2x}$, in which x can vary between 0, for which the formula is $UO_2O_{0.25}(OH)_{1.5}$ (or UO_3:0.75H_2O) and 0.25, for which the formula is $UO_2(OH)_2$ (or UO_3:H_2O) (Finch et al. 1998 [DIRS 106347]). One of the most commonly cited compositions for dehydrated schoepite is UO_3:0.9H_2O, which corresponds to x=0.15 in the structural formula.

The energetics among various "UO_3 hydrates" including alpha-UO_3:0.9H_2O [$UO_2O_{0.1}(OH)_{1.8}$], is discussed by Grenthe et al. (1992 [DIRS 101671], pp. 136 to 140) and Guillaumont et al. (2003 [DIRS 168382], Vol. 5, pp. 189 to 191). The value for $\Delta G_f°$ selected by Grenthe et al. (1992 [DIRS 101671]) and Guillaumont et al. (2003 [DIRS 168382]) for UO_3:0.9H_2O is -1374.56 (±2.46) kJ/mol. Applying this to the reaction:

$$UO_2O_{0.1}(OH)_{1.8} + 2\,H^+ = UO_2^{2+}\ 1.9\,H_2O \qquad \text{(Eq. 6-52)}$$

yields log K = 5.08, which is the value reported by O'Hare et al. (1988 [DIRS 113277]) for $UO_3·0.9H_2O$.

Guillaumont et al. (2003 [DIRS 168382]) does not select a value of $\Delta G_f°$ for UO_3:H_2O; however, Guillaumont et al. (2003 [DIRS 168382], p. 191) recalculated log K = 5.8 (±0.10) for the reaction:

$$UO_2(OH)_2 + 2\,H^+ = UO_2^{2+}\ 2\,H_2O \qquad \text{(Eq. 6-53)}$$

From this they derive a value of -1393.72 (±1.84) kJ/mol for $\Delta G_f°$ (UO_3:H_2O). Alternatively, by using a slightly different calculation, Guillaumont et al. (2003 [DIRS 168382]) derive -1396.0 (±4.2) for $\Delta G_f°$ (UO_3:H_2O), from which we calculate log K = 5.4 for reaction (6-52). Although Guillaumont et al. (2003 [DIRS 168382]) do not select either value of $\Delta G_f°$ for UO_3:H_2O, we opt to include the slightly less negative value for $\Delta G_f°$ (UO_3:H_2O) recalculated by Guillaumont et al. (2003 [DIRS 168382]) and used by them to determine log K = 5.8 for reaction (6-52).

We added a new data block in data0.ymp.R5 (Output DTN: SN0612T0502404.014) for $UO_3{:}H_2O$ to reflect both formulas discussed here, so that there are two data blocks for "dehydrated schoepite": $UO_3{:}H_2O$ and $UO_3{:}0.9H_2O$.

This Gibbs energy value was used with values of other thermodynamic parameters (molar volume, standard molar entropy, and Maier-Kelley heat capacity coefficients a, b, and c, to obtain the apparent Gibbs energy of formation on the EQ3/6 temperature grid (0-25-60-100-150-200-250-300°C), and thence to obtain log K values on the same temperature grid (see results for "data0.ymp.R5" in Tables 6-82 and 6-83). The molar volumes used to extrapolate log K values to other temperatures were calculated in *Usilicates_HC_S_KBH.xls* by using the density of metaschoepite (4.8 g/cm^3; Roberts et al. 1990 [DIRS 107105], p. 766) as an approximation. This approximation generated $V°$ values of 62.97 cm^3/mol and 36.34 cm^3/mol for $UO_3{:}0.9H_2O$ and $UO_3{:}1.0H_2O$, respectively. The standard molar entropy (S^o), and heat capacity values were estimated from the predictive correlation algorithms discussed above (at the beginning of Section 6.7.10). For calculational details, see spreadsheets *Minerals_cal_KBH_Usilicates.xls* and *Usilicates_HC_S_KBH.xls* in folder *\Uranyl_minerals_KBH* of Output DTN: SN0702T0502404.015. The entropy values obtained for $UO_3{:}0.9H_2O$ and $UO_3{:}1.0H_2O$ are 37.13 and 37.76 cal/mol-K, respectively. The heat capacity coefficients obtained are: a = 26.99, $b \times 10^3 = 13.39$, $c \times 10^{-5} = -2.61$ for $UO_3{:}0.9H_2O$, and a = 27.71, $b \times 10^3 = 14.21$, $c \times 10^{-5} = -2.61$ for $UO_3{:}1.0H_2O$ (all in units consistent with the heat capacity in cal/mol-K).

Post data0.ymp.R5 Corrections. The log K values calculated by us for both compounds differ from those calculated by Guillaumont et al. (2003 [DIRS 168382]), due to a small error in the value for the gas constant (R) used in workbook *Usilicates_HC_S_KBH.xls* in folder *\Uranyl_minerals_KBH* of Output DTN: SN0702T0502404.015 (8.331403 instead of the 8.314510 used by Guillaumont et al. 2003 [DIRS 168382]). Additionally, the density of metaschoepite (used in the calculation of unit-cell volume) is considerably less than that of dehydrated schoepite, being about two-thirds the value calculated by using the unit-cell constants for alpha-$UO_2(OH)_2$. The corrected calculations for unit-cell volume (45.19 cm^3/mol) for both dehydrated schoepites, and corresponding calculations to obtain log K between 0 and 300°C are given in workbooks *Usilicates_HC_S_KBH_rjf.xls* and *Minerals_cal_KBH_Usilicates_rjf.xls* located in folder *\Uranyl_minerals_KBH_RJF* of Output DTN: SN0702T0502404.015. Values for log K from both data blocks for "dehydrated schoepite" that are currently in data0.ymp.R5 (Output DTN: SN0612T0502404.014) are compared in the tables below with log K values recalculated by correcting the previously noted minor discrepancies in *R* and the error in the molar volume. It is apparent that the changes are relatively small and well within the uncertainties reported by Guillaumont et al. (2003 [DIRS 168382]). We have made no change to the current entries in data0.ymp.R5 (Output DTN: SN0612T0502404.014) but suggest these changes be made in the future.

Table 6-82. The data0.ymp.R5 and Corrected log K Values for UO_3:0.9H_2O

Temp. °C	0.01	25	60	100	150	200	250	300
data0.ymp.R5[a]	6.1471	5.0904	3.9109	2.8634	1.8498	1.0433	0.3578	-0.2709
Corrected[b]	6.0155	5.0800	4.0397	3.1193	2.2299	1.5201	0.9104	0.3407
Difference	0.1316	0.0104	-0.1288	-0.2559	-0.3801	-0.4768	-0.5526	-0.6116

[a] Output DTN: SN0702T0502404.015, folder: *\Uranyl_minerals_KBH*, workbook: *Minerals_cal_KBH_Usilicates.xls*.
[b] Output DTN: SN0702T0502404.015, folder: *\Uranyl_minerals_KBH_RJF*, worksheet: *Minerals_cal_KBH_Usilicates_rjf.xls*.

Table 6-83. The data0.ymp.R5 and Corrected log K Values for UO_3:H_2O

Temp. °C	0.01	25	60	100	150	200	250	300
data0.ymp.R5[a]	6.9145	5.8119	4.5816	3.4899	2.4351	1.5983	0.8898	0.2433
Corrected[b]	6.7786	5.8000	4.7121	3.7505	2.8228	2.0849	1.4539	0.8678
Difference	0.1359	0.0119	-0.1305	-0.2606	-0.3877	-0.4866	-0.5641	-0.6245

[a] Output DTN: SN0702T0502404.015, folder: *\Uranyl_minerals_KBH*, workbook *Minerals_cal_KBH_Usilicates.xls*.
[b] Output DTN: SN0702T0502404.015, folder: *\Uranyl_minerals_KBH_RJF*, workbook: *Minerals_cal_KBH_Usilicates_rjf.xls*.

Becquerelite: $Ca[(UO_2)_3O_2(OH)_3]_2$:8H_2O

Four solubility studies were reported in the literature for becquerelite (Sandino and Grambow 1994 [DIRS 113360]; Rai et al. 2002 [DIRS 168155]; Vochten and van Haverbeke 1990 [DIRS 113433]; Casas et al. 1997 [DIRS 102432]) and are discussed by Guillaumont et al. (2003 [DIRS 168382], Vol. 5, p. 180).

Sandino and Grambow (1994 [DIRS 113360]) measured becquerelite solubility at T=298.15 K in 1 molal $CaCl_2$ solution over a range of pH for the reaction:

$$\text{Becquerelite} + 14\ H^{+} = Ca^{2+} + 6\ UO_2^{2+} + 18\ H_2O \qquad (6\text{-}54)$$

From their measurements, they obtained log K= 43.8 (average of the 42.88 and 44.69 given in Sandino and Grambow 1994 [DIRS 113360]).

Guillaumont et al. (2003 [DIRS 168382]) recalculated this value by using the Specific Ion Interaction Theory (SIT) for extrapolating activity coefficients to infinite dilution. However, they were unable to obtain the same value when using the data presented in Sandino and Grambow (1994 [DIRS 113360]). Instead Guillaumont et al. (2003 [DIRS 168382]) report that log K = 39.5 (±1.0).

A more recent study by Rai et al. (2002 [DIRS 168155]) describes a well-characterized synthetic becquerelite sample in 2×10^{-2}, 0.1 and 0.5 M $CaCl_2$, at T = 296 (±2) K from pH = 4.4 to 9.

These authors used reference data from Grenthe et al. (1992 [DIRS 101671]) and applied a Pitzer model to their solubility data, from which they derived log K = 41.4 (±0.2).

Guillaumont et al. (2003 [DIRS 168382]) chose to select an average of the Sandino and Grambow (1994 [DIRS 113360]) data (as recalculated by SIT) and the Rai et al. 2002 [DIRS 168155]) data. This result is given by log K = 40.5 (±1.6).

Two additional studies of becquerelite solubility were reviewed and dismissed by Guillaumont et al. (2003 [DIRS 168382]), citing various experimental problems (Vochten and van Haverbeke, 1990 [DIRS 113433], Casas et al. 1997 [DIRS 102432]).

We added a new data block to data0.ymp.R5 (Output DTN: SN0612T0502404.014) that is consistent with the log K selected by Guillaumont et al. (2003 [DIRS 168382]). This Gibbs energy value was used with values of other thermodynamic parameters (molar volume, standard molar entropy, and Maier-Kelley heat capacity coefficients a, b, and c, to obtain the apparent Gibbs energy of formation on the EQ3/6 temperature grid (0-25-60-100-150-200-250-300°C), and thence to obtain log K values on the same temperature grid (see results for "data0.ymp.R5" in Table 6-84). The molar volume used to extrapolate log K values to other temperatures was calculated in *Usilicates_HC_S_KBH.xls* by using the density of becquerelite (5.14 g/cm^3; Roberts et al. 1990 [DIRS 107105], p. 78). This calculation generated a unit-cell molar volume of $V°$ = 383.35 cm^3/mol. The standard molar entropy (S^o), and heat capacity values were estimated from the predictive correlation algorithms discussed above (at the beginning of Section 6.7.10). For calculational details, see workbooks *Minerals_cal_KBH_Usilicates.xls* and *Usilicates_HC_S_KBH.xls* in folder *\Uranyl_minerals_KBH* of Output DTN: SN0702T0502404.015. The entropy value obtained for becquerelite is 313.31 cal/mol-K. The heat capacity coefficients obtained are: a = 247.77, b × 10^3 = 61.63, c × 10^{-5} = -17.21 (all in units consistent with the heat capacity in cal/mol-K).

<u>Post-data0.ymp.R5 Corrections</u>. Because of the previously noted small discrepancy in the value of the gas constant used in spreadsheet *Usilicates_HC_S_KBH.xls* in folder *\Uranyl_minerals_KBH* of Output DTN: SN0702T0502404.015, (8.331403 instead of 8.314510 used by Guillaumont et al. 2003 [DIRS 168382]) we recalculated the value for log K. Furthermore, a slight adjustment of the molar volume was made (to be consistent with the most recent structural data). The revised unit-cell molar volume of $V°$ = 385.96 cm^3/mol, and the corresponding revised calculations for S^o (314.46 cal/mol-K) and log K (40.50) are documented in workbooks *Minerals_cal_KBH_Usilicates_rjf.xls* and *Usilicates_HC_S_KBH_rjf.xls* in folder *\Uranyl_minerals_KBH_RJF* of Output DTN: SN0702T0502404.015. The revised values for log K are compared with those in data0.ymp.R5 (Output DTN: SN0612T0502404.014) in the following table, which shows that these differences are negligible and well within the uncertainty of the available data and our calculations. Therefore, we have made no change to the current entries in data0.ymp.R5 (Output DTN: SN0612T0502404.014).

Table 6-84. The data0.ymp.R5 and Corrected log K Values for Becquerelite

Temp. °C	0.01	25	60	100	150	200	250	300
data0.ymp.R5[a]	47.7429	40.5829	32.6393	25.6528	18.9750	13.7360	9.3308	5.3084
Corrected[b]	47.6761	40.5006	32.5393	25.5366	18.843	13.5917	9.1769	5.1471
Difference	0.0668	0.0823	0.1000	0.1162	0.1320	0.1443	0.1539	0.1613

[a] Output DTN: SN0702T0502404.015, folder: *\Uranyl_minerals_KBH*, workbook: *Minerals_cal_KBH_Usilicates.xls*.
[b] Output DTN: SN0702T0502404.015, folder: *\Uranyl_minerals_KBH_RJF*, workbook: *Minerals_cal_KBH_Usilicates_rjf.xls*.

Compreignacite: $K_2[(UO_2)_3O_2(OH)_3]:7H_2O$

We are aware of only one study of compreignacite solubility, that of Sandino and Grambow (1994 [DIRS 113360]). These authors conducted their study by using 1 molal KCl over a range of pH 3.12-5.83 at T = 298.15 K. For the reaction:

$$\text{Compreignacite} + 14H^+ = 2K^+ + 6UO_2^{2+} + 18H_2O \qquad \text{(Eq. 6-55)}$$

They reported log K = 38.7 (average of the 38.19 and 40.53 in Sandino and Grambow 1994 [DIRS 113360]).

Guillaumont et al. (2003 [DIRS 168382]) recalculated this value by using the data reported in Sandino and Grambow (1994 [DIRS 113360]) and SIT, deriving a slightly different solubility constant, log K = 37.1 (±0.5). This corresponds to a Gibbs energy of formation (calculated by Guillaumont et al. 2003 [DIRS 168382]) of ΔG_f° (compreignacite) = -10337.1 kJ/mol. Guillaumont et al. (2003 [DIRS 168382], Table 3-1, p. 63) adopt this value for the Gibbs energy of compreignacite.

This Gibbs energy value was used with values of other thermodynamic parameters (molar volume, standard molar entropy, and Maier-Kelley heat capacity coefficients a, b, and c, to obtain the apparent Gibbs energy of formation on the EQ3/6 temperature grid (0-25-60-100-150-200-250-300°C), and thence to obtain log K values on the same temperature grid (see results for "data0.ymp.R5" in Table 6-85). The molar volume used to extrapolate log K values to other temperatures was calculated in *Usilicates_HC_S_KBH.xls* by using the density of compreignacite (5.03 g/cm^3; Roberts et al. 1990 [DIRS 107105], p. 188). This calculation generated a unit-cell molar volume of V° = 399.31 cm^3/mol. The standard molar entropy (S^o), and heat capacity values were estimated from the predictive correlation algorithms discussed above (at the beginning of Section 6.7.10). For calculational details, see workbooks *Minerals_cal_KBH_Usilicates.xls* and *Usilicates_HC_S_KBH.xls* in folder *\Uranyl_minerals_KBH* of Output DTN: SN0702T0502404.015. The entropy value obtained for compreignacite is 322.42 cal/mol-K. The heat capacity coefficients obtained are: a = 254.61, $b \times 10^3 = 69.20$, $c \times 10^{-5} = -302.23$ (all in units consistent with the heat capacity in cal/mol-K). The resulting log K value at 25°C is calculated to be 37.18 (see *Minerals_cal_KBH_Usilicates.xls* in folder *\Uranyl_minerals_KBH* of Output DTN: SN0702T0502404.015).

Post-data0.ymp.R5 Corrections. The formula for compreignacite used by both Sandino and Grambow (1994 [DIRS 113360]) and Guillaumont et al. (2003 [DIRS 168382]) is incorrect and should contain seven H_2O groups in the interlayer structure, not eight (Burns 1998 [DIRS 127210]). This does not change the value of log K at 25°C since H_2O appears on both sides of the reaction in Equation 6-56. However, this change does affect values of log K extrapolated to temperatures other than 25°C. Furthermore, it changes the calculation of Gibbs energy of reaction (or ΔG_r) used to calculate $\Delta G_f°$ for compreignacite, since the dissolution reaction produces one fewer H_2O group (i.e., 17 instead of 18), see workbook *Usilicates_HC_S_KBH_RJF.xls* in Output DTN: SN0702T0502404.015. Thus the value for $\Delta G_f°$ for compreignacite (10337.1 kJ/mol) reported in Guillaumont et al. (2003 [DIRS 168382], p. 182) is incorrect. Based on log K = 37.1 for the reaction:

$$\text{Compreignacite} + 14\ H^+ = 2\ K^+ + 6\ UO_2^{2+} + 17\ H_2O \qquad \text{(Eq. 6-56)}$$

one obtains that $\Delta G_f°$ (compreignacite) = -10100.9 kJ/mol. (We note that this is essentially identical within expected uncertainty to the $\Delta G_f°$ for compreignacite calculated by using the method of Chen et al. 1999 [DIRS 123270]: 10005.3 kJ/mol).

We added a data block to data0.ymp.R5 (Output DTN: SN0612T0502404.014) that is consistent with the values of log K and $\Delta G_f°$ selected by Guillaumont et al. (2003 [DIRS 168382]). Due to this revision of the formula of compreignacite, the previously noted small discrepancy in the gas constant value (used in workbook *Usilicates_HC_S_KBH.xls* in folder *\Uranyl_minerals_KBH* in Output DTN: SN0702T0502404.015), and a slight adjustment of the molar volume (to be consistent with the most recent structural data, $V°$ = 391.30 cm^3/mol, Burns 1998 [DIRS 127210]), we compare the values of log K from data0.ymp.R5 (Output DTN: SN0612T0502404.014) with our corrected values. The corrected molar entropy is $S°$ = 307.82 cal/mol-K, and the recalculated heat capacity coefficient obtained is a = 254.61 cal/mol-K (b and c parameters are unchanged). The resulting corrected log K value at 25°C is 37.10. The corresponding calculations are documented in workbooks *Minerals_cal_KBH_Usilicates.xls* and *Usilicates_HC_S_KBH.xls* in folder *\Uranyl_minerals_KBH* of Output DTN: SN0702T0502404.015.

As can be seen in Table 6-85, these differences are very small and well within the uncertainty of our calculations. Therefore, we have made no change to the current entries in data.ymp.R5; however, we suggest these corrections be made in the future.

Table 6-85. The data0.ymp.R5 and Corrected log K Values for Compreignacite

Temp. °C	0.01	25	60	100	150	200	250	300
data0.ymp.R5[a]	42.9716	37.1759	30.8030	25.2616	20.0279	15.9592	12.5407	9.3835
Corrected[b]	42.9253	37.1001	30.6781	25.0744	19.7590	15.6072	12.1061	8.8676
Difference	0.0463	0.0758	0.1249	0.1872	0.2689	0.352	0.4346	0.5159

[a] Output DTN: SN0702T0502404.015, folder: *\Uranyl_minerals_KBH*, workbook: *Minerals_cal_KBH_Usilicates.xls*.
[b] Output DTN: SN0702T0502404.015, folder: *\Uranyl_minerals_KBH_RJF*, workbook: *Minerals_cal_KBH_Usilicates_rjf.xls*.

Weeksite-Na: $Na_2(UO_2)_2(Si_5O_{13}):3H_2O$

We are aware of only one study of the solubility of Na-weeksite (Nguyen et al. 1992 [DIRS 100809]) , which is discussed by Guillaumont et al. (2003 [DIRS 168382], pp. 256 and 440 to 443). This study was conducted in water at pH = 4.50 (±0.05), and an inert atmosphere. The solubility constant reported for the reaction:

$$\text{Weeksite-Na} + 3\ H^+ + 5\ H_2O = 2\ Na^+ + 2\ UO_2^{2+} + 6\ Si(OH)_4(aq) \qquad \text{(Eq. 6-57)}$$

is log K = 1.50 (±0.08). Nguyen et al. (1992 [DIRS 100809]) report the Gibbs energy of formation for Na-Weeksite as $\Delta G_f°$ = -9088.5 kJ/mol.

Guillaumont et al. (2003 [DIRS 168382]) note that the composition of the weeksite sample deviated very slightly from its expected stoichiometry, that there was considerable deviation from congruent dissolution, and that amorphous silica may have precipitated during the experiments (amorphous silica may have sorbed U at the experimental pH). Although Guillaumont et al. (2003 [DIRS 168382]) do not select this value of $\Delta G_f°$ for the reasons stated, they nevertheless consider it a best estimate.

Chen et al. (1999 [DIRS 123270]) also evaluated the experiments of Nguyen et al. (1992 [DIRS 100809]) and derived a very different value of $\Delta G_f°$ for Na-weeksite from the data. Chen et al. (1999 [DIRS 123270], p. 664), report that $\Delta G_f°$ (weeksite-Na) = -7993.9 (±9.8) kJ/mol. For the above reaction, this gives log K = 5.7.

Guillaumont et al. (2003 [DIRS 168382])called the treatment by Chen et al. (1999 [DIRS 123270]) tentative, and, although it is based in part on a re-evaluation of the structural formula for weeksite, it is unclear how Chen et al. (1999 [DIRS 123270]) performed their recalculation. Guillaumont et al. (2003 [DIRS 168382]) reproduced the $\Delta G_f°$ value from Chen et al. (1999 [DIRS 123270], p. 443) but did not select it.

The Gibbs energy for Na-weeksite calculated by Chen et al. (1999 [DIRS 123270], Table 5, p. 657) using their predictive method to estimate Gibbs energies of formation is -8001.8 kJ/mol. This derivation of $\Delta G_f°$ is more readily traced; it is also close to the -7993.9 ± 9.8 kJ/mol that Chen et al. (1999 [DIRS 123270]) obtained from their re-analysis of the experiments of Nguyen et al. (1992 [DIRS 100809]) (within the ±9.8 kJ/mol uncertainty). Therefore, this value of $\Delta G_f°$ (-8001.8 kJ/mol) is recommended here. This then gives log K = 4.33.

The data0.ymp.R5 database (Output DTN: SN0612T0502404.014) uses the log K value based on the recalculated value of $\Delta G_f°$ by Chen et al. (1999 [DIRS 123270]). This Gibbs energy value was used with values of other thermodynamic parameters (molar volume, standard molar entropy, and Maier-Kelley heat capacity coefficients a, b, and c) to obtain the apparent Gibbs energy of formation on the EQ3/6 temperature grid (0-25-60-100-150-200-250-300°C), and thence to obtain log K values on the same temperature grid (see results for "data0.ymp.R5" in Table 6-86). The molar volume used to extrapolate log K values to other temperatures was calculated in *Usilicates_yc_tls_ch_CFJC.xls* (Output DTN: SN0702T0502404.015) by using the density of K-weeksite (4.02 g/cm^3; Roberts et al. 1990 [DIRS 107105], p. 936), since no known density of Na-weeksite is available. This calculation generated a unit-cell molar volume of $V°$ = 246.04 cm^3/mol. The standard molar entropy (S^o), and heat capacity values were estimated from the predictive correlation algorithms discussed above (at the beginning of Section 6.7.10). For calculational details, see workbooks *Minerals_cal_YC_Usilicates_CFJC.xls* and *Usilicates_yc_tls_ch_CFJC.xls* in folder *\Uranyl_minerals_KBH* of Output DTN: SN0702T0502404.015. The entropy value obtained for Na-weeksite is 141.49 cal/mol-K. The heat capacity coefficients obtained are: a = 136.87, b × 10^3 = 82.55, c × 10^{-5} = -21.61 (all in units consistent with the heat capacity in cal/mol-K).

Post-data0.ymp.R5 Corrections. Three points of concern were found subsequent to inserting the current data block for weeksite-Na into data0.ymp.R5 (Output DTN: SN0612T0502404.014). There is the previously noted small discrepancy in the value of the gas constant; H_2O groups in the structural interlayer were incorrectly designated as "structural water" in the *Minerals_cal_YC_Usilicates_CFJC.xls* and *Usilicates_yc_tls_ch_CFJC.xls* in folder *\Uranyl_minerals_KBH* of Output DTN: SN0702T0502404.015 (using the terminology of Chen et al. 1996 [DIRS 123270]; an error in the original paper). The data were recalculated by correcting for the small discrepancy in R, re-assigning the three H_2O groups in weeksite-Na as "waters of hydration", and correcting the molar volume to be consistent with the most recent structural data (Jackson and Burns 2001 [DIRS 178824]) and documented in *Minerals_cal_YC_Usilicates_CFJC_rjf.xls* and *Usilicates_yc_tls_ch_CFJC_rjf.xls* in folder *\Uranyl_minerals_KBH_RJF* of Output DTN: SN0702T0502404.015. The revised thermodynamic data are: $V°$ = 272.00 cm^3/mol and $S°$ = 169.35 cal/mol-K. The corrected heat capacity coefficients obtained are: a = 149.74 and b × 10^3 = 57.83, ('c' parameter unchanged; all in units consistent with the heat capacity in cal/mol-K). The resulting corrected log K at 25°C = 4.33.

As can be seen in Table 6-86, differences between the current data block of log K values for weeksite-Na and the corrected log K values are considerable but probably within the uncertainty of our calculations. Therefore, we have made no change to the current entries in data0.ymp.R5 (Output DTN: SN0612T0502404.014); however, we suggest that corrected values be used in the future updates.

Table 6-86. The data0.ymp.R5 and Corrected log K Values for Weeksite-Na

Temp. °C	0.01	25	60	100	150	200	250	300
data0.ymp.R5[a]	6.1530	5.7031	4.9390	4.2980	3.8473	3.6236	3.4353	3.0362
Corrected[b]	5.2058	4.3295	3.0633	1.9517	1.0279	0.4265	-0.0665	-0.7119
Difference	0.9472	1.3736	1.8757	2.3463	2.8194	3.1971	3.5018	3.7481

[a] Output DTN: SN0702T0502404.015, folder: *\Uranyl_minerals_KBH*, workbook: *Minerals_cal_YC_Usilicates_CFJC.xls*.

[b] Output DTN: SN0702T0502404.015, folder: *\Uranyl_minerals_KBH_RJF*, workbook: *Minerals_cal_YC_Usilicates_CFJC_rjf.xls*.

Boltwoodite-Na: $Na[(UO_2)(SiO_3OH)]:1.5H_2O$

Only one study of the solubility of Boltwoodite-Na (Nguyen et al. (1992 [DIRS 100809])) is discussed in Guillaumont et al. (2003 [DIRS 168382], p. 256). Nguyen et al. (1992 [DIRS 100809]) conducted a study at pH = 4.50 (±0.05) in water and under an inert atmosphere. They report a minimum value for the solubility constant for the reaction:

$$\text{Boltwoodite-Na} + 3\ H^+ = Na^+ + UO_2^{2+} + Si(OH)_4(aq) + 2\ H_2O \qquad \text{(Eq. 6-58)}$$

They reported that log K > 5.82 (±0.16). Guillaumont et al. (2003 [DIRS 168382]) did not select this value, even though it is the only data available, citing sample impurity and the likelihood that the solution was supersaturated with respect to Si. The Gibbs energy value given in Guillaumont et al. (2003 [DIRS 168382]) is -2844.8 kJ/mol (-679923.5 cal/mol). Although this may be less than a perfect value, it should nevertheless provide a bounding limit on the solubility of Na-Boltwoodite. Its use would be conservative in applications modeling. This is sufficient to justify its use until better data become available.

This Gibbs energy value was used with values of other thermodynamic parameters (molar volume, standard molar entropy, and Maier-Kelley heat capacity coefficients a, b, and c) to obtain the apparent Gibbs energy of formation on the EQ3/6 temperature grid (0-25-60-100-150-200-250-300°C), and thence to obtain log K values on the same temperature grid (see results for “data0.ymp.R5” in Table 6-87). The molar volume of 97.04 cm^3/mol (through data0.ymp.R0; DTN: MO0009THRMODYN.001 [DIRS 152576]) originally from Strunz and Tennyson (1982 [DIRS 151259]) was used in the calculations. The standard molar entropy (S^o), and heat capacities were estimated from the predictive correlation algorithms discussed above (at the beginning of Section 6.7.10). For calculational details, see spreadsheets *Minerals_cal_YC_Usilicates.xls* and *Usilicates_yc_tls_ch_CFJC.xls* in folder *\Uranyl_minerals_KBH* of Output DTN: SN0702T0502404.015. The entropy value obtained is 71.09 cal/mol-K, and the heat capacity coefficients obtained are: $a = 61.60$, $b \times 10^3 = 20.74$, $c \times 10^{-5} = -6.75$ (all in units consistent with the heat capacity in cal/mol-K). The resulting log K at 25°C is 6.08.

<u>Post-data0.ymp.R5 Corrections</u>. As with Na-weeksite, H_2O groups in the structural interlayer were incorrectly designated as “structural water” in the calculations for Na-boltwoodite in the *Usilicates_yc_tls_ch_CFJC.xls* workbook in folder *\Uranyl_minerals_KBH* of Output

DTN: SN0702T0502404.015 (using the terminology of Chen et al. 1996 [DIRS 123270]); an error in the original paper). This error has been corrected in workbook *Usilicates_yc_tls_ch_CFJC_rjf.xls* in folder *\Uranyl_minerals_KBH_RJF* of Output DTN: SN0702T0502404.015.

More recently, Ilton et al. (2006 [DIRS 178810]) conducted solubility experiments with synthetic boltwoodite-Na and showed that boltwoodite-Na dissolution was nearly congruent and that its solubility and dissolution kinetics increased with increasing bicarbonate concentration and pH. These experiments were open to air, and a consistent set of solubility constants was derived from circum-neutral pH (no bicarbonate added) to alkaline pH (50 mM bicarbonate added). Their average values for log K of 5.86 (±0.24) and 5.85 (±0.26), calculated by using the Pitzer ion-interaction model or Davies equation, respectively, are similar to the value reported by Nguyen et al. (1992 [DIRS 100809]). We recommend the average of the two values reported by Ilton et al. (2006 [DIRS 178810]) yielding a log K = 5.855. The Gibbs energy of formation for Boltwoodite-Na can be calculated from the reaction stoichiometry and the data given in spreadsheets *Minerals_cal_YC_Usilicates.xls* and *Usilicates_yc_tls_ch_CFJC.xls* in folder *\Uranyl_minerals_KBH* of Output DTN: SN0702T0502404.015, giving $\Delta G_f°$ (Boltwoodite-Na) = -2846.08 kJ/mol. This is the value we recommend and is within expected uncertainty of the value reported by Chen et al. (1999 [DIRS 123270], Table 2): -2844.8 (±3.9) and is used in the calculations documented in spreadsheets *Minerals_cal_YC_Usilicates.xls* and *Usilicates_yc_tls_ch_CFJC.xls* in folder *\Uranyl_minerals_KBH* of Output DTN: SN0702T0502404.015. The corrected thermodynamic values recommended for Na-boltwoodite are: $S°$ = 77.88 cal/mol-K, $V°$ = 114.76 cm^3/mol, and the corresponding log K at 25°C is 5.86.

As can be seen in Table 6-87, differences between the current data block for all values of log K for Na-boltwoodite in data0.ymp.R5 (Output DTN: SN0612T0502404.014) and the corrected values are well within the uncertainty of the calculations. Therefore, we have made no change to the current entries in data0.ymp.R5 (Output DTN: SN0612T0502404.014).

Table 6-87. The data0.ymp.R5 and Corrected log K Values for Boltwoodite-Na

Temp. °C	0.01	25	60	100	150	200	250	300
data0.ymp.R5[a]	6.8394	6.0800	5.2024	4.4617	3.8165	3.3612	2.9931	2.6134
Corrected[b]	6.7297	5.8550	4.8451	3.9837	3.2204	2.6734	2.2334	1.7980
Difference	0.1097	0.2250	0.3573	0.4780	0.5961	0.6878	0.7597	0.8154

[a] Output DTN: SN0702T0502404.015, folder: *\Uranyl_minerals_KBH*, workbook: *Minerals_cal_YC_Usilicates_CFJC.xls*.
[b] Output DTN: SN0702T0502404.015, folder: *\Uranyl_minerals_KBH_RJF*, workbook: *Minerals_cal_YC_Usilicates_CFJC_rjf.xls*.

Studtite: $UO_2O_2{:}4H_2O$

Studtite ($UO_2O_2{:}4H_2O$) and metastudtite ($UO_2O_2{:}2H_2O$), are the only known peroxide minerals. Studtite has been reported as an alteration product of spent nuclear fuel and other radioactive "wastes" (Corbel et al. 2006 [DIRS 179135], Hanson et al. 2005 [DIRS 178026], McNamara et al. 2005 [DIRS 174068], Sattonnay et al. 2001 [DIRS 173091], Abrefah et al. 1998 [DIRS 178785], Burakov et al. 1997 [DIRS 178287]). One study reported that studtite was found on the surface of spent nuclear fuel that was reacted with deionized water for 1.5 years, and its growth was due to the incorporation of peroxide that formed during the radiolysis of water (McNamara et al. 2005 [DIRS 174068]). Another study reported that studtite was a prime corrosion product found on the Chernobyl "lavas" that formed in the aftermath of the nuclear plant accident (Burakov et al., 1997 [DIRS 178287]). Additionally, studtite has been observed in the tank wastes at Hanford (Abrefah et al. 1998 [DIRS 178785]). Recently the thermodynamic properties of studtite were investigated (Kubatko et al. 2003 [DIRS 173070]). The enthalpy of formation was determined from calorimetric experiments and is reported as: $\Delta H_f°$ (studtite, 298.15 K) = -2344.7 ± 4.0 kJ/mol

These authors also reported the results of a "solubility" experiment where $H_2O_2(aq)$ was titrated into a dilute uranyl solution (log $[UO_2^{2+}]$ = -5 to -8) with pH ≈ 3.0 (Kubatko et al. (2003 [DIRS 173070], Table 2). For the reaction:

$$UO_2O_2{:}4(H_2O) + 2\ H^+ = UO_2^{2+} + H_2O_2(aq) + 4\ H_2O \qquad \text{(Eq. 6-59)}$$

we have that $K_{sp} = [UO_2^{2+}][H_2O_2(aq)] / [H^+]^2 = 1.34\ (\pm 0.02) \times 10^{-3}$. The above value for the solubility product (K_{sp}) is an average of the values tabulated by Kubatko et al. (2003 [DIRS 173070]) and thus log K = -2.8729 ± 0.007. However, due to uncertainties about whether the solution compositions reported by Kubatko et al. (2003 [DIRS 173070]) represent equilibrium, this value remains in doubt Although, this value of log K is currently adopted in the data0.ymp.R5 (Output DTN: SN0612T0502404.014) data base for the dissolution reaction above at 298.15 K, we believe that the potential errors are considerably larger than those estimated by Kubatko et al. (2003 [DIRS 173070]) in their solubility experiments. No attempt to extrapolate log K to temperatures other than 298.15 K have been made.

Modeled Thermodynamic Data Incorporated into data0.ymp.R5

Several uranyl phases that have been reported from corrosion tests of CSNF and unirradiated UO_2 have no measured thermodynamic parameters (Wilson 1988 [DIRS 113473], Wronkiewicz et al. 1992 [DIRS 100493], Finch et al. 1999 [DIRS 106347]), including (though not limited to) haiweeite, sklodowskite, boltwoodite and weeksite. In the absence of thermodynamic data, several methods have been employed to estimate the thermodynamic properties of silicate minerals (Karpov and Kashik 1968 [DIRS 178827], Chen 1978 [DIRS 123270], Nriagu 1975 [DIRS 178321], Tardy and Garrels 1974 [DIRS 159209], Tardy and Garrels 1976 [DIRS 178272], Tardy and Garrels 1977 [DIRS 178273], Mattigod and Sposito 1978 [DIRS 159197], Hemingway et al. 1982 [DIRS 157905], Viellard and Tardy1998 [DIRS 178821]). Although the details of these methods vary, they generally employ a common approach based on observations that the fundamental formation thermodynamic quantities of Gibbs energy and enthalpy of formation ($\Delta G_f°$ and $\Delta H_f°$, respectively) can be approximated by summing the contributions of constituent component oxides. This type of approach has been applied to several uranyl oxy-hydroxides, silicates and carbonates (1997 [DIRS 106347]) and was updated by Chen et al. (1999 [DIRS 123270]) to include numerous additional uranyl compounds. Chen et al. (1999 [DIRS 123270]) used multiple linear regressions to determine the contributions of constituent oxides to the $\Delta G_f°$ and $\Delta H_f°$ for a large number of uranyl phases. This method averages across multiple phases to extract the thermodynamic quantities associated with individual component oxides. Although Chen et al. (1999 [DIRS 123270]) attempted to distinguish contributions to the Gibbs free energy or enthalpy (g_i or h_i values, respectively) from the constituent oxide, UO_3, for three distinct types of U coordination polyhedra, they noted that "no significant differences exist among the calculated g_i or h_i values for different uranyl polyhedra types ($Ur\Phi_4$, $Ur\Phi_5$ and $Ur\Phi_6$)" (Chen et al. 1999 [DIRS 123270], p. 655). For the purposes of the discussion that follows, this is a minor detail, because all the uranyl compounds described below possess only one type of U polyhedron, that which contains a five-coordinated uranyl ion: $Ur\Phi_5$. Therefore, we use "UO_3" to designate the U-oxide fictive component. In fact, it is not possible to assign uncertainties to values of ΔG (or the corresponding log Ks) estimated by using the method of Chen et al. (1999 [DIRS 123270]) because that paper does not provide estimates of uncertainties for g_i and h_i.

Boltwoodite: $K[(UO_2)(SiO_3OH)]{:}1.5H_2O$

Based on the structure of boltwoodite reported by Burns (1998 [DIRS 127210]), the boltwoodite structure may be broken down into five fictive structural components according to the reaction:

$$0.5\ K_2O_{(I)} + UO_{3(VI)} + SiO_{2(IV)} + 0.5\ H_2O_{(S)} + 1.5\ H_2O_{(H)} = K[(UO_2)(SiO_3OH)]{:}1.5H_2O \qquad (6\text{-}60)$$

Consistent with (Chen et al. 1999 [DIRS 123270], Table 1), in the above reaction, H_2O in the structural interlayer is considered water of hydration (designated as $H_2O_{(H)}$), whereas the hydroxyl in the structural unit is considered structural water (designated $H_2O_{(S)}$; i.e., one-half $H_2O_{(S)}$ for each (OH) in the formula). The ΔG_f^o may be estimated by summing the stoichiometric contributions of each of the components in the reaction above that are reported in Table 3, column 2 of Chen et al. (1999 [DIRS 123270]). This gives ΔG_f^o (boltwoodite) = -2814.355 kJ/mol. By using this value, we obtain for the following reaction:

$$K(UO_2)(SiO_3)(OH){:}1.5H_2O + 3\ H^+ = K^+ + UO_2^{2+} + SiO_2(aq) + 3.5\ H_2O \qquad (Eq.\ 6\text{-}61)$$

that ΔG_r^o(298.15 K) = -85730.15 kJ/mol and log K = 15.02.

This Gibbs energy value was used with values of other thermodynamic parameters (molar volume, standard molar entropy, and Maier-Kelley heat capacity coefficients a, b, and c) to obtain the apparent Gibbs energy of formation on the EQ3/6 temperature grid (0-25-60-100-150-200-250-300°C), and thence to obtain log K values on the same temperature grid (see results for "data0.ymp.R5" in Table 6-88). The molar volume of 119.23 cm^3/mol was calculated using the density of K-boltwoodite (3.6 g/cm^3; Roberts et al. 1990 [DIRS 107105], p. 103). The standard molar entropy (S^o), and heat capacity values were estimated from the predictive correlation algorithms discussed above (at the beginning of Section 6.7.10). For calculational details, see spreadsheets *Minerals_cal_KBH_Usilicates.xls* and *Usilicates_HC_S_KBH.xls* in folder *\Uranyl_minerals_KBH* of Output DTN: SN0702T0502404.015. The entropy value obtained is 78.50 cal/mol-K, and the heat capacity coefficients obtained are: a = 61.73, $b \times 10^3 = 22.62$, $c \times 10^{-5} = -5.75$ (all in units consistent with the heat capacity in cal/mol-K). The resulting log K at 25°C is 15.02.

Post-data0.ymp.R5 Corrections. Due to a the previously noted small discrepancy in the value for the gas constant (*R*), the log K value for K-boltwoodite required correction (see workbook *Minerals_cal_KBH_Usilicates_rjf.xls* in folder *\Uranyl_minerals_KBH_RJF* of Output DTN: SN0702T0502404.015. The values for entropy, unit-cell volume and heat capacity did not changes versus the data presented in data0.ymp.R5 (Output DTN: SN0612T0502404.014).

As can be seen in Table 6-88, differences between the current data block for all values of log K for boltwoodite in data0.ymp.R5 (Output DTN: SN0612T0502404.014) and the corrected values are negligible and well within the uncertainty of the calculations. Therefore, we have made no change to the current entries in data0.ymp.R5 (Output DTN: SN0612T0502404.014).

Table 6-88. The data0.ymp.R5 and Corrected log K Values for Boltwoodite

Temp. °C	0.01	25	60	100	150	200	250	300
data0.ymp.R5[a]	16.5341	15.0194	13.2543	11.6774	10.1797	9.0281	8.0811	7.2164
Corrected[b]	16.5339	15.0192	13.2542	11.6773	10.1796	9.0279	8.0810	7.2164
Difference	0.0002	0.0002	0.0001	0.0001	0.0001	0.0002	0.0001	-

[a] Output DTN: SN0702T0502404.015, folder: *\Uranyl_minerals_KBH*, workbook: *Minerals_cal_KBH_Usilicates.xls*.

[b] Output DTN: SN0702T0502404.015, folder: *\Uranyl_minerals_KBH_RJF*, workbook: *Minerals_cal_KBH_Usilicates_rjf.xls*.

Weeksite: $K_2[(UO_2)_2(Si_5O_{13})]:(3\text{-}x)H_2O$

The composition of weeksite can vary in both interlayer cation components and interlayered H_2O. Jackson and Burns (2001[DIRS 178824]) reported the crystal structure of a natural weeksite crystal: $K_{1.26}Ba_{0.25}Ca_{0.12}[(UO_2)2(Si_5O_{13})]:H_2O$; by contrast Baturin and Sidorenko (1985 [DIRS 178818]) reported the structure for a crystal with substantial Na but no Ba or Ca: $(K_{0.62}Na_{0.38})_2[(UO_2)_2Si_5O_{13}]:3H_2O$. The ideal potassium end-member composition would likely correspond to $K_2[(UO_2)_2(Si_5O_{13})]:(3\text{-}x)H_2O$, with $0 \leq \times < 2$. Based on the method of Chen et al. (1999 [DIRS 123270]), the weeksite structure may be broken down into four oxide components according to the reaction:

$$K_2O_{(I)} + 2\ UO_{3(VI)} + 5\ SiO_{2(IV)} + (3\text{-}x)\ H_2O_{(H)} = K_2[(UO_2)_2(Si_5O_{13})]:(3\text{-}x)H_2O \quad \text{(Eq. 6-62)}$$

Consistent with the discussion by Chen et al. (1999 [DIRS 123270], Table 1), all H_2O in weeksite is considered to be structural water. The ΔG_f^o may be estimated by summing the stoichiometric contributions of each of the components in the reaction above that are reported in column 2 of Table 3 in the study by Chen et al. (1999 [DIRS 123270]). This gives ΔG_f^o (weeksite) = -7943 kJ/mol for the fully hydrated (x=0) formula. Applying these values to the reaction:

$$K_2(UO_2)_2(Si_5O_{13}):(3\text{-}x)H_2O + (6\text{-}2x)H^+ = 2K^+ + 2UO_2^{2+} + 5SiO_2^{(aq)} + (6\text{-}x)H_2O \quad \text{(Eq. 6-63)}$$

gives ΔG_r^o (298.15 K) = -124.445 kJ/mol and log K = 21.80 for x = 0. We recommend using the log K value calculated for the fully hydrated formula (x = 0), as well as for extrapolating log K values for weeksite to temperatures other than 298.15 K.

This Gibbs energy value was used with values of other thermodynamic parameters (molar volume, standard molar entropy, and Maier-Kelley heat capacity coefficients a, b, and c) to obtain the apparent Gibbs energy of formation on the EQ3/6 temperature grid (0-25-60-100-150-200-250-300°C), and thence to obtain log K values on the same temperature grid (see results for "data0.ymp.R5" in Table 6-89). The molar volume of 248.96 cm^3/mol was calculated using the density of K-weeksite (4.1 g/cm^3; Roberts et al. 1990 [DIRS 107105], p. 936). The standard molar entropy (S^o), and heat capacity values were estimated from the predictive correlation algorithms discussed above (at the beginning of Section 6.7.10). For calculational details, see spreadsheets *Minerals_cal_KBH_Usilicates.xls* and *Usilicates_HC_S_KBH.xls* in folder *\Uranyl_minerals_KBH* of Output DTN: SN0702T0502404.015. The entropy value obtained is 142.60 cal/mol-K, and the heat capacity coefficients obtained are: a = 137.13, $b \times 10^3$ = 86.31, $c \times 10^{-5}$ = -19.60 (all in units consistent with the heat capacity in cal/mol-K). The resulting log K at 25°C is 21.80.

Post-data0.ymp.R5 Corrections. Due to the previously noted small discrepancy in the gas constant (*R*), and the fact that H_2O in the structural interlayer was assigned as "structural water" rather than "water of hydration" in that spreadsheet (terminology of Chen et al. 1999 [DIRS 123270]; error in the original paper) the values for log K in the data block for weeksite in data0.ymp.R5 (Output DTN: SN0612T0502404.014) differ from those calculated after correcting for the small discrepancy in *R* and re-assigning the three H_2O groups in weeksite as "waters of hydration." The corrected values are calculated in the workbooks *Usilicates_HC_S_KBH_rjf.xls* and *Minerals_cal_KBH_Usilicates_rjf.xls* in folder *\Uranyl_minerals_KBH_RJF* of Output DTN: SN0702T0502404.015. The corrected entropy is $S°$ = 160.96 cal/mol-K. The corrected heat capacity coefficients are a = 150.00 and $b \times 10^3$ = 61.59 (the "c" term remains unchanged; all in units consistent with the heat capacity in cal/mol-K). The resulting log K at 25°C is 20.14. As can be seen in Table 6-89, differences between the current data block of log K values for K-weeksite in data0.ymp.R5 (Output DTN: SN0612T0502404.014) and the corrected log K values are relatively small and probably within the uncertainty of our calculations. Therefore, we have made no change to the current entries in data0.ymp.R5 (Output DTN: SN0612T0502404.014); however, it is suggested that the corrected values be used in future updates.

Table 6-89. The data0.ymp.R5 and Corrected log K Values for Weeksite

Temp. °C	0.01	25	60	100	150	200	250	300
data0.ymp.R5[a]	23.3254	21.8020	19.7645	17.9092	16.2023	14.9368	13.8690	12.7214
Corrected[b]	21.8745	20.1409	17.8497	15.7505	13.7925	12.3223	11.0864	9.8000
Difference	1.4509	1.6611	1.9148	2.1587	2.4098	2.6145	2.7826	2.9214

[a] Output DTN: SN0702T0502404.015, folder: *\Uranyl_minerals_KBH*, workbook: *Minerals_cal_KBH_Usilicates.xls*.

[b] Output DTN: SN0702T0502404.015, folder: *\Uranyl_minerals_KBH_RJF*, workbook: *Minerals_cal_KBH_Usilicates_rjf.xls*.

Sklodowskite: $Mg[(UO_2)(SiO_3OH)]_2{:}6H_2O$

The sklodowskite structure may be broken down into six fictive structural components according to the reaction (Chen et al. 1999 [DIRS 123270], Table 1):

$$MgO_{(II)} + H_2O_{(S)} + 2\ UO_{3(VI)} + 2\ SiO_{2(IV)} + 6\ H_2O_{(H)} = Mg[(UO_2)(SiO_3OH)]_2{:}6H_2O \qquad \text{(Eq. 6-64)}$$

The ΔG_f^o may be estimated by summing the stoichiometric contributions of each of the components in the reaction above that are reported in Table 3, column 2 of Chen et al. (1999 [DIRS 123270]). This yields ΔG_f^o (sklodowskite) = -6303.73 kJ/mol. Applying this value to the reaction:

$$Mg[(UO_2)(SiO_3)(OH)]_2{:}6H_2O + 6\ H^+ = Mg^{2+} + 2\ UO_2^{2+} + 2\ SiO_2(aq) + 10\ H_2O \qquad \text{(Eq. 6-65)}$$

gives ΔG_r^o (298.15 K) = -23194.5 J/mol and log K = 17.0.

This Gibbs energy value was used with values of other thermodynamic parameters (molar volume, standard molar entropy, and Maier-Kelley heat capacity coefficients a, b, and c, to obtain the apparent Gibbs energy of formation on the EQ3/6 temperature grid (0-25-60-100-150-200-250-300°C), and thence to obtain log K values on the same temperature grid (see results for "data0.ymp.R5" in Table 6-87). The molar volume of 242.55 cm^3/mol was calculated using the density of sklodowskite (3.64 g/cm^3; Roberts et al. 1990 [DIRS 107105], p. 793). The standard molar entropy (S^o), and heat capacity values were estimated from the predictive correlation algorithms discussed above (at the beginning of Section 6.7.10). For calculational details, see spreadsheets *Minerals_cal_KBH_Usilicates.xls* and *Usilicates_HC_S_KBH.xls* in folder *\Uranyl_minerals_KBH* of Output DTN: SN0702T0502404.015. The entropy value obtained is 142.60 cal/mol-K, and the heat capacity coefficients obtained are: a = 149.95, $b \times 10^3 = 38.32$, $c \times 10^{-5} = -9.14$ (all in units consistent with the heat capacity in cal/mol-K). The resulting log K at 25°C is 17.00. An error appeared in workbook *Minerals_cal_KBH_Usilicates.xls* in Output DTN: SN0702T0502404.015; the "a" heat capacity coefficient was given the value of 149.95 instead of the correct value of 149.32 cal/mol-K.

data0.ymp.R5 Corrections. Due to the previously noted small discrepancy in the value of the gas constant (*R*), the value for log K at 298.15 K in data0.ymp.R5 (Output DTN: SN0612T0502404.014) is recalculated. The corrected values are calculated in the workbooks *Usilicates_HC_S_KBH_rjf.xls* and *Minerals_cal_KBH_Usilicates_rjf.xls* in folder *\Uranyl_minerals_KBH_RJF* of Output DTN: SN0702T0502404.015. The corrected entropy is *S*° = 191.02. The erroneous "a" heat capacity coefficient was corrected to 149.32 cal/mol-K. The resulting log K at 25°C is 17.00. This value differs in the fourth decimal place from that calculated after correcting for the small discrepancy. As can be seen Table 6-90, differences between the current data block for all values of log K for sklodowskite and the corrected values are negligible and well within the uncertainty of the calculations. Therefore, we have made no change to the current entries in data0.ymp.R5 (Output DTN: SN0612T0502404.014).

Table 6-90. The data0.ymp.R5 and Corrected log K Values for Sklodowskite

Temp. °C	0.01	25	60	100	150	200	250	300
data0.ymp.R5[a]	20.1556	17.0018	13.3689	10.1712	7.1851	4.9245	3.0773	1.3802
Corrected[b]	20.1559	17.0016	13.3695	10.1743	7.1926	4.9371	3.0955	1.4042
Difference	-0.0003	0.0002	-0.0006	-0.0031	-0.0075	-0.0126	-0.0182	-0.0240

[a] Output DTN: SN0702T0502404.015, folder: *\Uranyl_minerals_KBH*, workbook: *Minerals_cal_KBH_Usilicates.xls*.

[b] Output DTN: SN0702T0502404.015, folder: *\Uranyl_minerals_KBH_RJF*, workbook: *Minerals_cal_KBH_Usilicates_rjf.xls*.

6.7.11 Correction of Data for Some Additional Cr Species

Changes are made for some Cr species to obtain better consistency with the solubility of $Cr(OH)_3$(am) as a function of pH (Rai et al. 1987 [DIRS 163369]; Ball and Nordstrom 1998 [DIRS 163015]; Rai et al. 2004 [DIRS 179582]). The input data (Table 4-54) are taken from Ball and Nordstrom (1998 [DIRS 163015]) and Rai et al. (2004 [DIRS 179582]). The results of this development are given in Table 6-91. The species $Cr_2(OH)_2^{4+}$ and $Cr_3(OH)_4^{5+}$ are deleted, and the data for $CrOH^{2+}$, $Cr(OH)_3$(aq), and $Cr(OH)_3$(am) are changed. The case for deleting $Cr_3(OH)_4^{5+}$ and $Cr_2(OH)_2^{4+}$ is discussed by Ball and Nordstrom (1998 [DIRS 163015], p. 912). They cite earlier results reported by Rai et al. (1987 [DIRS 163369]) who found no measurable evidence of the formation of such complexes. As it is likely that such species do not exist, they have been deleted. The data recommended by Ball and Nordstrom (1998 [DIRS 163015]) for $Cr(OH)_3$(am) are adopted without change (see Table 6-91). Their data for $Cr(OH)_3$(aq) (Table 4-4) have been adapted by reversing the reaction for consistency with EQ3/6 format and changing the sign of the log K (Table 6-91).

Another change concerns the log K value for the reaction $CrOH^{2+} + H^+ = Cr^{3+} + H_2O$. The thermodynamic data recommended for $Cr(OH)^{2+}$ by Ball and Nordstrom (1998 [DIRS 163015]) are based on the solubility measurements of Rai et al. (1987 [DIRS 163369]). They give (Table 4-54) a log K value of -3.57 for the reverse reaction, which corresponds to a value of 3.57 for the desired reaction. This datum was determined by analyzing the solubility of $Cr(OH)_3$(am) at relatively low pH (less than about 4). The solubility curve in this region decreases sharply with increasing pH at a slope consistent with $Cr(OH)_3(am) + 2\ H^+ = CrOH^{2+} + 2\ H_2O$ as the controlling reaction (Rai et al. 1987 [DIRS 163369]). Rai et al. (2004 [DIRS 179582]) present newer solubility measurements in which the solubility curve in this low pH region has the same slope but is shifted in the direction of lower pH. One may compare Figure 1 of Rai et al. (2004 [DIRS 179582]) with Figure 2 of Rai et al. (1987 [DIRS 163369]). The low-pH limb in the former figure is shifted substantially to the left, by about 1.7 pH units. Other parts of the solubility curve in this figure are essentially unchanged. Rai et al. (2004 [DIRS 179582]) attribute this changed result at low pH to more closely attaining a state of equilibrium in this region than in the earlier study. Rai et al. (2004 [DIRS 179582]) give log K = -10.93 for the reaction $CrOH^{2+} + 2\ H_2O = Cr(OH)_3(aq) + 2\ H^+$ (Table 4-54). Ball and Nordstrom (1998 [DIRS 163015]) give log K = 16.19 for the reaction $Cr(OH)_3(aq) + 3\ H^+ = Cr^{3+} + 3\ H_2O$ (Table 4-54). Adding these reactions gives the desired reaction $CrOH^{2+} + H^+ = Cr^{3+} + H_2O$ and log K = -10.93 + 16.29 = 5.26. This value is adopted in Table 6-91. It compares with the 3.57 that would be obtained from the recommendation of Ball and Nordstrom (1998 [DIRS 163015]).

Table 6-91. Equilibrium Constants (298.15 K) for Some Additional Chromium-Bearing Species

Species	Chemical Reaction	log K	Source
$Cr_2(OH)_2^{4+}$	species deleted	---	1
$Cr_3(OH)_4^{5+}$	species deleted	---	1
$Cr(OH)_3(am)$	$Cr(OH)_3(am) + 3H^+ = Cr^{3+} + 3H_2O$	9.35	1
$CrOH^{2+}$	$CrOH^{2+} + H^+ = Cr^{3+} + H_2O$ [a]	5.26 [a]	1
$Cr(OH)_3(aq)$	$Cr(OH)_3(aq) + 3H^+ = Cr^{3+} + 3H_2O$ [b]	16.19 [b]	1[a]

Sources: (1) Ball and Nordstrom 1998 [DIRS 163015], Table 8 (p. 910) and Table 10 (p. 911); (2) Rai et al. 2004 [DIRS 179582], p. 1223.

[a] These data were obtained by combining reactions from the two sources. See text.

[b] The reaction has been reversed and the log K sign changed.

6.7.12 Summary Table of New Data for data0.ymp.R5

Table 6-92 summarizes the new and recalculated log K temperature grids for aqueous species. Table 6-93 does the same for log K temperature grids for solids.

Table 6-92. Log K Temperature Grids for Aqueous Species Added or Recalculated in data0.ymp.R5

Species Name	Reaction	0.01°C	25°C	60°C	100°C	150°C	200°C	250°C	300°C
$H_2PO_4^-$	$H_2PO_4^- = HPO_4^{2-} + H^+$	-7.3200	-7.2120	-7.2065	-7.3155	-7.5638	-7.9129	-8.3711	-8.9931
$H_3PO_4(aq)$	$H_3PO_4(aq) = HPO_4^{2-} + 2H^+$	-9.3536	-9.3517	-9.5386	-9.8927	-10.4715	-11.1851	-12.0698	-13.2546
PO_4^{3-}	$PO_4^{3-} + H^+ = HPO_4^{2-}$	12.6494	12.3504	12.1600	12.1319	12.2803	12.5821	13.0271	13.6515
$H_2P_2O_7^{2-}$	$H_2P_2O_7^{2-} + H_2O = 2HPO_4^{2-} + 2H^+$	-12.5130	-12.6713	-13.2037	-14.0214	-15.2162	-16.5560	-18.0631	-19.8540
$H_4P_2O_7(aq)$	$H_4P_2O_7(aq) = H_2P_2O_7^{2-} + 2H^+$	-3.0852	-3.2494	-3.5335	-3.8917	-4.3852	-4.9566	-5.6718	-6.6952
$H_3P_2O_7^-$	$H_3P_2O_7^- = H_2P_2O_7^{2-} + H^+$	-2.2358	-2.2496	-2.3114	-2.4162	-2.5903	-2.8207	-3.1356	-3.6092
$HP_2O_7^{3-}$	$HP_2O_7^{3-} + H^+ = H_2P_2O_7^{2-}$	6.7452	6.6506	6.6488	6.7509	6.9824	7.3108	7.7482	8.3537
$P_2O_7^{4-}$	$P_2O_7^{4-} + 2H^+ = H_2P_2O_7^{2-}$	16.3346	16.0506	16.0856	16.4575	17.2247	18.2395	19.4980	21.0983
HPO_3^{2-}	$HPO_3^{2-} + 0.5\ O_2(g) = HPO_4^{2-}$	55.0715	49.8056	43.7088	38.0942	32.5162	28.0698	24.4329	21.3946
$H_2PO_3^-$	$H_2PO_3^- = HPO_3^{2-} + H^+$	-6.1715	-6.1206	-6.1677	-6.3132	-6.5858	-6.9450	-7.4062	-8.0318
$H_3PO_3(aq)$	$H_3PO_3(aq) = HPO_3^{2-} + 2\ H^+$	-7.9129	-7.9165	-8.0716	-8.3623	-8.8436	-9.4520	-10.2323	-11.3242
$H_2PO_2^-$	$H_2PO_2^- + O_2(g) = HPO_4^{2-} + H^+$	113.2127	102.2889	89.6099	77.8991	66.2095	56.8152	49.0212	42.3246
$H_3PO_2(aq)$	$H_3PO_2(aq) = H_2PO_2^- + H^+$	-1.9249	-1.9791	-2.0903	-2.2415	-2.4592	-2.7171	-3.0429	-3.5096
$NiCO_3(aq)$	$NiCO_3(aq) + H^+ = Ni^{2+} + HCO_3^-$	-	6.3288	-	-	-	-		
$CaSeO_4(aq)$	$CaSeO_4(aq) = Ca^{2+} + SeO_4^{2-}$	-	2.0000	-	-	-	-	-	-
CrO_3Cl^-	$CrO_3Cl^- + H_2O = CrO4^{2-} + 2H^+ + Cl^-$	-6.8731	-6.8964	-7.1882	-7.7066	-8.5214	-9.4874	-10.6333	-12.0844
$KP_2O_7^{3-}$	$KP_2O_7^{3-} + 2H^+ = K^+ + H_2P_2O_7^{2-}$	14.5840	13.9506	13.3301	12.8671	12.5426	12.4325	12.5151	12.8279
$MgP_2O_7^{2-}$	$MgP_2O_7^{2-} + 2H^+ = H_2P_2O_7^{2-} + Mg^{2+}$	9.5756	8.9000	8.1241	7.4156	6.7184	6.1685	5.7237	5.3565
$NiP_2O_7^{2-}$	$NiP_2O_7^{2-} + 2H^+ = H_2P_2O_7^{2-} + Ni^{2+}$	8.8363	9.0050	9.1987	9.3756	9.5497	9.6870	9.7981	9.8897
$PbH_2PO_4^+$	$PbH_2PO_4^+ = Pb^{2+} + HPO_4^{2-} + H^+$	-	-8.7120	-	-	-	-	-	-
$AmH_2PO_4^{2+}$	$AmH_2PO_4^{2+} = HPO_4^{2-} + Am^{3+} + H^+$	-	-10.2120	-	-	-	-	-	-
$CaPO_4^-$	$CaPO_4^- + H^+ = Ca^{2+} + HPO_4^{2-}$	-	5.8905	-	-	-	-	-	-
$Ce(PO_4)_2^{3-}$	$Ce(PO_4)_2^{3-} + 2\ H^+ = Ce^{3+} + 2HPO_4^{2-}$	-	6.2010	-	-	-	-	-	-
$CeH_2PO_4^{2+}$	$CeH_2PO_4^{2+} = H^+ + Ce^{3+} + HPO_4^{2-}$	-	-9.7121	-	-	-	-	-	-
$CePO_4(aq)$	$CePO_4(aq) + H^+ = Ce^{3+} + HPO_4^{2-}$	-	1.0005	-	-	-	-	-	-
$Dy(PO_4)_2^{3-}$	$Dy(PO_4)_2^{3-} + 2\ H^+ = Dy^{3+} + 2HPO_4^{2-}$	-	3.5010	-	-	-	-	-	-

Table 6-92. Log K Temperature Grids for Aqueous Species Added or Recalculated in data0.ymp.R5 (Continued)

Species Name	Reaction	0.01°C	25°C	60°C	100°C	150°C	200°C	250°C	300°C
$DyH_2PO_4^{++}$	$DyH_2PO_4^{2+} = H^+ + Dy^{3+} + HPO_4^{2-}$	-	-9.6121	-	-	-	-	-	-
$DyPO_4(aq)$	$DyPO_4(aq) + H^+ = Dy^{3+} + HPO_4^{2-}$	-	-0.1495	-	-	-	-	-	-
$Er(PO_4)_2^{3-}$	$Er(PO_4)_2^{3-} + 2H^+ = Er^{3+} + 2HPO_4^{2-}$	-	3.3010	-	-	-	-	-	-
$ErH_2PO_4^{2+}$	$ErH_2PO_4^{2+} = H^+ + Er^{3+} + HPO_4^{2-}$	-	-9.6121	-	-	-	-	-	-
$ErPO_4(aq)$	$ErPO_4(aq) + H^+ = Er^{3+} + HPO_4^{2-}$	-	-0.3495	-	-	-	-	-	-
$Eu(PO_4)_2^{3-}$	$Eu(PO_4)_2^{3-} + 2H^+ = Eu^{3+} + 2HPO_4^{2-}$	-	4.0410	-	-	-	-	-	-
$EuH_2PO_4^{2+}$	$EuH_2PO_4^{2+} = H^+ + Eu^{3+} + HPO_4^{2-}$	-	-9.6121	-	-	-	-	-	-
$EuPO_4(aq)$	$EuPO_4(aq) + H^+ = Eu^{3+} + HPO_4^{2-}$	-	0.1505	-	-	-	-	-	-
$Gd(PO_4)_2^{3-}$	$Gd(PO_4)_2^{3-} + 2H^+ = Gd^{3+} + 2HPO_4^{2-}$	-	4.0012	-	-	-	-	-	-
$GdH_2PO_4^{2+}$	$GdH_2PO_4^{2+} = Gd^{3+} + 2HPO_4^{2-} + H^+$	-	-9.6120	-	-	-	-	-	-
$GdPO_4(aq)$	$GdPO_4(aq) + H^+ = Gd^{3+} + HPO_4^{2-}$	-	0.1505	-	-	-	-	-	-
$Ho(PO_4)_2^{3-}$	$Ho(PO_4)_2^{3-} + 2H^+ = Ho^{3+} + 2HPO_4^{2-}$	-	3.4010	-	-	-	-	-	-
$HoH_2PO_4^{2+}$	$HoH_2PO_4^{2+} = H^+ + Ho^{3+} + HPO_4^{2-}$	-	-9.5121	-	-	-	-	-	-
$HoPO_4(aq)$	$HoPO_4(aq) + H^+ = Ho^{3+} + HPO_4^{2-}$	-	-0.2495	-	-	-	-	-	-
$La(PO_4)_2^{3-}$	$La(PO_4)_2^{3-} + 2H^+ = La^{3+} + 2HPO_4^{2-}$	-	7.1010	-	-	-	-	-	-
$LaH_2PO_4^{2+}$	$LaH_2PO_4^{2+} = H^+ + La^{3+} + HPO_4^{2-}$	-	-9.7121	-	-	-	-	-	-
$LaPO_4(aq)$	$LaPO_4(aq) + H^+ = La^{3+} + HPO_4^{2-}$	-	1.3905	-	-	-	-	-	-
$Lu(PO_4)_2^{3-}$	$Lu(PO_4)_2^{3-} + 2H^+ = Lu^{3+} + 2HPO_4^{2-}$	-	2.8010	-	-	-	-	-	-
$LuH_2PO_4^{2+}$	$LuH_2PO_4^{2+} = H^+ + Lu^{3+} + HPO_4^{2-}$	-	-9.7121	-	-	-	-	-	-
$LuPO_4(aq)$	$LuPO_4(aq) + H^+ = Lu^{3+} + HPO_4^{2-}$	-	-0.6495	-	-	-	-	-	-
$Nd(PO_4)_2^{3-}$	$Nd(PO_4)_2^{3-} + 2H^+ = Nd^{3+} + 2HPO_4^{2-}$	-	5.2010	-	-	-	-	-	-
$NdH_2PO_4^{2+}$	$NdH_2PO_4^{2+} = H^+ + Nd^{3+} + HPO_4^{2-}$	-	-9.6121	-	-	-	-	-	-
$NdPO_4(aq)$	$NdPO_4(aq) + H^+ = Nd^{3+} + HPO_4^{2-}$	-	0.5505	-	-	-	-	-	-
$Pm(PO_4)_2^{3-}$	$Pm(PO_4)_2^{3-} + 2H^+ = Pm^{3+} + 2\ HPO_4^{2-}$	-	4.7410	-	-	-	-	-	-
$PmH_2PO_4^{2+}$	$PmH_2PO_4^{2+} = H^+ + Pm^{3+} + HPO_4^{2-}$	-	-9.6121	-	-	-	-	-	-
$PmPO_4(aq)$	$PmPO_4(aq) + H^+ = Pm^{3+} + HPO_4^{2-}$	-	0.4005	-	-	-	-	-	-
$Pr(PO_4)_2^{3-}$	$Pr(PO_4)_2^{3-} + 2H^+ = Pm^{3+} + 2HPO_4^{2-}$	-	5.6210	-	-	-	-	-	-
$PrH_2PO_4^{2+}$	$PrH_2PO_4^{2+} = H^+ + Pm^{3+} + HPO_4^{2-}$	-	-9.6621	-	-	-	-	-	-

Table 6-92. Log K Temperature Grids for Aqueous Species Added or Recalculated in data0.ymp.R5 (Continued)

Species Name	**Reaction**	**0.01°C**	**25°C**	**60°C**	**100°C**	**150°C**	**200°C**	**250°C**	**300°C**
$PrPO_4(aq)$	$PrPO_4(aq) + H^+ = Pm^{3+} + HPO_4^{2-}$	-	0.7505	-	-	-	-	-	-
$Sm(PO_4)_2^{3-}$	$Sm(PO_4)_2^{3-} + 2H^+ = Sm^{3+} + 2HPO_4^{2-}$	-	4.3010	-	-	-	-	-	-
$SmH_2PO_4^{2+}$	$SmH_2PO_4^{2+} = H^+ + Sm^{3+} + HPO_4^{2-}$	-	-9.5621	-	-	-	-	-	-
$SmPO_4(aq)$	$SmPO_4(aq) + H^+ = Sm^{3+} + HPO_4^{2-}$	-	0.2505	-	-	-	-	-	-
$Tb(PO_4)_2^{3-}$	$Tb(PO_4)_2^{3-} + 2H^+ = Tb^{3+} + 2HPO_4^{2-}$	-	3.7010	-	-	-	-	-	-
$TbH_2PO_4^{2+}$	$TbH_2PO_4^{2+} = H^+ + Tb^{3+} + HPO_4^{2-}$	-	-9.6121	-	-	-	-	-	-
$TbPO_4(aq)$	$TbPO_4(aq) + H^+ = Tb^{3+} + HPO_4^{2-}$	-	-0.0495	-	-	-	-	-	-
$Tm(PO_4)_2^{3-}$	$Tm(PO_4)_2^{3-} + 2H^+ = Tm^{3+} + 2HPO_4^{2-}$	-	3.1010	-	-	-	-	-	-
$TmH_2PO_4^{2+}$	$TmH_2PO_4^{2+} = H^+ + Tm^{3+} + HPO_4^{2-}$	-	-9.7121	-	-	-	-	-	-
$TmPO_4(aq)$ (a)	$TmPO_4(aq) + H^+ = Tm^{3+} + HPO_4^{2-}$	-	-0.0495	-	-	-	-	-	-
$Y(PO_4)_2^{3-}$	$Y(PO_4)_2^{3-}- + 2H^+ = Y^{3+} + 2HPO_4^{2-}$	-	3.3010	-	-	-	-	-	-
$YH_2PO_4^{2+}$	$YH_2PO_4^{2+} = H^+ + Y^{3+} + HPO_4^{2-}$	-	-9.6121	-	-	-	-	-	-
$YPO_4(aq)$	$YPO_4(aq) + H^+ = Y^{3+} + HPO_4^{2-}$	-	-0.2495	-	-	-	-	-	-
$Yb(PO_4)_2^{3-}$	$Yb(PO_4)_2^{3-} + 2H^+ = Yb^{3+} + 2HPO_4^{2-}$	-	2.8010	-	-	-	-	-	-
$YbH_2PO_4^{2+}$	$YbH_2PO_4^{2+} = H^+ + Yb^{3+} + HPO_4^{2-}$	-	-9.6121	-	-	-	-	-	-
$YbPO_4(aq)$	$YbPO_4(aq) + H^+ = Yb^{3+} + HPO_4^{2-}$	-	-0.5495	-	-	-	-	-	-
$UO_2PO_4^-$	$UO_2PO_4^- + H^+ = UO_2^{2+} + HPO_4^{2-}$	-	-0.8689	-	-	-	-	-	-
$UO_2HPO_4(aq)$	$UO_2HPO_4(aq) = UO_2^{2+} + HPO_4^{2-}$	-	-7.2290	-	-	-	-	-	-
$UO_2H_3PO_4^{2+}$	$UO_2H_3PO_4^{2+} = UO_2^{2+} + HPO_4^{2-} + 2H^+$	-	-10.1011	-	-	-	-	-	-
$UO_2H_2PO_4^+$	$UO_2H_2PO_4^+ = UO_2^{2+} + HPO_4^{2-} + H^+$	-	-10.4611	-	-	-	-	-	-
$UO_2(H_2PO_4)_2(aq)$	$UO_2(H_2PO_4)_2(aq) = UO_2^{2+} + 2HPO_4^{2-} + 2H^+$	-	-19.3331	-	-	-	-	-	-
$UO_2(H_2PO_4)(H_3PO_4)^+$	$UO_2(H_2PO_4)(H_3PO_4)^+ = UO_2^{2+} + 2HPO_4^{2}- + 3H^+$	-	-20.3430	-	-	-	-	-	-
$NpO_2H_2PO_4^+$	$NpO_2H_2PO_4^+ = NpO_2^{2+} + HPO_4^{2-} + H^+$	-	-10.5247	-	-	-	-	-	-
$H_2PO_3F(aq)$	$H_2PO_3F(aq) + H_2O = HPO_4^{2-} + 3H^+ + F^-$	-9.3961	-9.7896	-10.5474	-11.5346	-12.8721	-14.3292	-15.9798	-18.0257
HPO_3F^-	$HPO_3F^- + H_2O = HPO_4^{2-} + 2H^+ + F^-$	-9.0936	-9.2465	-9.6574	-10.2584	-11.1265	-12.1096	-13.2452	-14.6552

Table 6-92. Log K Temperature Grids for Aqueous Species Added or Recalculated in data0.ymp.R5 (Continued)

Species Name	Reaction	0.01°C	25°C	60°C	100°C	150°C	200°C	250°C	300°C
PO_3F^{2-}	$PO_3F^{2-} + H_2O = HPO_4^{2-} + H^+ + F^-$	-4.3678	-4.4461	-4.6532	-4.9539	-5.3855	-5.8710	-6.4283	-7.1171
$HPO_2F_2(aq)$	$HPO_2F_2(aq) + 2\ H_2O = HPO_4^{2-} + 4H^+ + 2F^-$	-8.2884	-9.0606	-10.3705	-11.9734	-14.0524	-16.2396	-18.6453	-21.5432
$PO_2F_2^-$	$PO_2F_2^- + 2H_2O = HPO_4^{2-} + H^+ + 2F^-$	-8.0863	-8.7627	-9.8920	-11.2606	-13.0197	-14.8506	-16.8366	-19.1774
$CaP_2O_7^{2-}$	$CaP_2O_7^{2-} + 2H^+ = Ca^{2+} + H_2P_2O_7^{2-}$	-	9.3000	-	-	-	-	-	-
$CdP_2O_7^{2-}$	$CdP_2O_7^{2-} + 2H^+ = Cd^{2+} + H_2P_2O_7^{2-}$	-	7.4000	-	-	-	-	-	-
$Na_2P_2O_7^{2-}$	$Na_2P_2O_7^{2-} + 2H^+ = 2\ Na^+ + H_2P_2O_7^{2-}$	-	12.8	-	-	-	-	-	-
$NaHP_2O_7^{2-}$	$NaHP_2O_7^{2-} + H^+ = Na^+ + H_2P_2O_7^{2-}$	-	5.3	-	-	-	-	-	-
$NaP_2O_7^{3-}$	$NaP_2O_7^{3-} + 2H^+ = Na^+ + H_2P_2O_7^{2-}$	-	13.81	-	-	-	-	-	-
$NiHP_2O_7^-$	$NiHP_2O_7^- + H^+ = Ni^{2+} + H_2P_2O_7^{2-}$	-	2.8029	-	-	-	-	-	-
$PbP_2O_7^{2-}$	$PbP_2O_7^{2-} + 2H^+ = Pb^{2+} + H_2P_2O_7^{2-}$	-	4.6573	-	-	-	-	-	-
$SrP_2O_7^{2-}$	$SrP_2O_7^{2-} + 2H^+ = Sr^{2+} + H_2P_2O_7^{2-}$	-	10.7000	-	-	-	-	-	-
$Th(OH)_4(aq)$	$Th(OH)_4(aq) + 4H^+ = Th^{4+} + 4H_2O$	-	16.9804	-	-	-	-	-	-
$Th(OH)_3^+$	$Th(OH)_3^+ + 3H^+ = Th^{4+} + 3H_2O$	-	11.3853	-	-	-	-	-	-
$Th(OH)_3CO_3^-$	$Th(OH)_3CO_3^- + 4H^+ = Th^{4+} + HCO_3^- + 3H_2O$	-	13.8141	-	-	-	-	-	-
$Th(OH)_2^{2+}$	$Th(OH)_2^{2+} + 2H^+ = Th^{4+} + 2H_2O$	-	6.5902	-	-	-	-	-	-
$Th(OH)^{3+}$	$Th(OH)^{3+} + H^+ = Th^{4+} + H_2O$	-	2.1951	-	-	-	-	-	-
$Th(OH)(CO_3)_4^{5-}$	$Th(OH)(CO_3)_4^{5-} + 5H^+ = Th^{4+} + H_2O + 4HCO_3^-$	-	19.5103	-	-	-	-	-	-
$Th(OH)_2CO_3(aq)$	$Th(OH)_2CO_3(aq) + 3H^+ = Th^{4+} + 2H_2O + HCO_3^-$	-	7.6190	-	-	-	-	-	-
$Th(OH)_2(CO_3)_2^{2-}$	$Th(OH)_2(CO_3)_2^{2-} + 4H^+ = Th^{4+} + 2H_2O + 2HCO_3^-$	-	11.6478	-	-	-	-	-	-
$Th(OH)_3(CO_3)^-$	$Th(OH)_3(CO_3)^- + 4H^+ = Th^{4+} + 3H_2O + HCO_3^-$	-	13.8141	-	-	-	-	-	-
$Th(OH)_4CO_3^{2-}$	$Th(OH)_4CO_3^{2-} + 5H^+ = Th^{4+} + 4H_2O + HCO_3^-$	-	25.7092	-	-	-	-	-	-

Table 6-92. Log K Temperature Grids for Aqueous Species Added or Recalculated in data0.ymp.R5 (Continued)

Species Name	**Reaction**	**0.01°C**	**25°C**	**60°C**	**100°C**	**150°C**	**200°C**	**250°C**	**300°C**
$Sn(OH)_4(aq)$	$Sn(OH)_4(aq) + 4H^+ = Sn^{4+} + 4H_2O$	-1.0516	-0.8863	-0.6586	-0.4108	-0.1540	0.0100	0.0468	-0.0723
$Sn(OH)_5^-$	$Sn(OH)_5^- + 5H^+ = Sn^{4+} + 5H_2O$	-	6.7637	-	-	-	-	-	-
$Sn(OH)_6^{2-}$	$Sn(OH)_6^{2-} + 6H^+ = Sn^{4+} + 6\ H_2O$	-	17.4237	-	-	-	-	-	-
$Cr_2(OH)_2^{4+}$	Species deleted	-	-	-	-	-	-	-	-
$Cr_3(OH)_4^{5+}$	Species deleted	-	-	-	-	-	-	-	-
$CrOH^{2+}$	$CrOH^{2+} + H^+ = Cr^{3+} + H_2O$	-	3.57	-	-	-	-	-	-
$Cr(OH)_3(aq)$	$Cr(OH)_3(aq) + 3H^+ = Cr^{3+} + 3H_2O$	-	16.19	-	-	-	-	-	-

Source: Output DTN: SN0702T0502404.015, except that data for CrOH2+ and Cr(OH)3(aq) are taken from Ball and Nordstrom (1998 [DIRS 163015]), Table 10 (p. 911).

[a] A data entry error (-12.4 instead of -12.8) was made in calculating the log K value for $TmPO_4(aq)$.

Table 6-93. Log K Temperature Grids for Solids Added or Recalculated in data0.ymp.R5

Species Name	Reaction	0.01°C	25°C	60°C	100°C	150°C	200°C	250°C	300°C
Eskolaite	$Cr_2O_3 + 6H^+ = 2Cr^{3+} + 3H_2O$	15.0621	11.5662	7.5022	3.7591	0.0033	-3.0908	-5.7941	-8.2945
CrO_2	CrO2 + $3H^+ = Cr^{3+} + 1.5H_2O$ + 0.25 O_2(g)	4.2955	3.0034	1.4774	0.0463	-1.4240	-2.6725	-3.8001	-4.8782
Kogarkoite	$Na_3SO_4F = 3\ Na^+ + SO_4^{2-} + F^-$	-2.2018	-2.0247	-2.0694	-2.3260	-2.8603	-3.6269	-4.6979	-6.2783
Sepiolite(am)	Sepiolite(am) + $8H^+ = 4Mg^{2+}$ + $6SiO_2$(aq) + $11H_2O$	39.5037	37.5600	34.2871	31.0129				
Palygorskite	$Mg_{2.84}Al_{1.8}Si_{7.73}O_{20}(OH)_2(OH_2)4$: $4H_2O + 11.08H^+ = 2.84Mg^{2+}$ + $1.8Al^{3+}$ + $7.73SiO_2$(aq) + $14.54H_2O$	-	26.4078	-	-	-	-	-	-
Poorly Crystalline Antigorite	$Mg_3Si_2O_5(OH)_4 + 6H^+ = 3Mg^{2+}$ + $2SiO_2$(aq) + $5H_2O$	37.3589	34.5025	31.2224	28.2271	25.2793	22.9545	21.0741	19.5218
Nickel Molybdate	$NiMoO_4 = Ni^{2+} + MoO_4^{2-}$	-5.8328	-6.5033	-6.6098	-6.1013	-5.1146	-4.1164	-3.3380	-2.9911
$NiCO_3$	$NiCO_3 + H^+ = Ni^{2+} + HCO_3^-$	-	-0.8712	-	-	-	-	-	-
$NiCO_3$:5.5H_2O	$NiCO_3$:5.5$H_2O + H^+ = Ni^{2+} + HCO_3^-$ + 5.5H_2O	-	2.8040	-	-	-	-	-	-
$Ca_3(PO_4)_2$	$Ca_3(PO_4)_2 + 2H^+ = 2HPO_4^{2-}$ + $3Ca^{2+}$	-4.5510	-6.0658	-8.2529	-10.7018	-13.7096	-16.7712	-20.0744	-23.9669
$FePO_4$:2H_2O [(a)]	$FePO_4$:2$H_2O + H^+ = HPO_4^{2-} + Fe^{3+}$ + $2H_2O$	-11.8075	-12.2416	-12.9308	-13.7531	-14.8382	-16.0358	-17.4293	-19.1736
$SrHPO_4$ [(b)]	$SrHPO_4 = HPO_4^{2-} + Sr^{2+}$	-4.6845	-5.0417	-5.6104	-	-	-	-	-
$Ni_3(PO_4)_2$	$Ni_3(PO_4)_2 + 2H^+ = 2\ HPO_4^{2-} + 3Ni^{2+}$	-	-4.2415	-	-	-	-	-	-
$Ni_2P_2O_7$	$Ni_2P_2O_7 + 2H^+ = H_2P_2O_7^{2-} + 2Ni^{2+}$	-	6.1721	-	-	-	-	-	-
$Ca_5(PO_4)_3OH$	$Ca_5(PO_4)_3OH + 4\ H^+ = 3HPO_4^{2-}$ + $5Ca^{2+}$ + H2O	-6.0753	-8.4110	-11.6996	-15.3187	-19.7242	-24.2039	-29.0620	-34.8365
$Ca_5(PO_4)_3F$	$Ca_5(PO_4)_3F + 3H^+ = 3HPO_4^{2-} + F^-$ + $5Ca^{2+}$	-24.0888	-25.1410	-27.3075	-30.2732	-34.4609	-39.1564	-44.5401	-51.1241
Berlinite ($AlPO_4$)	$AlPO_4 + H^+ = HPO_4^{2-} + Al^{3+}$	-5.1902	-6.6228	-8.5260	-10.5218	-12.8272	-15.0379	-17.2880	-19.7663
$PuPO_4$(s, hyd)	$PuPO_4$(s, hyd) + $H^+ = Pu^{3+} + HPO_4^{2-}$	-	-12.2500	-	-	-	-	-	-
PuP [(b)]	PuP + H^+ $2O_2$(g) = $Pu^{3+} + HPO_4^{2-}$	263.5911	238.4760	209.4201	-	-	-	-	-
$Pu(HPO_4)_2$(am,hyd)	$Pu(HPO_4)_2$(am,hyd) = $2HPO_4^{2-}$ + Pu^{4+}	-	-30.4500	-	-	-	-	-	-

Table 6-93. Log K Temperature Grids for Solids Added or Recalculated in data0.ymp.R5 (Continued)

Species Name	**Reaction**	**0.01°C**	**25°C**	**60°C**	**100°C**	**150°C**	**200°C**	**250°C**	**300°C**
$AmPO_4(am)$ (c)	$AmPO_4(am) + H^+ = HPO_4^{2-} + Am^{3+}$	-11.9105	-12.4399	-13.2919	-14.3128	-15.6390	-17.0571	-18.6454	-20.5555
$UO_2HPO_4{:}4H_2O_{(c)}$	$UO_2HPO_4{:}4H_2O_{(c)} = 4H_2O + HPO_4^{2-} + UO_2^{2+}$	-12.0044	-11.8123	-11.7278	-11.7885	-12.0459	-12.4980	-13.1868	-14.2419
$U(HPO_4)_2{:}4H_2O$ (b)	$U(HPO_4)_2{:}4H_2O = 4H_2O + 2HPO_4^{2-} + U^{4+}$	-30.5483	-30.4577	-30.4594	-	-	-	-	-
$(UO_2)_3(PO_4)_2{:}6H_2O$	$(UO_2)_3(PO_4)_2{:}6H_2O + 2H^+ = 3UO_2^{2+} + 2HPO_4^{2-} + 6H_2O$	-24.0012	-24.5489	-25.4829	-26.6570	-28.2782	-30.1400	-32.3899	-35.3388
$(UO_2)_3(PO_4)_2{:}4H_2O$	$(UO_2)_3(PO_4)_2{:}4H_2O + H^+ = 4H_2O + 2HPO_4^{2-} + 3UO_2^{2+}$	-23.7849	-24.6023	-25.8763	-27.3957	-29.3976	-31.5968	-34.1504	-37.3763
$(UO_2)_3(PO_4)_2$	$(UO_2)_3(PO_4)_2 + 2H^+ = 2HPO_4^{2-} + 3UO_2^{2+}$	-9.1253	-11.5914	-14.8191	-18.1923	-22.1081	-25.9038	-29.8323	-34.2790
$(UO_2)_2P_2O_7$	$(UO_2)_2P_2O_7 + 2H^+ = 2UO_2^{2+} + H_2P_2O_7^{2-}$	1.9694	0.4105	-1.4420	-3.2388	-5.2068	-7.0394	-8.9016	-11.0099
UP_2O_7 (d)	$UP_2O_7 + 2H^+ = H_2P_2O_7^{2-} + U^{4+}$	-17.4200	-17.9135	-18.5384	-19.1979	-20.0200	-20.9256	-22.0167	-23.4534
$YbPO_4{:}2H_2O$	$YbPO_4{:}2H_2O + H^+ = HPO_4^{2-} + Yb^{3+} + 2H_2O$	-	-11.7495	-	-	-	-	-	-
$(VO)_3(PO_4)_2$	$(VO)_3(PO_4)_2 + 2H^+ = 2HPO_4^{2-} + 3VO^{2+}$	-	51.1865	-	-	-	-	-	-
UPO_5	$UPO_5 + H_2O = HPO_4^{2-} + UO_2^+ + H^+$	-18.9104	-18.3752	-18.0559	-18.0580	-18.4231	-19.0939	-20.0568	-21.4062
UP_2 (b)	$UP_2 + 3.25O_2(g) + 1.5H_2O = 2HPO_4^{2-} + U^{3+} + H^+$	390.8556	353.3199	309.7469	-	-	-	-	-
UP (b)	$UP + 2O_2(g) + H^+ = HPO_4^{2-} + U^{3+}$	252.8822	228.6555	200.5830	-	-	-	-	-
U_3P_4 (b)	$U_3P_4 + 7.25O_2(g) + 1.5H_2O + H^+ = 4\ HPO_4^{2-} + 3\ U^{3+}$	896.6230	810.6242	710.8952	-	-	-	-	-
$TmPO_4{:}2H_2O$	$TmPO_4\ 2H_2O + H^+ = HPO_4^{2-} + Tm^{3+} + 2\ H_2O$	-	-11.8495	-	-	-	-	-	-
$Th_{0\cdot75}PO_4$	$Th_{0\cdot75}PO_4 + H^+ = HPO_4^{2-} + 0.75Th^{4+}$	-	-15.6495	-	-	-	-	-	-
$TbPO_4{:}2H_2O$	$TbPO_4\ 2H_2O + H^+ = HPO_4^{2-} + Tb^{3+} + 2H_2O$	-	-11.9495	-	-	-	-	-	-

Table 6-93. Log K Temperature Grids for Solids Added or Recalculated in data0.ymp.R5 (Continued)

Species Name	Reaction	0.01°C	25°C	60°C	100°C	150°C	200°C	250°C	300°C
$SmPO_4{:}H_2O$	$SmPO_4\ H_2O + H^+ = HPO_4^{2-} + Sm^{3+} + H_2O$	-	-12.1495	-	-	-	-	-	-
$Pb_5(PO_4)_3OH$	$Pb_5(PO_4)_3OH + 4\ H^+ = 3HPO_4^{2-} + 5Pb^{2+} + Cl^- + H_2O$	-	-25.7534	-	-	-	-	-	-
$Pb_5(PO_4)_3Cl$	$Pb_5(PO_4)_3Cl + 3H^+ = 3HPO_4^{2-} + 5Pb^{2+} + Cl^-$	-	-47.3485	-	-	-	-	-	-
$PrPO_4{:}H_2O$	$PrPO_4{:}H_2O + H^+ = HPO_4^{2-} + Pr^{3+} + H_2O$	-	-12.2495	-	-	-	-	-	-
$PmPO_4{:}1.5H_2O$	$PmPO_4{:}1.5H_2O + H^+ = HPO_4^{2-} + Pm^{3+} + 1.5\ H_2O$	-	-12.1495	-	-	-	-	-	-
$PbHPO_4$	$PbHPO_4 = HPO_4^{2-} + Pb^{2+}$	-	-15.6308	-	-	-	-	-	-
$Pb_4O(PO_4)_2$	$Pb_4O(PO_4)_2 + 4\ H^+ = 2\ HPO_4^{2-} + 4Pb^{2+} + H_2O$	-	-12.1753	-	-	-	-	-	-
$Pb_3(PO_4)_2$	$Pb_3(PO_4)_2 + 2H^+ = 2HPO_4^{2-} + 3Pb^{2+}$	-	-19.5780	-	-	-	-	-	-
$NdPO_4{:}H_2O$	$NdPO_4{:}H_2O + H^+ = HPO_4^{2-} + Nd^{3+} + H_2O$	-	-12.1495	-	-	-	-	-	-
$LuPO_4{:}0.5H_2O$	$LuPO_4{:}0.5H_2O + H^+ = HPO_4^{2-} + Lu^{3+} + 0.5\ H_2O$	-	-11.6495	-	-	-	-	-	-
$LaPO_4{:}H_2O$	$LaPO_4{:}H_2O + H^+ = HPO_4^{2-} + La^{3+} + H_2O$	-	-12.3495	-	-	-	-	-	-
$Zn_3(PO_4)_2{:}4H_2O$	$Zn_3(PO_4)_2{:}4H_2O + 2H^+ = 2HPO_4^{2-} + 3Zn^{2+} + 4H_2O$	-	-10.5990	-	-	-	-	-	-
$HoPO_4{:}2H_2O$	$HoPO_4{:}2H_2O + H^+ = HPO_4^{2-} + Ho^{3+} + 2H_2O$	-	-11.8495	-	-	-	-	-	-
$GdPO_4{:}2H_2O$	$GdPO_4{:}2H_2O + H^+ = HPO_4^{2-} + Gd^{3+} + 2H_2O$	-	-11.9495	-	-	-	-	-	-
$EuPO_4{:}H_2O$	$EuPO_4{:}H_2O + H^+ = HPO_4^{2-} + Eu^{3+} + H_2O$	-	-12.0495	-	-	-	-	-	-
$ErPO_4{:}2H_2O$	$ErPO_4{:}2H_2O + H^+ = HPO_4^{2-} + Er^{3+} + 2H_2O$	-	-11.8495	-	-	-	-	-	-

Table 6-93. Log K Temperature Grids for Solids Added or Recalculated in data0.ymp.R5 (Continued)

Species Name	Reaction	0.01°C	25°C	60°C	100°C	150°C	200°C	250°C	300°C
$DyPO_4:2H_2O$	$DyPO_4:2H_2O + H^+ = HPO_4^{2-} + Dy^{3+} + 2H_2O$	-	-11.9495	-	-	-	-	-	-
$Cu_3(PO_4)_2$	$Cu_3(PO_4)_2 + 2H^+ = 2HPO_4^{2-} + 3Cu^{2+}$	-	-12.1707	-	-	-	-	-	-
$CoHPO_4$	$CoHPO_4 = HPO_4^{2-} + Co^{2+}$	-	-6.7187	-	-	-	-	-	-
$Co_3(PO_4)_2$	$Co_3(PO_4)_2 + 2H^+ = 2HPO_4^{2-} + 3Co^{2+}$	-	-10.0036	-	-	-	-	-	-
$CePO_4:H_2O$	$CePO_4:H_2O + H^+ = HPO_4^{2-} + Ce^{3+} + H_2O$	-	-12.2495	-	-	-	-	-	-
$Ce_3(PO_4)_4$	$Ce_3(PO_4)_4 + 4H^+ = 4HPO_4^{2-} + 3Ce^{4+}$	-	-40.6980	-	-	-	-	-	-
$Cd_3(PO_4)_2$	$Cd_3(PO_4)_2 + 2H^+ = 2HPO_4^{2-} + 3Cd^{2+}$	-	-7.9124	-	-	-	-	-	-
Ag_3PO_4	$Ag_3PO_4 + H^+ = HPO_4^{2-} + 3Ag^+$	-	-5.1995	-	-	-	-	-	-
$CaSeO_4:2H_2O$	$CaSeO_4:2H_2O = Ca^{2+} + SeO_4^{2-} + 2H_2O$	-	-2.8960	-	-	-	-	-	-
$ThO_2 \cdot 2H_2O$(am)	$ThO_2 \cdot 2H_2O(am) + 4H^+ = Th^{4+} + 4H_2O$	-	8.1804	-	-	-	-	-	-
SnO_2(am)	$SnO_2(am) + 4H^+ = Sn^{4+} + 2H_2O$	-	-8.3463	-	-	-	-	-	-
K-Boltwoodite	$K(UO_2)(SiO_3)(OH):1.5H_2O + 3H^+ = K^+ + UO_2^{2+} + SiO_2(aq) + 3.5H_2O$	16.5341	15.0194	13.2543	11.6774	10.1797	9.0281	8.0811	7.2164
K-Weeksite	$K_2(UO_2)_2(Si_5O_{13}):3H_2O + 6H^+ = 2K^+ + 2UO_2^{2+} + 5SiO_2(aq) + 6H_2O$	23.3254	21.8020	19.7645	17.9092	16.2023	14.9368	13.8690	12.7214
Becquerelite	$Ca(UO_2)_6O_4(OH)_6:8H_2O + 14H^+ = Ca^{2+} + 6UO_2^{2+} + 18H_2O$	47.7429	40.5829	32.6393	25.6528	18.9750	13.7360	9.3308	5.3084
Compreignacite	$K_2(UO_2)_6O_4(OH)_6:8H_2O + 14H^+ = 2K^+ + 6UO_2^{2+} + 18H_2O$	42.9716	37.1759	30.8030	25.2616	20.0279	15.9592	12.5407	9.3835
Sklodowskite	$Mg[(UO_2)(SiO_3)(OH)]_2:6H_2O + 6H^+ = Mg^{2+} + 2UO_2^{2+} + 2SiO_2(aq) + 10H_2O$	20.1556	17.0018	13.3689	10.1712	7.1851	4.9245	3.0773	1.3802
Dehydrated Schoepite (0.9)	$UO_3:0.9H_2O + 2H^+ = UO_2^{2+} + 1.9H_2O$	6.1471	5.0904	3.9109	2.8634	1.8498	1.0433	0.3578	-0.2709

Table 6-93. Log K Temperature Grids for Solids Added or Recalculated in data0.ymp.R5 (Continued)

Species Name	Reaction	0.01°C	25°C	60°C	100°C	150°C	200°C	250°C	300°C
Dehydrated Schoepite (1.0)	$UO_3{:}H_2O + 2H^+ = UO_2^{2+} + 2H_2O$	6.9145	5.8119	4.5816	3.4899	2.4351	1.5983	0.8898	0.2433
Na-boltwoodite	$Na(UO_2)(SiO_3)(OH){:}1.5H_2O + 3H^+ = Na^+ + UO_2^{2+} + SiO_2(aq) + 3.5H_2O$	6.8394	6.0800	5.2024	4.4617	3.8165	3.3612	2.9931	2.6134
Na-weeksite	$Na_2(UO_2)_2(Si_5O_{13}){:}3H_2O + 6H^+ = 2Na^+ + 2UO_2^{2+} + 5\ SiO_2(aq) + 6H_2O$	6.1530	5.7031	4.9390	4.2980	3.8473	3.6236	3.4353	3.0362
Soddyite	$(UO_2)_2(SiO_4){:}2H_2O + 4H^+ = SiO_2(aq) + 2UO_2^{2+} + 4H_2O$	7.7967	6.2767	4.5264	2.9733	1.4919	0.3254	-0.6815	-1.6652
Uranophane	$Ca(UO_2)_2(SiO_3OH)_2{:}5H_2O + 6H^+ = Ca^{2+} + 2SiO_2(aq) + 2UO_2^{2+} + 9H_2O$	14.7917	12.2810	9.3729	6.8112	4.4178	2.5963	1.0843	-0.3513
$Cr(OH)_3$(am)	$Cr(OH)_3(am) + 3H^+ = Cr^{3+} + 3H_2O$	-	9.35	-	-	-	-	-	-

Source: Output DTN: SN0702T0502404.015, except that data for $Cr(OH)_3$(am) are taken from Ball and Nordstrom (1998 [DIRS 163015]), Table 8 (p. 910).

[a] The data shown for the $FePO_4{:}2H_2O$ (strengite) reaction were based on heat capacity coefficients erroneously fit to entropy data from the source. See Section 6.8 for a correction. Corrected data are given in Table 6-96.

[b] Extrapolated from 25°C to 0.01°C and to 60°C in the absence of heat capacity data for the solid that appears in the reaction. See Appendix D for justification.

[c] In the calculation of the log K grid for $AmPO_4$(am),a heat capacity coefficient for a term in T^2 was omitted. The log K values for temperatures other than 25°C are affected. This is discussed in Section 6.8. See Table 6-98 for a corrected grid.

[d] In the calculation of the log K grid for UP_2O_7, the c heat capacity coefficient was incorrectly entered as -1.7827×10^{-5} instead of -17.827×10^{-5} (values consistent with heat capacity in units of J/mol-K). The log K values for temperatures other than 25°C are affected. This is discussed in Section 6.8. See Table 6-97 for a corrected grid.

6.8 POST-DATA0.YMP.R5 CORRECTIONS

This review of thermodynamic parameters has identified a host of improvements to the thermodynamic database used in YMP calculations, and the vast majority of these have been incorporated into data0.ymp.R5 (Output DTN: SN0612T0502404.014). Several identified in the later stages of the process have not. The non-included data fall into two categories: (1) revised log K values from the review of uranium mineral stabilities (Section 6.7.10), and (2) data input errors (see Table 6-94). The uranium log K values were not updated because the change from the existing values were typically small and within the overall uncertainty. The data input errors involve species/elements that (1) do not exist under Yucca Mountain conditions (e.g., thulium phosphate, metal-bearing gas species), and/or (2) involve temperatures outside of the range being considered at Yucca Mountain.

The analysis of uranium mineral thermochemistry was done to assess the uncertainty in uranium mineral log Ks used in Yucca Mountain calculations and to point the way for potential future database development. Updated values are documented in Tables 6-80 to 6-90 for, respectively, uranophane, soddyite, two forms of dehydrated schoepite (UO_3:0.9H_2O and UO_3:H_2O), becquerelite, compreignacite, sodium weeksite, sodium boltwoodite, boltwoodite, weeksite, and sklodowskite, but are not incorporated into data0.ymp.R5 (Output DTN: SN0612T0502404.014), as the difference between the existing and the updated values is generally small compared to the actual uncertainties (Section 6.7.10).

Only one notable error is known and this concerns the solid ferrimolybdite ($Fe_2(MoO_4)_3$). The database data0.ymp.R2 (DTN: MO0302SPATHDYN.000 [DIRS 161756]) contains the reaction $Fe_2(MoO_4)_3 = 2\ Fe^{3+} + 3\ MoO_4^{2-}$ and a log K value of −38.520. This datum has carried through into data0.ymp.R4 (Output DTN: SN0410T0510404.002) and data0.ymp.R5 (Output DTN: SN0612T0502404.014). As noted in Section 4.1, the source input for this datum cannot be justified. It is now recommended that this datum not be used. It is thought to be non-impacting on YMP calculations. The use of this datum would only impact the results if the ferrimolybdite solid were to precipitate. This would only occur given sufficient activities of dissolved Fe and MoO_4, which would mean that other precipitates such as ferrihydrite ($Fe(OH)_3$), powellite ($CaMoO_4$), and $NiMoO_4$(s) (Section 6.7.5), would not be limiting. However, in future code calculations using any of these databases, solid ferrimolybdite should be suppressed (equivalent to removing it from the database).

Table 6-94. Non-YMP Affecting Data Input Errors

Phase/Species	Explanation
Witherite ($BaCO_3$)	0.01°C log K value of 1.9041 mistakenly left as 1.9014.
$CoCr_2O_4$	60°C value of 10.1319 mistakenly entered as 10.1379.
Ferrite-Cu	300°C value of 9.1921 mistakenly entered as 9.9121.
Ferrite-Ca	log K grid was uncorrected. Values should be: 25.8315, 21.5945, 16.7047, 12.2304, 7.7701, 4.1185, 0.9419, -2.0036; instead of: 25.8281, 21.5945, 16.7003, 12.2140, 7.7348, 4.0632, 0.8671, -2.0967
$MgCl_2$	150°C log K value of 12.7237 mistakenly entered as 12.7273.
$NiWO_4$	250°C value of -13.6275 mistakenly entered as -13.6272.
Ti_3O_5	100°C value of 26.0351 mistakenly entered as 25.0351; 250°C value of 10.2524 mistakenly entered as 9.9524.

Table 6-94. Non-YMP Affecting Data Input Errors (Continued)

Phase/Species	Explanation
$UOBr_2$	200°C value of -2.9518 mistakenly entered as -3.9518.
$UOCl_3$	250°C value of -1.7874 mistakenly entered as -1.7974.
$UO_2PO_4^-$	25°C value of -0.8689 mistakenly entered as -1.3668.
UO_2HPO_4(aq)	25°C value of -7.2290 mistakenly entered as -7.2092l.
$UO_2H_3PO_4^{2+}$	25°C value of -10.1011 mistakenly entered as -10.0813.
$UO_2H_2PO_4^+$	25°C value of -10.4611 mistakenly entered as -10.4413.
$UO_2(H_2PO_4)_2$(aq)	25°C value of -19.3331 mistakenly entered as -19.2935.
$UO_2(H_2PO_4)(H_3PO_4)^+$	25°C value of -20.3430 mistakenly entered as -20.3034.
$NpO_2H_2PO_4^+$	25°C value of -10.5247 mistakenly entered as -10.5049
Metal gas species	Log K grids corrected. See Table 6-43.
Phosphorus solid	Log K grid was not corrected for consistency with new phosphate data.
$TmPO_4$(aq)	25°C Log K corrected.
Strengite ($FeHPO_4$:$2H_2O$)	Heat capacity coefficients, log K grids corrected.
$Fe_2(SO_4)_3$	Log K grid corrected.
UP_2O_7	Heat capacity coefficients, log K grid corrected.
$AmPO_4$	Heat capacity coefficients, log K grid corrected.
$NiMoO_4$	Heat capacity coefficients, log K grid corrected.

The errors identified in Table 6-94 have no material impact on Yucca Mountain Project calculations. Errors in log K values for solids tend to be numerically small and then only for high temperatures (starting in the range 100°C to 200°C). Moreover, none of the solids is expected to be significant at Yucca Mountain. The metal gas species are likewise unimportant and the log K differences are minor (less than 0.2 unit). The errors for aqueous species again are small numerically, except in the case of the 25°C value for $UO_2PO_4^-$. The error in the log K value here is about 0.5 unit, and would make this complex somewhat more abundant than it should be. This species is probably not significant at Yucca Mountain, though, because of low phosphate levels. The latter also limits the importance of the minor errors found in the log K values for solid phosphorus, strengite, UP_2O_7, and $AmPO_4$. For completeness, the corrections in the latter phases (except phosphorus) are documented below. The log Ks for $NiMoO_4$ and $Fe_2(SO_4)_3$ were likewise corrected – the changes being minor to non-existent at 25°C, the temperature where the bulk of Yucca Mountain calculations are performed.

Phosphorus. The data for the solid "Phosphorus" were not updated for consistency with the phosphate correction (Section 6.7.8). Corrected log K values have not been calculated for this solid. The correction would follow the change in the assumed stability of HPO_4^{2-} (~6800 J/mol, changing the log K by about 1.2 units; see Appendix A, Table A-7).

Strengite ($FeHPO_4$:$2H_2O$). The heat capacity coefficients obtained in Table 6-70 were obtained from heat capacity tabulated as a function of temperature in Table 4-45. However, the entropy values tabulated as a function of temperature were taken from the source instead of the heat capacity values. Consequently, the heat capacity coefficients in Table 6-70 are in error, as is the log K grid as shown in both Tables 6-71 and 6-93. Table 6-95 gives the correct tabulation of heat capacity as a function of temperature from the source, and Table 6-96 gives the corresponding heat capacity coefficients. Table 6-97 gives the log K grid from data0.ymp.R5 (Output DTN: SN0612T0502404.014) and the corrected log K grid. The differences are relatively small up to 100°C.

Table 6-95. Heat Capacity (Cp) Data for Strengite ($FePO_4.2H_2O$) (Corrected)

Temp K	*Cp* (Joule/mol-K)
298.15	180.540
300	181.200
400	206.338
500	220.933
600	231.378

Source: Barin and Platzki 1995 [DIRS 157865], p. 711.

Table 6-96. Fitted Heat Capacity (Cp) Coefficients for Strengite (Corrected)

Solid	*a*	*b*	*c*
Strengite	2.0953E+02	5.5101E-02	-4.0377E+06

Source: Output DTN: SN0702T0502404.015, folder: *\Phosphate*, worksheet: *Cp_Solids_j_Phosphates_Set1.xls*.

NOTE: Data are consistent with Cp in units of Joule/mol-K. for the equation: $Cp = a + bT + cT^{-2}$.

Table 6-97. The data0.ymp.R5 and Corrected log K Values for Strengite

Temp. °C	0.01	25	60	100	150	200	250	300
data0.ymp.R5	-11.8075	-12.2416	-12.9308	-13.7531	-14.8382	-16.0358	-17.4293	-19.1736
Corrected	-11.8291	-12.2416	-12.9634	-13.8817	-15.1394	-16.5422	-18.1576	-20.1314

Source: Output DTN: SN0702T0502404.015, folder: *\Phosphate*, workbook: *Minerals_j_Phosphates_Set1.xls*.

UP_2O_7. In the calculation of the log K grid shown in Tables 6-72 and 6-93, the c heat capacity coefficient was incorrectly entered as -1.7827×10^{-5} (consistent with heat capacity in units of J/mol-K). The correct value is -17.827×10^{-5} (consistent with the same units). Table 6-97 gives the log K grid from data0.ymp.R5 (Output DTN: SN0612T0502404.014) and the corrected log K grid. The differences are relatively small up to 250°C.

Table 6-98. The data0.ymp.R5 and Corrected log K Values for UP_2O_7.

Temp. °C	0.01	25	60	100	150	200	250	300
data0.ymp.R5	-17.4200	-17.9135	-18.5384	-19.1979	-20.0200	-20.9256	-22.0167	-23.4534
Corrected	-17.4161	-17.9135	-18.5332	-19.1788	-19.9788	-20.8612	-21.9295	-23.3449

Source: Output DTN: SN0702T0502404.015, folder: *\Phosphate*, workbook: *Minerals_j_Phosphates_Set1.xls*.

$AmPO_4$(am). Worksheet "Americium Phosphate" of workbook *Estim_Cp_solids_j_phosphates_ Set1.xls* (in folder *\Phosphate* of Output DTN: SN0702T0502404.015) provides a four heat capacity coefficient model for $AmPO_4$(am). The calculational template used to calculate the log K grid for this solid in workbook *Minerals_j_Phosphates_Set1.xls* (also in folder *\Phosphate* of Output DTN: SN0702T0502404.015) only allows the use of the three-term Maier-Kelley coefficient. The T^2 term coefficient (-1.15×10^{-5}) was not used there. Therefore, only the 25°C log K value is technically correct. The values at the other grid temperatures are in error. These statements apply to Tables 6-72 and 6-93. The magnitude of the error is however small. Table 6-99 shows gives the log K data grid used in data0.ymp.R5 (Output DTN: SN0612T0502404.014) along with a corrected grid.

Table 6-99. The data0.ymp.R5 and Corrected log K Values for $AmPO_4$(am)

Temp. °C	0.01	25	60	100	150	200	250	300
data0.ymp.R5	-11.9105	-12.4399	-13.2919	-14.3128	-15.6390	-17.0571	-18.6454	-20.5555
Corrected	-11.9103	-12.4399	-13.2916	-14.3114	-15.6352	-17.0502	-18.6347	-20.5401

Source: Output DTN: SN0702T0502404.015, folder: *\Phosphate*, workbook: *Minerals_j_Phosphates_Set1.xls*.

$NiMoO_4$. In the calculation of the log K grid, the T^{-2} term heat capacity coefficient of -1.5788×10^7 (consistent with heat capacity in units of J/mol-K) was incorrectly entered as -1.5788×10^8. Table 6-100 gives the log K grid from data0.ymp.R5 (Output DTN: SN0612T0502404.014) and the corrected log K grid. The differences are not highly significant up to 100°C. Fundamentally, $NiMoO_4$ is not very soluble. However, the log K grid used in data0.ymp.R5 (Output DTN: SN0612T0502404.014) predicts a trend of increasing solubility with increasing temperature, such that above 100°C this phase appears moderately soluble. The corrected data show a trend of decreasing solubility and very low solubility above 100°C.

Table 6-100. The data0.ymp.R5 and Corrected log K Values for $NiMoO_4$

Temp. °C	0.01	25	60	100	150	200	250	300
data0.ymp.R5	-5.8328	-6.5033	-6.6098	-6.1013	-5.1146	-4.1164	-3.3380	-2.9911
Corrected	-6.1822	-6.5033	-7.0706	-7.7878	-8.7575	-9.8273	-11.0601	-12.6017

Source: Output DTN: SN0702T0502404.015, folder: *\Nickel*, workbook: *Solids_j_NiMoO4_CFJC.xls*.

7. CONCLUSIONS

This report supports the qualified use of the thermochemical databases data0.ymp.R2, data0.ymp.R4, and data0.ymp.R5. It qualifies the data0.ymp.R2 database and supporting calculations, and documents the development of the data0.ymp.R4 and data0.ymp.R5 databases as successive improvements. All three of these databases are qualified without supersession in order to maintain support for database applications throughout the suite of analysis/model reports and calculations that support the license application.

This section summarizes the status of the three databases, beginning with the data0.ymp.R2 database, then the data0.ymp.R4 database, which comprises an earlier set of changes, and finally the data0.ymp.R5 database, which includes additional changes. The changes in successive versions of the database incorporate corrections, updates based on new data, and other improvements. Additional information is provided below on the general uncertainty of modeling with thermodynamic databases, and the application of thermodynamic modeling to performance assessment for a Yucca Mountain repository.

In the following discussion, the reader is referred to Table 7-1 for the data tracking numbers and other citation information for the data0.ymp.R2, data0.ymp.R4, and data0.ymp.R5 databases and their supporting calculations packages.

7.1 QUALIFICATION OF DATA0.YMP.R2 AND DEVELOPMENT OF DATA0.YMP.R4

The data sets listed in Table 7-1 were qualified or developed in the course of this analysis. For the data0.ymp.R2 database, the sources used were evaluated and justified. The data0.ymp.R0 database (DTN: MO0009THRMODYN.001 [DIRS 152576]) is the major, qualified source for data used in data0.ymp.R2. In addition handbooks, compilations, and published technical literature were incorporated in the data0.ymp.R2 database by its developers, and were reevaluated in this analysis.

The qualified data0.ymp.R2 database can be used for a broad range of chemical modeling systems. Some errors or discrepancies were identified in the data0.ymp.R2 database, related to some of the sources or the manner of use of data from the sources. These conditions are summarized below and discussed in more detail in Section 6. The presence of errors or problems in the database does not prevent its use as long as the proscriptions itemized below are observed. The affected data are mostly revised or corrected in the data0.ymp.R4 database, which was first issued as output from Rev. 00 of this report. Additional updates and corrections to the data0.ymp.R4 database, and the more recent data0.ymp.R5 database, are discussed in Section 7.2.

Table 7-1. Qualification Status of Thermodynamic Databases

Title	Data Package	Status*	Description
data0.ymp.R2	DTN: MO0302SPATHDYN.000 [DIRS 161756]	Qualified	Thermodynamic database (input)
Supporting Calculations for data0.ymp.R2	DTN: MO0302SPATHDYN.001 [DIRS 161886]	Qualified	Spreadsheets and SUPCRT92 files used to develop data0.ymp.R2 (input)
data0.ymp.R4	DTN: SN0410T0510404.002	Qualified	Corrected (R4) thermodynamic database (output)
Supporting Calculations for data0.ymp.R4	DTN: SN0410T0510404.001	Qualified	Additional spreadsheets supporting data0.ymp.R4 (output)
data0.ymp.R5	DTN: SN0612T0502404.014	Qualified	Corrected (R5) thermodynamic database (output)
Supporting Calculations for data0.ymp.R5	DTN: SN0702T0502404.015	Qualified	Additional spreadsheets supporting data0.ymp.R5 (output)

*as a result of this report.

With respect to qualification of the data0.ymp.R2 database, in addition to the criteria discussed in Section 4.2, the assessment in this report has addressed the following criteria:

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

The data have been cross-checked within the data0.ymp.R2 database to ensure that the data are internally consistent. The change to the "Rimstidt" paradigm for quartz solubility (Section 6.1.5) which was implemented in data0.ymp.R4, 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. Although multiple sources of input data were used in the data0.ymp.R2 database, 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. An inconsistency in key phosphate data was addressed in the development of data0.ymp.R5 (Section 6.7.8).

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 quality assurance program?*

The data used to create the data0.ymp.R2 database using major input from the data0.ymp.R0 database (DTN: MO0009THRMODYN.001 [DIRS 152576]) 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 were 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. These conditions also hold for the additional data used to develop the data0.ymp.R4 database and its supporting calculations package, and the data0.ymp.R5 database and its supporting calculations package (see Table 7-1).

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, are compatible with the previous data0.ymp.R0 database which 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. The changes used to create the data0.ymp.R2 database, and the justification for those changes, are documented in this report. These conditions also hold for the additional data used to develop the data0.ymp.R4 database and its supporting calculations package, and the data0.ymp.R5 database and its supporting calculations package (see Table 7-1), in which a series of improvements have been made in the quality of the data and in adding new data to assure completeness in applications of the data.

Molar volume data for many phases were included in the data0.ymp.R2 database 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, 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 differences are expected because of the variable hydration condition of measured clay mineral samples, which affects the unit-cell structure data.

As a result of the data evaluation described in Section 6, various errors and discrepancies have been 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. 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 potential applications for the database that are affected by such errors or discrepancies, such as modeling of gaseous species, cement phases, etc., are identified in the summary below. Similar known problems with the data0.ymp.R4 database, and also the data0.ymp.R5 database, are also identified and discussed in this report.

7.1.1 Summary of Known Limitations for the data0.ymp.R2 Database

The errors, discrepancies, and uncertainties found in qualification of the data0.ymp.R2 database (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, caused potentially significant differences in the log K values. 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. The magnitude of differences between data0.ymp.R2 and data0.ymp.R4 was assessed, and the differences were found to be largest at higher temperatures. Section 6.3.2 provides further details including tabulation of corrected log K values and listing of the differences (Δlog 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 and data0.ymp.R5, which should be used instead for this purpose.

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 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 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 Ca-gismondine in data0.ymp.R2 are incorrect. No corroborating data are available for Na-gismondine, but the same conclusion is drawn by analogy to Ca-gismondine.

The data block for the cement phase "Friedl salt" (Section 6.3.3.4) is inactive in the data0.ymp.R2 database; the data for this phase in data0.ymp.R2 were 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; these species appear in the data0.ymp.R4 database the same as in data0.ymp.R2, and are not recommended for use.

The log K value for syngenite at 25°C presented in data0.ymp.R2 could not 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 thermodynamic database, data0.ypf (DTN: SN0302T0510102.002 [DIRS 162572]) was identified. The difference between the value in data0.ymp.R2 and this alternative value (0.15 log units) is insignificant. Therefore the syngenite log K value in data0.ymp.R2 may be used at 25°C.

Correction of Stoichiometry for the Pu Phase $PuO_2(OH)_2{\cdot}H_2O$ – A modification of the Pu solid $PuO_2(OH)_2{:}H_2O$ was made to correct an error found in data0.ymp.R2 related to the stoichiometry of this species (the incorrect $PuO_2(OH)_2{:}2H_2O$ was corrected to $PuO_2(OH)_2{:}H_2O$). This correction is consistent with the usage in Lemire (2001 [DIRS 159027], Section 17.2.2.1). The correction is carried into the new data0.ymp.R4 and data0.ymp.R5 databases.

Correction to log K Values for HF_2^- 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 with respect to the reaction given in the source. The protonated form of hydrofluoric acid (HF) is related to the formation of HF_2^- (Equation 6-36). Aqueous dissociation of hydroflouric 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 data0.ymp.R4 and data0.ymp.R5 databases.

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); see 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 log K values, for the data0.ymp.R4 and data0.ymp.R5 databases. 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 and data0.ymp.R5 databases, 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 Δlog 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 (Δlog K). The corrected values are not included in the updated data0.ymp.R4 database, but are included in data0.ymp.R5.

In summary, the most substantial errors for active data blocks in data0.ymp.R2 pertain to the zeolites, the gismondine cement species (Na and Ca), and the corrected stoichiometry of the Pu phase $PuO_2(OH)_2 \cdot H_2O$. The error associated with HF_2^- is potentially significant depending on the pH range and fluoride activity.

In addition to the qualification findings summarized above, a number of other assumptions and approximations associated with the data0.ymp.R2 database were identified, which can affect use of the database:

Thermodynamic Data for Steam – As identified in Section 6.1.2, thermodynamic data for steam 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.

SUPCRT92 Properties for High-pH Aqueous Silica Species – Reevaluation of SUPCRT92 properties was not performed for high-pH aqueous silica species (see Section 6.1.5) because these species 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.

Correction of Silicate Data to the Rimstidt Paradigm – Thermodynamic data for 28 silicon-bearing minerals and two silicon-bearing gas species were not corrected to the Rimstidt paradigm (Section 6.1.5). The relevant species are identified in Table 7-2. 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.

Thermodynamic Data for Clays – The thermodynamic data for clays have some additional uncertainties (Section 6.3.1) because clay species in the data0.ymp.R2 database have idealized formulae, and the mineralogical compositions of clays can be uncertain, especially in nature. Also, the temperature dependence of Gibbs energies for exchangeable components in clays are approximate. Additional detailed information on uncertainty associated with thermodynamic properties of clay minerals is provided in Section 6.3.1.

Temperature Range of Data for Clays – 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 500 K (except for NH_4-clinoptilolite, which was measured only at 25°C).

Minor Errors in Data for Uranium Silicates – 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 are qualified for use.

Table 7-2. List of Silicon-Containing Solids and Gases in data0.ymp.R2 for Which Thermodynamic Data Have Not Been Revised for Consistency with the Rimstidt Paradigm

Species Name	Chemical Formula
Alamosite	$PbSiO_3$
Ba2Si3O8	$Ba_2Si_3O_8$
Ba2SiO4	Ba_2SiO_4
BaSiF6	$BaSiF_6$
CdSiO3	$CdSiO_3$
Co2SiO4	Co_2SiO_4
Coffinite	$USiO_4$
Dicalcium_silicate	Ca_2SiO_4
Eucryptite	$LiAlSiO_4$
Hatrurite	Ca_3SiO_5
Larnite	Ca_2SiO_4
Mordenite-dehy	$Ca_{0.2895}Na_{0.361}Al_{0.94}Si_{5.06}O_{12}$
Na2SiO3	Na_2SiO_3
Na4SiO4	Na_4SiO_4
Na6Si2O7	$Na_6Si_2O_7$
Natrosilite	$Na_2Si_2O_5$
Pb2SiO4	Pb_2SiO_4
Petalite	$LiAlSi_4O_{10}$
Rankinite	$Ca_3Si_2O_7$
Rhodonite	$MnSiO_3$
Sanbornite	$BaSi_2O_5$
Silicon	Si
Spodumene	$LiAlSi_2O_6$
Sr2SiO4	Sr_2SiO_4
SrSiO3	$SrSiO_3$
Tridymite	SiO_2
Zircon	$ZrSiO_4$
Zn2SiO4	Zn_2SiO_4
Si(g)	Si(g)
SiF4(g)	SiF_4(g)

NOTE: The data for these species have not been subsequently revised in data0.ymp.R4 (Output DTN: SN0410T0510404.002) or data0.ymp.R5 (Output DTN: SN0612T0502404.014).

7.1.2 Corrections Implemented in the data0.ymp.R4 Database

For users of the data0.ymp.R2 database (DTN: MO0302SPATHDYN.000 [DIRS 161756]), given the conditions identified in Section 7.1.1, this report provides a corrected data0.ymp.R4 database (Output DTN: SN0410T0510404.002) plus tabulation of the log K differences for all affected species not included in the data0.ymp.R4 database (Output DTN: SN0410T0510404.002). The corrections include the following changes as discussed above: corrected zeolite log K values; corrected log K values for HF_2^- dissociation; corrected stoichiometry for $PuO_2(OH)_2{\cdot}H_2O$; and corrected log K values for Np and Pu solids. The cement phases gismondine (Na and Ca) could not be corrected, nor could data for “Friedl salt.” Data for syngenite are suitable for use and did not require correction in data0.ymp.R4. Corrected log K values for certain metal-gas species and associated solids were produced (see Section 6.3.4.5) but were not incorporated in data0.ymp.R4.

For additional problems identified subsequent to data0.ymp.R4, this report also provides the data0.ymp.R5 database (Output DTN: SN0612T0502404.014) discussed in Section 7.2.

7.1.3 Use of Cement Data

Many of the cement mineral phases (e.g., portlandite, tobermorite, and gyrolite) included in the data0.ymp.R2 database and the data0.ymp.R4 database are naturally occurring minerals and could be formed if thermodynamically or kinetically possible. However, some other cement phases in the data0.ymp.R2 database 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 formed by alteration of cement, 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 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.

7.2 ADDITIONAL CORRECTIONS IMPLEMENTED IN THE DATA0.YMP.R5 DATABASE

Other errors, discrepancies, or uncertainties have been noted in the data0.ymp.R4 database, and addressed in data0.ymp.R5. Some of these involve a set of Condition Reports (CRs): CR 6489, CR 6731, CR 7542, and CR 7756) described in *Technical Work Plan for: Thermodynamic Databases for Chemical Modeling* (BSC 2006 [DIRS 177885]). These CRs have been addressed in the data0.ymp.R5 database, as described in the following paragraphs.

CR 6489: Sensitivity Studies on Form of Sepiolite Used in ANL-EBS-MD-000074, Rev. 01, (BSC 2005 [DIRS 175058]). The text of this CR that applies to the data0.ymp.R5 database is as follows:

> The IDPS model (EQ3/6 simulations) is used in the Analysis of Dust Deliquescence for FEP Screening, ANL-EBS-MD-000074 Rev 00. The IDPS model uses the precipitation of the mineral, sepiolite as the primary mechanism controlling magnesium concentrations in brines. The thermodynamic data base, data0.ypf.R0 contains the log K value for crystalline sepiolite. Validation of the IDPS model in In-Drift Precipitates/Salt Model, ANL-EBS-MD-000045 REV 02, Section 7.1.1, required changing the log K value for sepiolite by 6 log units to match experimental data. The modified log K represents an amorphous form of sepiolite rather than the crystalline form…Modifying the IDPS model

> with the revised log K for amorphous sepiolite and running the simulations of the brine formed by evaporation would improve the confidence in the results of the model as it applied to dust deliquescence.

The IDPS model (SNL 2007 [DIRS 177411]) uses a log K for amorphous sepiolite as an important mechanism limiting total magnesium concentration in brines. The species Sepiolite(am) ($Mg_4Si_6O_{15}(OH)_2{:}6H_2O$) was added to the data0.ymp.R5 database, with a limited log K data grid spanning the temperature range 0°C to 100°C. As this is a metastable amorphous phase, it is probably reasonable to limit the log K grid to this range (this phase should transform to something else, such as crystalline sepiolite, at higher temperature). The related phase palygorskite ($Mg_{2.84}Al_{1.8}Si_{7.73}O_{20}(OH)_2{:}4H_2O$) was also added to the database, but is represented only by a 25°C log K value. This is not inappropriate as this is a strictly low-temperature phase. Another related solid, antigorite(am) ($Mg_3Si_2O_5(OH)_4$) was also added, and is represented by a log K grid spanning the full 0°C to 300°C. This phase probably does not exist in the higher end of this temperature range, so this is more than sufficient.

CR 6731: Discrepancy in thermodynamic data for phosphate species. The text of this CR that is relevant to the data0.ymp.R5 database is as follows:

> [the originator has identified]….discrepancies in key thermodynamic data used to develop the data0.ymp.R0 and successor data0.ymp.R2 thermochemical databases (see ANL-WIS-GS-000003 Rev. 00). The data0.ymp.R0 database is used as a starting point for a Pitzer database in the In-Drift Precipitates/Salts AMR (ANL-EBS-MD-000045 Rev. 02) which is applied in the seepage evaporation abstraction for TSPA (ANL-EBS-MD-000033 Rev. 05). Phosphate species are not included in these models, and are likely to be very scarce in the EBS chemical environment. In other models, however, phosphate may be a significant reactant. Because phosphate forms insoluble precipitates with certain actinides (e.g., U) and other important elements (e.g., Gd), discrepant thermodynamic data for phosphate species may be significant to TSPA abstractions or FEP exclusion (see ANL-EBS-MD-000037 Rev. 04)…[in addition, we are] unable to verify the stoichiometry of $GdPO_4{:}10H_2O$ from the source cited in the data0.ymp.R2 database (ANL-WIS-GS-000003 Rev. 00). This is a different but related issue to the one identified in the attachment, and the two issues should be evaluated together.

The phosphate aqueous and solid species data have been revised (Section 6.7.8) where necessary to achieve consistency in the data0.ymp.R5 database with the CODATA (Cox et al. 1989 [DIRS 150874]) recommendations for key phosphate data. This resolution addresses the strong inconsistency between the recommendations of CODATA (Cox et al. 1989 [DIRS 150874]) and the *NBS Tables* (Wagman et al. 1982 [DIRS 159216]), and achieves consistency with the recommendations of the OECD/NEA data volumes (e.g., Grenthe et al. 1992 [DIRS 101671]; Silva et al. 1995 [DIRS 102087]; Lemire 2001 [DIRS 159027]) which adopt the CODATA recommendations for key phosphate data. Not all phosphate data required modification to achieve this consistency. Another issue regarding the number of waters of hydration of trivalent rare earth phosphate solids is also resolved (Section 6.7.8) with the result that most such solids have only one or two waters of hydration.

CR 7542: Thermodynamic database (data0.ymp.R4) update [$NiCO_3$ solid]. The text of this CR as it pertains to the data0.ymp.R5 database is as follows:

> The solid mineral $NiCO_3$ (nickel carbonate) has been identified as needing an update in the data0.ymp.R4 thermodynamic database(DTN: SN0410T0510404.002). The ymp.R4 data leads to a very high nickel solubility and is realized in the in-package chemistry calculations (ANL-EBS-MD-000037 REV 04). A recent NAGRA 2002 report (02-16; TIC 253421) states how previous databases commonly contained this incorrect solubility product…The updated value from NAGRA is already contained within data0.ypf.R2 (DTN: SN0504T0502205.008).

The data for $NiCO_3$(s) at 25°C were updated in the data0.ymp.R5 database, consistent with the recommendations of Hummel et al. (2002 [DIRS 161904]). Data for the species $NiCO_3$(aq) at 25°C were also added using data from the same source. Data for the related solid $NiCO_3$:5.5H_2O (25°C only, based on Gamsjäger et al. 2005 [DIRS 178266]) were also added.

CR 7756: **Add mineral phases observed in UO_2 drip tests and natural analogue to EQ3/6 databases**. The text of this CR that is relevant to the data0.ymp.R5 database is as follows:

> A number of secondary minerals observed in UO_2 dissolution experiments and/or at the Pena Blanca uraninite deposit are not included in YMP thermodynamic databases such as data0.ymp.R4 used in TSPA. They include [the following listed species]: haiweeite, dehydrated schoepite (UO_3:0.8-1.0H_2O), becquerelite, compreignacite, sklodowskite, boltwoodite ($KH(UO_2)SiO_4$:1.5H_2O), beta-uranophane (same formula as uranophane), palygorskite, ianthinite, and weeksite ($K_2(UO_2)_2Si_6O_{15}$:4H_2O). Because these minerals are observed to form under conditions similar to conditions that could develop at the repository, they should be added to the databases, if data are available. Without these phases in the databases, one cannot predict their potential formation and accumulation nor their potential effects on water composition.

Data for various secondary uranium minerals were added to data0.ymp.R5 database (Section 6.7.10). Data for some other secondary uranium minerals which had already been added to data0.ymp.R4 were re-examined and recalculated. The present representation of secondary uranium minerals has been significantly improved in terms of the set of such solids known to occur with reasonable frequency in natural uranium deposits. This representation should also produce somewhat more realistic results of secondary mineral formation resulting from spent fuel degradation.

The data0.ymp.R5 database also implements other improvements to data0.ymp.R4, addressing the following items as called out in the TWP (BSC 2006 [DIRS 177885]):

New Data for Se(VI) and Sn(IV) Species. The data0.ymp.R4 database includes data for aqueous and solid species involving these two components, but additional data were added to data0.ymp.R5 (Sections 6.7.2 and 6.7.4) to expand the stability range and number of possible solid and aqueous species. The aqueous species $CaSeO_4$(aq) and the solid $CaSeO_4$:2H_2O(s) were added, with $CaSeO_4$:2H_2O(s) replacing the species named *CaSeO4* in data0.ymp.R4. The solid SnO_2(s) and aqueous complexes $Sn(OH)_5^-$ and $Sn(OH)_6^{2-}$ were also added to data0.ymp.R5.

Addition of the Phase $NiMoO_4(s)$. Thermodynamic data for this Ni-bearing phase recently reported by Morishita and Navrotsky (2003 [DIRS 176846]) were added to data0.ymp.R5 (Section 6.7.5). Thermodynamic data for this phase as a function of temperature can be used with data for aqueous species already in the database to calculate a log K value for the hydrolysis reaction (subject to the limitations noted in Section 6.8).

Review of Complexation Data for the Species $Th(CO_3)_5^{6-}$. The species *ThO2(am)* is replaced by *ThO2.2H2O(am)* in data0.ymp.R5, giving a formula that is more explicit regarding water content (Section 6.7.6). The species *Th(CO3)5(6-)* is deleted from data0.ymp.R5, and data for the species *Th(OH)3+*, *Th(OH)4(aq)*, and *Th(OH)3(CO3)-* are revised. These changes are directed to more defensible solubility calculations, since the activity model for highly charged species can have a strong effect on solubility, particularly where there is a high concentration of dissolved carbonate in solution.

Add Kogarkoite (Na_3SO_4F) to the Databases. This phase has been identified as a product of the experimental evaporation of synthetic seepage solutions, and is added to data0.ymp.R5 (Section 6.7.3).

Changes Involving Reactions for Some Cr Species. The reactions for the aqueous species CrO_3Cl^- and the solids Cr_2O_3 (eskolaite) and CrO_2 are changed in data0.ymp.R5, to preserve the oxidation state of the Cr in typical modeling applications, to the extent possible. These changes facilitate suppressions in the problem definition in the computer software package EQ3/6 input file.

Changes Involving Some Other Cr Species. Changes are made for some Cr species in data0.ymp.R5 to obtain better consistency with the solubility of $Cr(OH)_3(am)$ as a function of pH (Section 6.7.11). The species $Cr_3(OH)_4^{5+}$ and $Cr_2(OH)_2^{4+}$ are deleted, and the data for $CrOH^{2+}$, $Cr(OH)_3(aq)$, and $Cr(OH)_3(am)$ are changed.

Incorporate Tabulated Data Corrections. The corrected log K grids for gas species listed in Table 6-42, were added to data0.ymp.R5 to correct an interpretation error in the heat capacity coefficients (Section 6.4).

In a number of instances, qualified data have different values in different versions of the database described in this analysis report. All known errors, discrepancies, or uncertainties with these databases are documented in this report, and corrected values have been calculated or the magnitudes of the errors are otherwise constrained. These errors are small numerically, are significant only at temperatures above the range of interest to the Yucca Mountain Project, or involve species not expected to be relevant to Yucca Mountain Project systems, and are thus generally non-impacting for Yucca Mountain Project use. Only one notable error is known and this concerns the 25°C log K value for the solid ferrimolybdite ($Fe_2(MoO_4)_3$). These errors are summarized in Section 6.8.

7.3 EVALUATION OF UNCERTAINTY AND RECOMMENDED USE OF THE DATABASES

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, and the updated data0.ymp.R4 and data0.ymp.R5 databases to determine the appropriate assemblage of clay minerals 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.

7.3.1 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 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 PuO_2 and NpO_2 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 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 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 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 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 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 statistical rigor. Apparent bounds or an informally defined scale of measurement are the approaches most typically used.

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 energies of formation at 298.15 K 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 Östhols 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 and its successors, and is therefore of special interest. With regard to other methods which have been used previously, the reader is referred to other sources, particularly the NEA guidelines on temperature extrapolations (Puigdomenech et al. 1997 [DIRS 159204], 1999 [DIRS 159205]). That source recommends use of the isocoulombic/ isoelectric method to about 275°C.

The isocoulombic/isoelectric method requires as inputs Gibbs energies (or log K values) and entropies, normally for 298.15 K. 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 energy of formation for Am^{3+} which is a basis species for this element in the data0.ymp.R2 database. While the example is limited, the comparison is instructive.

Calculation of the apparent Gibbs energy of formation using the isocoulombic/isoelectric method is addressed, given a choice of different reference reactions. The Am^{3+} ion is not in the SUPCRT92 database, so the Gibbs energy grid was calculated for the normal library worksheets. The basic 25°C data (Gibbs energy of formation and entropy) for the Am^{3+} were taken from Silva et al. (1995 [DIRS 102087], p. 37). All other data were taken from the SUPCRT92 database. Calculations were done in spreadsheet *BasisSpecies_j_TJW_1.xls* (DTN: MO0302SPATHDYN.001 [DIRS 161886]). The following reference reactions were considered:

$$2Am^{3+} + Cr_2O_3 = 2Cr^{3+} + Am_2O_3 \quad \text{(Eq. 7-1)}$$

$$2Am^{3+} + Fe_2O_3 = 2Fe^{3+} + Am_2O_3 \quad \text{(Eq. 7-2)}$$

$$2Am^{3+} + Ce_2O_3 = 2Ce^{3+} + Am_2O_3 \quad \text{(Eq. 7-3)}$$

$$2Am^{3+} + Gd_2O_3 = 2Gd^{3+} + Am_2O_3 \quad \text{(Eq. 7-4)}$$

$$2Am^{3+} + Lu_2O_3 = 2Lu^{3+} + Am_2O_3 \quad \text{(Eq. 7-5)}$$

$$2Am^{3+} + UO_2 = 2U^{3+} + AmO_2 \quad \text{(Eq. 7-6)}$$

The results are shown in Tables 7-3 and 7-4. 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 analogues considered here. The properties of Fe^{3+}, U^{3+} and the trivalent rare earths are difficult to obtain because ferric iron is rather insoluble; those of U^{3+} 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 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 7-3. Isocoulombic Extrapolation of the Calculated Apparent Gibbs Energy Grids of Am^{3+} Comparing Extrapolations Using Various Reference Reactions

T (°C)	Cr^{3+} Analogue	Fe^{3+} Analogue	Ce^{3+} Analogue	Gd^{3+} Analogue	Lu^{3+} Analogue	U^{3+} Analogue	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

Source: DTN: MO0302SPATHDYN.001 [DIRS 161886], spreadsheet: *BasisSpecies_j_TJW_1.xls*.

NOTE: Characterized by analogues; see text for details. Units are Joules/mole.

Table 7-4. Isocoulombic Extrapolation of the Calculated Apparent Gibbs Energy Deviations from Mean of Am^{3+}

T (°C)	Cr^{3+} Analogue	Fe^{3+} Analogue	Ce^{3+} Analogue	Gd^{3+} Analogue	Lu^{3+} Analogue	U^{3+} Analogue
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

Source: DTN: MO0302SPATHDYN.001 [DIRS 161886], spreadsheet: *BasisSpecies_j_TJW_1.xls*.

NOTE: Characterized by analogues; see text for details. Units are Joules/mole.

INTENTIONALLY LEFT BLANK

8. INPUTS AND REFERENCES

The following is a list of the references cited in this document. Column 1 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.

8.1 DOCUMENTS CITED

178785 Abrefah, J.; Marschman, S.C.; and Jenson, E.D. 1998. *Examination of the Surface Coatings Removed from K-East Basin Fuel Elements.* PNNL-11806. Richland, Washington: Pacific Northwest National Laboratory. ACC: MOL.20070109.0009.

173048 Altmaier, M.; Neck, V.; Müller, R.; and Fanghänel, Th. 2005. "Solubility of $ThO_2 \cdot xH_2O(am)$ in Carbonate Solution and the Formation of Ternary Th(IV) Hydroxide-Carbonate Complexes." *Radiochimica Acta, 93,* 83-92. München, Germany: Oldenbourg Wissenschaftsverlag. TIC: 257060.

103750 Altman, W.D.; Donnelly, J.P.; and Kennedy, J.E. 1988. *Qualification of Existing Data for High-Level Nuclear Waste Repositories: Generic Technical Position.* NUREG-1298. Washington, D.C.: U.S. Nuclear Regulatory Commission. TIC: 200652.

103597 Altman, W.D.; Donnelly, J.P.; and Kennedy, J.E. 1988. *Peer Review for High-Level Nuclear Waste Repositories: Generic Technical Position.* NUREG-1297. Washington, D.C.: U.S. Nuclear Regulatory Commission. TIC: 200651.

176843 Amaya, T.; Chiba, T.; Suzuki, K.; Oda, C.; Yoshikawa, H.; and Yui, M. 1997. "Solubility of Sn(IV) Oxide in Dilute $NaClO_4$ Solution at Ambient Temperature." *Scientific Basis for Nuclear Waste Management XX, Symposium held December 2-6, 1996, Boston, Massachusetts.* Gray, W.J. and Triay, I.R., eds. *465,* 751-758. Pittsburgh, Pennsylvania: Materials Research Society. TIC: 238884.

153209 Anthony, J.A.; Kaur, H.; Kemnitz, C.R.; and Baron, D. 2000. "Precipitation/Dissolution Equilibria in the System Fe(III)-Cr(VI)-H2O." Boulder, Colorado: Geological Society of America. Accessed December 20, 2000. TIC: 249236. URL: http://rock.geosociety.org/absindex/annual/2000/20583.htm

179602 Assaaoudi, H.; Ennaciri, A.; and Rulmont, A. 2001. "Vibrational Spectra of Hydrated Rare Earth Orthophosphates." *Vibrational Spectroscopy, 25,* (1), 81-90. New York, New York: Elsevier. TIC: 259201.

177992 Assaaoudi, H.; Ennaciri, A.; Rulmont, A.; and Harcharras, M. 2000. “Vibrational Spectra and Structure of Rare Earth Orthophosphates Weinschenkite Type.” *Phase Transitions, 72,* 1-13. New York, New York: Overseas Publishers Association. TIC: 258626.

177936 Assaoudi, H. and Ennaciri, A. 1997. “Vibrational Spectra and Structure of Rare Earth Orthophosphates Weinschenkite Type.” *Spectrochimica Acta, Part A,* (53), 895-902. New York, New York: Elsevier. TIC: 258620.

100700 Atkins, M.; Bennett, D.; Dawes, A.; Glasser, F.; Kindness, A.; and Read, D. 1992. *A Thermodynamic Model for Blended Cements.* DoE/HMIP/RR/92/005. London, England: Department of the Environment. TIC: 233334.

116979 Atkins, M.; Glasser, F.P.; Kindness, A.; and Macphee, D.E. 1991. *Solubility Data for Cement Hydrate Phases (25(SUP O)C). Experimental Data Generated at Aberdeen University During 1987-1990.* DOE/HMIP/RR/91/032. London, England: Department of the Environment, Her Majesty's Inspectorate of Pollution. TIC: 241636.

131758 Atkins, M.; Glasser, F.P.; Moroni, L.P.; and Jack, J.J. 1993. *Thermodynamic Modelling of Blended Cements at Elevated Temperatures (50-90°C).* DoE/HMIP/RR/94/011. Aberdeen, United Kingdom: Aberdeen University. TIC: 235985.

116981 Babushkin, V.I.; Matveyev, G.M.; and Mchedlov-Petrossyan, O.P. 1985. *Thermodynamics of Silicates.* Mchedlov-Petrossyan, O.P., ed. Berlin, Germany: Springer-Verlag. TIC: 244843.

157860 Baes, C.F., Jr. and Mesmer, R.E. 1976. *The Hydrolysis of Cations.* Pages 1, 6, 7, 176, 177, 180, 181, 184-191. New York, New York: John Wiley & Sons. TIC: 217440.

100702 Baes, C.F., Jr. and Mesmer, R.E. 1986. *The Hydrolysis of Cations.* Malabar, Florida: Krieger Publishing Company. TIC: 223481.

163015 Ball, J.W. and Nordstrom, D.K. 1998. "Critical Evaluation and Selection of Standard State Thermodynamic Properties for Chromium Metal and its Aqueous Ions, Hydrolysis Species, Oxides, and Hydroxides." *Journal of Chemical & Engineering Data, 43,* (6), 895-918. Washington, D.C.: American Chemical Society. TIC: 254015.

160926 Barin, I. and Knacke, O. 1973. *Thermochemical Properties of Inorganic Substances.* New York, New York: Springer-Verlag. TIC: 248490.

157865 Barin, I. and Platzki, G. 1995. *Thermochemical Data of Pure Substances.* 3rd Edition. Two volumes. New York, New York: VCH Publishers. TIC: 251934.

172415 Barthelmy, D. 2004. “Beidellite.” Beidellite Mineral Data. Spring, Texas: David Barthelmy. Accessed October 25, 2004. TIC: 256691. URL: http://www.webmineral.com/data/Beidellite.shtml

172410 Barthelmy, D. 2004. “Chabazite.” Chabazite Mineral Data. Spring, Texas: David Barthelmy. Accessed October 25, 2004. TIC: 256692. URL: http://www.webmineral.com/data/Chabazite.shtml

172414 Barthelmy, D. 2004. “Erionite.” Erionite Mineral Data. Spring, Texas: David Barthelmy. Accessed October 25, 2004. TIC: 256693. URL: http://www.webmineral.com/data/Erionite.shtml

172412 Barthelmy, D. 2004. “Ferrimolybdite.” *Ferrimolybdite Mineral Data.* Spring, Texas: David Barthelmy. Accessed October 25, 2004. TIC: 256694. URL: http://www.webmineral.com/data/Ferrimolybdite.shtml

172407 Barthelmy, D. 2004. “Ferro-Aluminoceladonite Mineral Data.” Spring, Texas: David Barthelmy. Accessed October 25, 2004. TIC: 256695. URL: http://webmineral.com/data/Ferro-aluminoceladonite.shtml

172408 Barthelmy, D. 2004. “Ferroceladonite.” *Ferroceladonite Mineral Data.* Spring, Texas: David Barthelmy. Accessed October 25, 2004. TIC: 256696. URL: http://www.webmineral.com/data/Ferroceladonite.shtml

172413 Barthelmy, D. 2004. “Montmorillonite.” *Montmorillonite Mineral Data.* Spring, Texas: David Barthelmy. Accessed October 25, 2004. TIC: 256697. URL: http://www.webmineral.com/data/Montmorillonite.shtml

156182 Batchelor, B. and Wu, K. 1993. “Effects of Equilibrium Chemistry on Leaching of Contaminants from Stabilized/Solidified Wastes.” Chapter 9 of *Chemistry and Microstructure of Solidified Waste Forms.* Spence, R.D., ed. Boca Raton, Florida: Lewis Publishers. TIC: 250621.

178818 Baturin, S.V. and Sidorenko, G.A. 1985. “Crystal Structure of Wicksite $(K_{0.62}Na_{0.38})_2(UO_2)_2[Si_5O_{13}]\cdot 3H_2O$.” *Soviet Physics Doklady, 30,* (6), 435 - 437. New York, New York: American Institute of Physics. TIC: 259084.

116990 Bennett, D.G.; Read, D.; Atkins, M.; and Glasser, F.P. 1992. “A Thermodynamic Model for Blended Cements. II: Cement Hydrate Phases; Thermodynamic Values and Modelling Studies.” *Journal of Nuclear Materials, 190,* 315-325. Amsterdam, The Netherlands: Elsevier. TIC: 246493.

100707 Berner, U. 1990. A Thermodynamic Description of the Evolution of Pore Water Chemistry and Uranium Speciation During the Degradation of Cement. PSI-Bericht 62. Wurenlingen und Villigen, Switzerland: Paul Scherrer Institut. TIC: 238928.

116991 Berner, U.R. 1987. "Modeling Porewater Chemistry in Hydrated Portland Cement." *Scientific Basis for Nuclear Waste Management X, Symposium held December 1-4, 1986, Boston, Massachusetts.* Bates, J.K. and Seefeldt, W.B., eds. *84,* 319-330. Pittsburgh, Pennsylvania: Materials Research Society. TIC: 203663.

158955 Binnewies, M. and Milke, E. 1999. *Thermochemical Data of Elements and Compounds.* New York, New York: Wiley-VCH. TIC: 251818.

178647 Birley, G.I. and Skinner, H.A. 1968. "Heat of Hydrolysis of Phosphorus Pentachloride, and Heat of Formation of Aqueous Orthophosphoric Acid." *Transactions of the Faraday Society, 64,* (552), 3232-3234. London, England: Faraday Society. TIC: 258902.

178220 Birsoy, R. 2002. "Formation of Sepiolite-Palygorskite and Related Minerals from Solution." *Clays and Clay Minerals, 50,* (6), 736-745. Aurora, Colorado: Clay Minerals Society. TIC: 258823.

149834 Bourcier, W.L.; Knauss, K.G.; and Jackson, K.J. 1993. "Aluminum Hydrolysis Constants to 250°C from Boehmite Solubility Measurements." *Geochimica et Cosmochimica Acta, 57,* 747-761. New York, New York: Pergamon Press. TIC: 235219.

105235 Brindley, G.W. and Brown, G. 1980. *Crystal Structures of Clay Minerals and Their X-Ray Identification.* Mineralogical Society Monograph No. 5. London, England: Mineralogical Society. TIC: 243417.

100710 Bruton, C.J.; Meike, A.; Viani, B.E.; Martin, S.; and Phillips, B.L. 1993. "Thermodynamic and Structural Characteristics of Cement Minerals at Elevated Temperature." *Proceedings of the Topical Meeting on Site Characterization and Model Validation, FOCUS '93, September 26-29, 1993, Las Vegas, Nevada.* Pages 150-156. La Grange Park, Illinois: American Nuclear Society. TIC: 102245.

170268 BSC (Bechtel SAIC Company) 2004. *Data Qualification for Thermodynamic Data Used to Support THC Calculations.* ANL-NBS-HS-000043 REV 00. Las Vegas, Nevada: Bechtel SAIC Company. ACC: DOC.20041118.0004.

169860 BSC 2004. *Engineered Barrier System: Physical and Chemical Environment.* ANL-EBS-MD-000033 REV 03. Las Vegas, Nevada: Bechtel SAIC Company. ACC: DOC.20041201.0001; DOC.20050411.0004.

170031 BSC 2004. *Mineralogic Model (MM3.0) Report.* MDL-NBS-GS-000003 REV 01. Las Vegas, Nevada: Bechtel SAIC Company. ACC: DOC.20040908.0006.

169565 BSC 2004. *Multiscale Thermohydrologic Model.* ANL-EBS-MD-000049 REV 02. Las Vegas, Nevada: Bechtel SAIC Company. ACC: DOC.20041014.0008.

171916 BSC 2004. Qualification of Thermodynamic Data for Geochemical Modeling of Mineral–Water Interactions in Dilute Systems. ANL-WIS-GS-000003 REV 00. Las Vegas, Nevada: Bechtel SAIC Company. ACC: DOC.20041129.0006.

174223 BSC (Bechtel SAIC Company) 2005. *Pitzer Database Expansion to Include Actinides and Transition Metal Species (data0.ypf.R1).* ANL-WIS-GS-000001 REV 00. Las Vegas, Nevada: Bechtel SAIC Company. ACC: DOC.20050427.0005.

161237 BSC (Bechtel SAIC Company) 2004. *Environment on the Surfaces of the Drip Shield and Waste Package Outer Barrier.* ANL-EBS-MD-000001 REV 01. Las Vegas, Nevada: Bechtel SAIC Company. ACC: DOC.20041116.0005.

175058 BSC 2005. *Analysis of Dust Deliquescence for FEP Screening.* ANL-EBS-MD-000074 REV 01. Las Vegas, Nevada: Bechtel SAIC Company. ACC: DOC.20050829.0002.

174583 BSC 2005. *In-Package Chemistry Abstraction.* ANL-EBS-MD-000037 REV 04. Las Vegas, Nevada: Bechtel SAIC Company. ACC: DOC.20050714.0003; DOC.20051130.0007.

172402 BSC 2004. *Technical Work Plan for: Near-Field Environment and Transport In-Drift Geochemistry Analyses.* TWP-MGR-PA-000013 REV 02. Las Vegas, Nevada: Bechtel SAIC Company. ACC: DOC.20041101.0001.

177885 BSC 2006. *Technical Work Plan for: Thermodynamic Databases for Chemical Modeling.* TWP-MGR-PA-000039 REV 01. Las Vegas, Nevada: Bechtel SAIC Company. ACC: DOC.20060912.0005.

178287 Burakov, B.E.; Strykanova, E.E.; and Anderson, E.B. 1997. "Secondary Uranium Minerals on the Surface of Chernobyl 'LAVA'." *Scientific Basis for Nuclear Waste Management XX, Symposium held December 2-6 1996, Boston Massachusetts.* Gray, W.J. and Triay, I.R., eds. *465,* 1309 -1311. Pittsburgh, Pennsylvania: Materials Research Society. TIC: 238884.

127210	Burns, P.C. 1998. "The Structure of Boltwoodite and Implications of Solid Solution Toward Sodium Boltwoodite." *The Canadian Mineralogist, 36,* 1069-1075. Ottawa, Ontario, Canada: Mineralogical Association of Canada. TIC: 246038.
172265	Calvo, C. and Faggiani, R. 1975. "Structure of Nickel Orthophosphate." *Canadian Journal of Chemistry, 53,* (10), 1516-1520. Ottawa, Canada: National Research Council of Canada. TIC: 252224.
105213	Carlos, B.A.; Chipera, S.J.; Bish, D.L.; and Raymond, R. 1995. "Distribution and Chemistry of Fracture-Lining Zeolites at Yucca Mountain, Nevada." *Natural Zeolites '93: Occurrence, Properties, Use, Proceedings of the 4th International Conference on the Occurrence, Properties, and Utilization of Natural Zeolites, June 20-28, 1993, Boise, Idaho.* Ming, D.W. and Mumpton, F.A., eds. Pages 547-563. Brockport, New York: International Committee on Natural Zeolites. TIC: 243086.
100714	Casas, I.; Bruno, J.; Cera, E.; Finch, R.J.; and Ewing, R.C. 1994. *Kinetic and Thermodynamic Studies of Uranium Minerals - Assessment of the Long-Term Evolution of Spent Nuclear Fuel.* SKB TR-94-16. Stockholm, Sweden: Svensk Kärnbränsleförsörjning A.B. TIC: 213723.
102432	Casas, I.; Perez, I.; Torrero, E.; Bruno, J.; Cera, E.; and Duro, E. 1997. *Dissolution Studies of Synthetic Soddyite and Uranophane.* SKB TR-97-15. Stockholm, Sweden: Svensk Kärnbränsleförsörjning A.B. TIC: 237591.
157874	Chase, M.W., Jr. 1998. *NIST-JANAF Thermochemical Tables.* 4th Edition. Monograph No. 9. Woodbury, New York: American Chemical Society. TIC: 249978.
145440	Chen, F.; Burns, P.C.; and Ewing R.C. 1999. "79Se: Geochemical and Crystallo-Chemical Retardation Mechanisms." *Journal of Nuclear Materials, 275,* 81-94. Amsterdam, The Netherlands: Elsevier. TIC: 247104.
106346	Chen, F.; Ewing R.C.; and Clark S.B. 1999. "The Gibbs Free Energies and Enthalpies of Formation of U6+ Phases: An Empirical Method of Prediction." *American Mineralogist, 84,* (4), 650-664. Washington, D.C.: American Mineralogist. TIC: 245800.
123270	Chen, F.; Ewing, R.C.; and Clark, S.B. 1999. "Errata--The Gibbs Free Energies and Enthalpies of Formation of Uranium(VI) Phases: An Empirical Method of Prediction." *American Mineralogist, 84,* (7-8), 1208. Washington, D.C.: Mineralogical Society of America. TIC: 246579.

171017 Chipera S.J. and Apps, J.A. 2001. “Geochemical Stability of Natural Zeolites.” In *Natural Zeolites: Occurrence, Properties, Applications,* Bish, D.L. and Ming, D.W.; eds, Chapter 13 of *Reviews in Mineralogy and Geochemistry.* Volume 45. Washington, D.C.: Mineralogical Society of America. TIC: 256369.

100025 Chipera, S.J.; Bish, D.L.; and Carlos, B.A. 1995. “Equilibrium Modeling of the Formation of Zeolites in Fractures at Yucca Mountain, Nevada.” *Natural Zeolites '93: Occurrence, Properties, Use, Proceedings of the 4th International Conference on the Occurrence, Properties, and Utilization of Natural Zeolites, June 20-28, 1993, Boise, Idaho.* Ming, D.W. and Mumpton, F.A., eds. Pages 565-577. Brockport, New York: International Committee on Natural Zeolites. TIC: 243086.

153163 Clark, S.P., Jr., ed. 1966. *Handbook of Physical Constants.* Memoir 97. New York, New York: Geological Society of America. TIC: 244868.

180863 Cloke, P.L. 1964. "Discussion, Some Behavioral Aspects of Molybdenum in the Supergene Environment, by S.R. Titley." *Transactions, Society of Mining Engineers, 229,* (1), 36-39. New York, New York: Society of Mining Engineers. TIC: 259388.

179135 Corbel, C.; Sattonnay, G.; Guilbert, S.; Garrido, F.; Barthe, M.-F.; and Jegou, C. 2006. “Addition Versus Radiolytic Production Effects of Hydrogen Peroxide on Aqueous Corrosion of UO_2.” *Journal of Nuclear Materials, 348,* 1-17. New York, New York: Elsevier. TIC: 259117.

150874 Cox, J.D.; Wagman, D.D.; and Medvedev, V.A., eds. 1989. *CODATA Key Values for Thermodynamics.* CODATA Series on Thermodynamic Values. New York, New York: Hemisphere Publishing Company. TIC: 248308.

152575 CRWMS M&O 2000. *Data Qualification Report for Thermodynamic Data File, Data0.ympR0 for Geochemical Code, EQ3/6.* TDR-EBS-MD-000012 REV 00. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.20001016.0004.

144866 Damidot, D.; Stronach, S.; Kindness, A.; Atkins, M.; and Glasser, F.P. 1994. “Thermodynamic Investigation of the CaO-Al2O3-CaCO3-H2O Closed System at 25°C and Influence of Na2O.” *Cement and Concrete Research, 24,* (3), 563-572. New York, New York: Elsevier. TIC: 248189.

100134 Delany, J.M. 1985. *Reaction of Topopah Spring Tuff with J-13 Water: A Geochemical Modeling Approach Using the EQ3/6 Reaction Path Code.* UCRL-53631. Livermore, California: Lawrence Livermore National Laboratory. ACC: HQS.19880517.2419.

158973 de Ligny, D. and Navrotsky, A. 1999. “Energetics of Kaolin Polymorphs.” *American Mineralogist, 84,* (4), 506-516. Washington, D.C.: Mineralogical Society of America. TIC: 252470.

180859 DeMartin, F.; Gramaccioli, C.M.; and Pilati, T. 1992. "The Importance of Accurate Crystal Structure Determination of Uranium Minerals. II. Soddyite (UO2)2(SiO4).2H2O." *Acta Crystallographica, C48,* 1-4. Copenhagen, Denmark: International Union of Crystallography.

163286 Deer, W.A.; Howie, R.A.; and Zussman, J. 1992. *An Introduction to the Rock-Forming Minerals.* 2nd Edition. New York, New York: Prentice Hall. TIC: 221918.

151392 Dellien, I.; Hall, F.M.; and Hepler, L.G. 1976. “Chromium, Molybdenum, and Tungsten: Thermodynamic Properties, Chemical Equilibria, and Standard Potentials.” *Chemical Reviews, 76,* (3), 283-310. Washington, D.C.: American Chemical Society. TIC: 248458.

172266 Douglass, R.M. 1956. “Tetrasodium Uranyl Tricarbonate, $Na_4UO_2(CO_3)_3$.” *Analytical Chemistry, 28,* (10), 1635. Washington, D.C.: American Chemical Society. TIC: 252227.

178626 Egan, E.P., Jr. and Luff, B.B. 1964. Heats of Formation of Phosphorus Oxides, Progress Report on Work Performed in the Period June 1, 1963, to November 30, 1963, Under Contract CMLMC-PA-2B-RFP-129. Wilson Dam, Alabama: Tennessee Valley Authority, Office of Agricultural and Chemical Development. ACC: MOL.20070109.0011.

178568 Egan, E.P., Jr.; Wakefield, Z.T.; and Elmore, K.L. 1950. “High-Temperature Heat Content of Hydroxyapatite.” *Journal of the American Chemical Society, 72,* (6), 2418-2421. Washington, D.C.: American Chemical Society. TIC: 258939.

178570 Egan, E.P., Jr.; Wakefield, Z.T.; and Elmore, K.L. 1951. “Thermodynamic Properties of Fluorapatite, 15 to 1600°K.” *Journal of the American Chemical Society, 73,* (12), 5581-5582. Washington, D.C.: American Chemical Society. TIC: 258941.

159230 Ellis, A.J. and Mahon, W.A.J., eds. 1977. “Table 8.4. Distribution of HF Between Steam and Water at Various Temperatures.” *Chemistry and Geothermal Systems.* New York, New York: Academic Press. TIC: 252725.

179395 Elrashidi, M.A.; Adriano, D.C.; and Lindsay, W.L. 1989. “Solubility, Speciation, and Transformations of Selenium in Soils.” Chapter 3 of *Selenium in Agriculture and the Environment.* SSSA Special Publication 23. Pages 51-63. Madison, Wisconsin: Soil Science Society of America. TIC: 259165.

177660 Felmy, A.R. and MacLean, G.T. 2001. *Development of an Enhanced Thermodynamic Database for the Pitzer Model in ESP: The Fluoride and Phosphate Components.* PNWD-3120. Richland, Washington: Battelle Pacific Northwest Division. ACC: MOL.20060928.0081.

179410 Fernández-González, A.; Andara, A.; Alía, J.M.; and Prieto, M. 2006. "Miscibility in the $CaSO_4 \cdot 2H_2O$-$CaSeO_4 \cdot 2H_2O$ System: Implications for the Crystallisation and Dehydration Behaviour." *Chemical Geology, 225,* 256-265. New York, New York: Elsevier. TIC: 259071.

161651 Fernandez-Prini, R.J.; Corti, H.R.; and Japas, M.L. 1992. *High-Temperature Aqueous Solutions: Thermodynamic Properties.* Pages 124-127. Boca Raton, Florida: CRC Press. TIC: 253048.

158975 Fialips, C.-I.; Navrotsky, A.; and Petit, S. 2001. "Crystal Properties and Energetics of Synthetic Kaolinite." *American Mineralogist, 86,* (3), 304-311. Washington, D.C.: Mineralogical Society of America. TIC: 252471.

106347 Finch, R.J. 1997. "Thermodynamic Stabilities of U(VI) Minerals: Estimated and Observed Relationships." *Scientific Basis for Nuclear Waste Management XX, Symposium held December 2-6, 1996, Boston, Massachusetts.* Gray, W.J. and Triay, I.R., eds. *465,* 1185-1192. Pittsburgh, Pennsylvania: Materials Research Society. TIC: 238884.

160956 Fournier, R.O. and Potter, R.W., II. 1982. "An Equation Correlating the Solubility of Quartz in Water from 25° to 900° at Pressures up to 10,000 Bars." *Geochimica et Cosmochimica Acta, 46,* 1969-1973. New York, New York: Pergamon. TIC: 223170.

160460 Fridriksson, T.; Neuhoff, P.S.; Arnórsson, S.; and Bird, D.K. 2001. "Geological Constraints on the Thermodynamic Properties of the Stilbite—Stellerite Solid Solution in Low-Grade Metabasalts." *Geochimica et Cosmochimica Acta, 65,* (21), 3993-4008. New York, New York: Elsevier. TIC: 253460.

158026 Fujii, K. and Kondo, W. 1981. "Heterogeneous Equilibrium of Calcium Silicate Hydrate in Water at 30 °C." *Journal of the Chemical Society, Dalton Transactions, A,* (2), 645-651. London, England: Chemical Society. TIC: 251812.

144876 Fujii, K. and Kondo, W. 1983. "Estimation of Thermochemical Data for Calcium Silicate Hydrate (C-S-H)." *Journal of the American Ceramic Society, 66,* (12), C220-C221. Columbus, Ohio: American Ceramic Society. TIC: 240838.

172360 Gaines, R.V.; Skinner, H.C.W.; Foord, E.E.; Mason, B.; and Rosenzweig, A. 1997. *Dana's New Mineralogy, The System of Mineralogy of James Dwight Dana and Edward Salisbury Dana.* 8th Edition. New York, New York: John Wiley & Sons. TIC: 256455.

178266 Gamsjäger, H.; Bugajski, J.; Gajda, T.; Lemire, R.J.; and Preis, W. 2005. *Chemical Thermodynamics of Nickel.* Chemical Thermodynamics. Volume 6. New York, New York: Elsevier. TIC: 257921.

144877 Garrels, R.M. and Christ, C.L. 1990. *Solutions, Minerals, and Equilibria.* Boston, Massachusetts: Jones and Bartlett Publishers. TIC: 223483.

144879 Gartner, E.M. and Jennings, H.M. 1987. “Thermodynamics of Calcium Silicate Hydrates and Their Solutions.” *Journal of the American Ceramic Society, 70,* (10), 743-749. Westerville, Ohio: American Ceramic Society. TIC: 248682.

180758 Ginderow, P.D 1988. "Structure de l'uranophane alpha, Ca(UO2)2(SiO3OH)2.5H2O." *Acta Crystallographica, C44,* 421-424. Copenhagen, Denmark: International Union of Crystallography.

118111 Glasser, F. P.; E. E. Lachowski; and D. E. MacPhee 1987. “Compositional Model for Calcium Silicate Hydrate (C-S-H) Gels, Their Solubilities, and Free Energies of Formation.” *Journal of the American Ceramic Society, 70,* (7), 481-485. Westerville, Ohio: American Ceramic Society. TIC: 246777.

158976 Gong, W.L.; Wang, L.M.; Ewing, R.C.; Vernaz, E.; Bates, J.K.; and Ebert, W.L. 1998. “Analytical Electron Microscopy Study of Surface Layers Formed on the French SON68 Nuclear Waste Glass During Vapor Hydration at 200°C.” *Journal of Nuclear Materials, 254,* (2-3), 249-265. New York, New York: Elsevier. TIC: 252351.

152684 Greenberg, J.P. and Moller, N. 1989. “The Prediction of Mineral Solubilities in Natural Waters: A Chemical Equilibrium Model for the Na-K-Ca-Cl-SO4-H2O System to High Concentration from 0 to 250°C.” *Geochimica et Cosmochimica Acta, 53,* 2503–2518. New York, New York: Pergamon Press. TIC: 249020.

144989 Greenberg, S.A. and Chang, T.N. 1965. “Investigation of the Colloidal Hydrated Calcium Silicates. II. Solubility Relationships in the Calcium Oxide-Silica-Water System at 25°.” *Journal of Physical Chemistry, 69,* (1), 182-188. Easton, Pennsylvania: American Chemical Society. TIC: 248686.

101671 Grenthe, I.; Fuger, J.; Konings, R.J.M.; Lemire, R.J.; Muller, A.B.; Nguyen-Trung, C.; and Wanner, H. 1992. *Chemical Thermodynamics of Uranium.* Volume 1 of *Chemical Thermodynamics.* Wanner, H. and Forest, I., eds. Amsterdam, The Netherlands: North-Holland Publishing Company. TIC: 224074.

168382 Guillaumont, R.; Fanghänel, T.; Fuger, J.; Grenthe, I.; Neck, V.; Palmer, D.A.; and Rand, M.H. 2003. *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium.* Mompean, F.J.; Illemassene, M.; Domenech-Orti, C.; and Ben Said, K., eds. Chemical Thermodynamics 5. Amsterdam, The Netherlands: Elsevier. TIC: 255230.

160465 Gunnarsson, I. and Arnórsson, S. 2000. "Amorphous Silica Solubility and the Thermodynamic Properties of $H_4SiO^o_4$ in the Range of 0° to 350°C at P_{sat}." *Geochimica et Cosmochimica Acta, 64,* (13), 2295-2307. New York, New York: Elsevier. TIC: 250506.

176844 Gunnarsson, I.; Arnórsson, S.; and Jakobsson, S. 2005. "Precipitation of Poorly Crystalline Antigorite Under Hydrothermal Conditions." *Geochimica et Cosmochimica Acta, 69,* (11), 2813-2828. New York, New York: Elsevier. TIC: 258287.

176845 Gurevich, V.M.; Gorbunov, V.E.; Gavrichev, K.S.; and Khodakovskii, I.L. 1999. "A Calorimeter for Heat Capacity Measurements from 50 to 300 K: The Heat Capacities of Kogarkoite Na_3SO_4F(cr) at Low Temperatures." *Geochemistry International, 37,* (4), 367-377. Moscow, Russia: MAHK Nauka/Interperiodica. TIC: 258290.

158983 Haas, J.L., Jr. and Fisher, J.R. 1976. "Simultaneous Evaluation and Correlation of Thermodynamic Data." *American Journal of Science, 276,* 525-545. New Haven, Connecticut: Yale University, Kline Geology Laboratory. TIC: 239706.

178026 Hanson, B.; McNamara, B.; Buck, E.; Friese, J.; Jenson, E.; Krupka, K.; and Arey, B. 2005. "Corrosion of Commercial Spent Nuclear Fuel. 1. Formation of Studtite and Metastudtite." *Radiochimica Acta, 93,* 159-168. München, Germany: Oldenbourg Wissenschaftsverlag. TIC: 257130.

100350 Hardin, E.L. 1998. *Near-Field/Altered-Zone Models Report.* UCRL-ID-129179 DR. Livermore, California: Lawrence Livermore National Laboratory. ACC: MOL.19980504.0577.

118163 Harvie, C.E.; Moller, N.; and Weare, J.H. 1984. "The Prediction of Mineral Solubilities in Natural Waters: The Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O System to High Ionic Strengths at 25°C." *Geochimica et Cosmochimica Acta, 48,* (4), 723-751. New York, New York: Pergamon Press. TIC: 239849.

178456 Head, A.J. and Lewis, G.B. 1970. “Thermodynamic Properties of Phosphorus Componds 3. The Enthalpy of Formation of Aqueous Orthophosphoric Acid.” *Journal of Chemical Thermodynamics, 2,* 701-716. New York, New York: Elsevier. TIC: 258827.

137246 Helgeson, H.C. 1969. “Thermodynamics of Hydrothermal Systems at Elevated Temperatures and Pressures.” *American Journal of Science, 267,* (6), 729-804. New Haven, Connecticut: Scholarly Publications. TIC: 241817.

157904 Helgeson, H.C. and Kirkham, D.H. 1974. “Theoretical Prediction of the Thermodynamic Behavior of Aqueous Electrolytes at High Pressures and Temperatures: II. Debye-Hückel Parameters for Activity Coefficients and Relative Partial Molal Properties.” *American Journal of Science, 274,* (7), 1199-1261. New Haven, Connecticut: Yale University, Kline Geology Laboratory. TIC: 240952.

101596 Helgeson, H.C.; Delany, J.M.; Nesbitt, H.W.; and Bird, D.K. 1978. “Summary and Critique of the Thermodynamic Properties of Rock Forming Minerals.” *American Journal of Science, 278-A.* New Haven, Connecticut: Yale University, Kline Geology Laboratory. TIC: 220013.

106024 Helgeson, H.C.; Kirkham, D.H.; and Flowers, G.C. 1981. "Theoretical Prediction of the Thermodynamic Behavior of Aqueous Electrolytes at High Pressures and Temperatures: IV. Calculation of Activity Coefficients, Osmotic Coefficients, and Apparent Molal and Standard and Relative Partial Molal Properties to 600ºC and 5 kb." *American Journal of Science, 281,* (10), 1249-1516. New Haven, Connecticut: Yale University, Kline Geology Laboratory. TIC: 238264.

157905 Hemingway, B.S. 1982. Thermodynamic Properties of Selected Uranium Compounds and Aqueous Species at 298.15 K and 1 Bar and at Higher Temperatures--Preliminary Models for the Origin of Coffinite Deposits. Open-File Report 82-619. Denver, Colorado: U.S. Geological Survey. TIC: 211709.

177990 Hezel, A. and Ross, S.D. 1966. “Forbidden Transitions in the Infra-Red Spectra of Tetrahedral Anions—III. Spectra-Structure Correlations in Perchlorates, Sulphates and Phosphates of the Formula MXO_4.” *Spectrochimica Acta, 22,* 1949-1961. New York, New York: Pergamon. TIC: 258623.

178227 Hezel, A. and Ross, S.D. 1967. “X-Ray Powder Data and Cell Dimensions of Some Rare Earth Orthophosphates.” *Journal of Inorganic and Nuclear Chemistry, 29,* 2085-2089. Oxford, New York: Pergamon Press. TIC: 258793.

178649 Holmes, W.S. 1962. “Heat of Combustion of Phosphorus and the Enthalpies of Formation of P_4O_{10} and H_3PO_4.” *Transactions of the Faraday Society, 58,* (478), 1916-1925. London, England: Faraday Society. TIC: 258903.

161904 Hummel, W.; Berner, U.; Curti, E.; Pearson, F.J.; and Thoenen, T. 2002. *Nagra/PSI Chemical Thermodynamic Data Base 01/01.* Parkland, Florida: Universal Publishers. TIC: 253421.

178810 Ilton, E.S.; Liu, C.; Yantasee, W.; Wang, Z.; Moore, D.A.; Felmy, A.R.; and Zachara, J.M. 2006. “The Dissolution of Synthetic Na-Boltwoodite in Sodium Carbonate Solutions.” *Geochimica et Cosmochimica Acta, 70,* 4836-4849. New York, New York: Elsevier. TIC: 259016.

180858 International Centre for Diffraction Data 1986. *Mineral Powder Diffraction File, Data Book.* pg. 460. Swarthmore, Pennsylvania: International Centre for Diffraction Data. Order Requested

178679 Irving, R.J. and McKerrell, H. 1967. “Standard Heat of Formation of Aqueous Orthophosphoric Acid.” *Transactions of the Faraday Society, 63,* (11), 2582-2585. London, England: Faraday Society. TIC: 259028.

178824 Jackson, J.M. and Burns, P.C. 2001. “A Re-Evaluation of the Structure of Weeksite, A Uranyl Silicate Framework Mineral.” *The Canadian Mineralogist, 39,* 187 -195. Ottawa, Ontario, Canada: Mineralogical Association of Canada. TIC: 259086.

151264 Jackson, K.J. and Helgeson, H.C. 1985. “Chemical and Thermodynamic Constraints on the Hydrothermal Transport and Deposition of Tin: II. Interpretation of Phase Relations in the Southeast Asian Tin Belt.” *Economic Geology and the Bulletin of the Society of Economic Geologists, 80,* (5), 1365-1378. Lancaster, Pennsylvania: Economic Geology Publishing. TIC: 248473.

178846 Jacques, J.K. 1963. “The Heats of Formation of Fluorapatite and Hydroxyapatite.” *Journal of the Chemical Society, III,* 3820-3822. London, England: The Chemical Society. TIC: 259094.

101632 Johnson, J.W.; Oelkers, E.H.; and Helgeson, H.C. 1992. “SUPCRT92: A Software Package for Calculating the Standard Molal Thermodynamic Properties of Minerals, Gases, Aqueous Species, and Reactions from 1 to 5000 Bar and 0 to 1000°C.” *Computers & Geosciences, 18,* (7), 899-947. New York, New York: Pergamon Press. TIC: 234273.

178827 Karpov, I.K. and Kashik, S.A. 1968. “Computer Calculation of Standard Isobaric-Isothermal Potentials of Silicates by Multiple Regression from a Crystallochemical Classification.” *Geochemistry International, 5,* 706-713. Moscow, Russia: Geochemical Society. TIC: 259088.

158992 Kashik, S.A.; Karpov, I.K.; and Kozlova, G.V. 1979. "An Empirical Method of Calculating Free Energies for Layer Silicates." *Geochemistry International, 15,* (2), 70-74. Washington, D.C.: Scripta Publishing. TIC: 252608.

151237 Kielland, J. 1937. "Individual Activity Coefficients of Ions in Aqueous Solutions." *Journal of the American Chemical Society, 59,* (9), 1675-1678. Easton, Pennsylvania: The American Chemical Society. TIC: 248309.

172352 Kiseleva, I.A.; Navrotsky, A.; Belitsky, I.A.; and Fursenko, B.A. 2001. "Thermodynamic Properties of the Calcium Zeolites Stilbite and Stellerite." *Geochemistry International, 39,* (2), 170-176. Moscow, Russia: MAIK Nauka/Interperiodica. TIC: 256731.

158998 Knauss, K.G.; Dibley, M.J.; Bourcier, W.L.; and Shaw, H.F. 2001. "Ti(IV) Hydrolysis Constants Derived from Rutile Solubility Measurements Made from 100 to 300°C." *Applied Geochemistry, 16,* (9-10), 1115-1128. New York, New York: Elsevier. TIC: 252032.

172387 Krishnamachari, N. and Calvo, C. 1972. "The Crystal Structure of Cobalt Diphosphate." *Acta Crystallographica, B28,* 2883-2885. Copenhagen, Denmark: Munksgaard. TIC: 256736.

173070 Kubatko, K-A.H.; Helean, K.B.; Navrotsky, A.; and Burns, P.C. 2003. "Stability of Peroxide-Containing Uranyl Minerals." *Science, 302,* 1191-1193. Washington, D.C.: American Association for the Advancement of Science. TIC: 257044.

101703 Langmuir, D. 1978. "Uranium Solution-Mineral Equilibria at Low Temperatures with Applications to Sedimentary Ore Deposits." *Geochimica et Cosmochimica Acta, 42,* (6), 547-569. New York, New York: Pergamon Press. TIC: 217857.

179363 Larson, J.W. and Su, B. 1994. "Thermodynamics of Formation of Aqueous Monofluoro-, Difluoro- and Amidofluorophosphoric Acids." *Journal of Chemical and Engineering Data, 39,* (1), 36-38. Washington, D.C.: American Chemical Society. TIC: 258867.

179362 Larson, J.W. and Su, B. 1994. "Thermodynamics of Ionization of Monofluoro- and Difluorophosphoric Acids." *Journal of Chemical and Engineering Data, 39,* (1), 33-35. Washington, D.C.: American Chemical Society. TIC: 258869.

159034 Li, G.; Peacor, D.R.; Coombs, D.S.; and Kawachi, Y. 1997. "Solid Solution in the Celadonite Family: The New Minerals Ferroceladonite, $K_2Fe^{2}_{2}+Fe^{3}_{2}+Si_8O_{20}(OH)_4$, and Ferroaluminoceladonite, $K_2Fe^{2}_{2}+Al_2Si_8O_{20}(OH)_4$." *American Mineralogist, 82,* (5-6), 503-511. Washington, D.C.: Mineralogical Society of America. TIC: 252472.

178081 Lide, D.R., ed. 2006. *CRC Handbook of Chemistry and Physics.* 87th Edition. Boca Raton, Florida: CRC Press. TIC: 258634.

159038 Lindsay, W.T., Jr. 1980. "Estimation of Concentration Quotients for Ionic Equilibria in High Temperature Water: The Model Substance Approach." *Official Proceedings, The International Water Conference, 41st Annual Meeting, October 20, 21, & 22, 1980, Pittsburgh, Pennsylvania.* Pages 284-294. Pittsburgh, Pennsylvania: Engineers' Society of Western Pennsylvania. TIC: 252705.

153210 Lindsay, W.L. 2001. *Chemical Equilibria in Soils.* 1st Edition. Caldwell, New Jersey: Blackburn Press. TIC: 5873.

172264 Loopstra, B.O. and Rietveld, H.M. 1969. "The Structure of Some Alkaline-Earth Metal Uranates." *Acta Crystallographica, B25,* (4), 787-791. Copenhagen, Denmark: Munksgaard. TIC: 252223.

177244 Lothenbach, B.; Ochs, M.; and Hager, D. 2000. "Thermodynamic Data for the Solubility of Tin(IV) in Aqueous Cementitious Environments." *Radiochimica Acta, 88,* 521-526. München, Germany: Oldenbourg Wissenschaftsverlag. TIC: 258463.

145004 MacPhee, D.E.; Luke, K.; Glasser, F.P.; and Lachowski, E.E. 1989. "Solubility and Aging of Calcium Silicate Hydrates in Alkaline Solutions at 25ºC." *Journal of the American Ceramic Society, 72,* (4), 646-654. Westerville, Ohio: American Ceramic Society. TIC: 248232.

101691 Maier, C.G. and Kelley, K.K. 1932. "An Equation For The Representation Of High Temperature Heat Content Data." *Journal of the American Chemical Society, 54,* 3243-3246. Washington, D.C.: American Chemical Society. TIC: 239023.

159196 Martell, A.E. and Smith, R.M. 1982. *First Supplement.* Volume 5 of *Critical Stability Constants.* New York, New York: Plenum Press. TIC: 248488.

172343 Mattigod S.V. and McGrail, B.P. 1999. "Estimating the Standard Free Energy of Formation of Zeolites Using the Polymer Model." *Microporous and Mesoporous Materials, 27,* 41-47. New York, New York: Elsevier. TIC: 256728.

159197 Mattigod, S.V. and Sposito, G. 1978. "Improved Method for Estimating the Standard Free Energies of Formation ($\Delta G^{O}_{f,298.15}$) of Smectites." *Geochimica et Cosmochimica Acta, 42,* (12), 1753-1762. New York, New York: Pergamon. TIC: 252609.

172346 McKenzie, W.F.; Richard, L.; and Salah, S. 2001. "Gibbs Free Energies of Formation of Uranyl Silicates at 298.15 K." *Proceedings of the Tenth International Symposium on Water-Rock Interaction/ WRI-10/ Villasimius/ Italy/ 10-15 July 2001.* Cidu, R., ed. *1,* 299-303. Exton, Pennsylvania: A.A. Balkema. TIC: 253823.

174068 McNamara, B.; Hanson, B.; Buck, E.; and Soderquist, C. 2005. "Corrosion of Commercial Spent Nuclear Fuel. 2. Radiochemical Analyses of Metastudtite and Leachates." *Radiochimica Acta, 93,* 169-175. München, Germany: Oldenbourg Wissenschaftsverlag. TIC: 257131.

106349 Moll, H.; Geipel, G.; Matz, W.; Bernhard, G.; and Nitsche, H. 1996. "Solubility and Speciation of (UO2)2SiO4·2H2O in Aqueous Systems." *Radiochimica Acta, 74,* 3-7. Munich, Germany: R. Oldenbourg Verlag. TIC: 236975.

159198 Morey, G.W.; Fournier, R.O.; and Rowe, J.J. 1962. "The Solubility of Quartz in Water in the Temperature Interval from 25° to 300°C." *Geochimica et Cosmochimica Acta, 26,* 1029-1043. New York, New York: Pergamon Press. TIC: 250706.

176846 Morishita, M. and Navrotsky, A. 2003. "Calorimetric Study of Nickel Molybdate: Heat Capacity, Enthalpy, and Gibbs Energy of Formation." *Journal of the American Ceramic Society, 86,* (11), 1927-1932. Westerville, Ohio: American Ceramic Society. TIC: 258286.

144449 Murphy, W.M. and Pabalan, R.T. 1995. *Review of Empirical Thermodynamic Data for Uranyl Silicate Minerals and Experimental Plan.* CNWRA 95-014. San Antonio, Texas: Center for Nuclear Waste Regulatory Analyses. TIC: 233385.

159200 Murray, R.C., Jr. and Cobble, J.W. 1980. "Chemical Equilibria in Aqueous Systems at High Temperatures." *The International Water Conference, 41st Annual Meeting, October 20, 21, & 22, 1980, Pittsburgh, Pennsylvania.* Pages 295-310. Pittsburgh, Pennsylvania: Engineers' Society of Western Pennsylvania. TIC: 252705.

100807 Neall, F.B. 1994. *Modelling of the Near-Field Chemistry of the SMA Repository at the Wellenberg Site.* PSI Bericht 94-18. Wurenlingen und Villigen, Switzerland: Paul Scherrer Institute. TIC: 238927.

144784 Neall, F.B. 1996. “Modelling the Long-Term Chemical Evolution of Cement-Groundwater Systems.” *Scientific Basis for Nuclear Waste Management XIX, Symposium held November 27-December 1, 1995, Boston, Massachusetts.* Murphy, W.M. and Knecht, D.A., eds. *412,* 483-490. Pittsburgh, Pennsylvania: Materials Research Society. TIC: 233877.

168259 Neck, V.; Müller, R.; Bouby, M.; Altmaier, M.; Rothe, J.; Denecke, M.A.; and Kim, J.I. 2002. “Solubility of Amorphous Th(IV) Hydroxide – Application of LIBD to Determine the Solubility Product and EXAFS for Aqueous Speciation.” *Radiochimica Acta, 90,* (09/11), 485-494. München, Germany: Oldenbourg Wissenchaftsverlag. TIC: 255812.

172354 Neuhoff, P.S.; Hovis, G.L.; Balassone, G.; and Stebbins, J.F. 2004. “Thermodynamic Properties of Analcime Solid Solutions.” *American Journal of Science, 304,* (1), 21-66. New Haven, Connecticut: Yale University, Kline Geology Laboratory. TIC: 256733.

172385 Ng, H.N.; Calvo, C.; and Faggiani, R. 1978. “A New Investigation of the Structure of Silver Orthophosphate.” *Acta Crystallographica, B34,* 898 - 899. Copenhagen, Denmark: Munksgaard. TIC: 256735.

100809 Nguyen, S.N.; Silva, R.J.; Weed, H.C.; and Andrews, J.E., Jr. 1992. “Standard Gibbs Free Energies of Formation at the Temperature 303.15 K of Four Uranyl Silicates: Soddyite, Uranophane, Sodium Boltwoodite, and Sodium Weeksite.” *Journal of Chemical Thermodynamics, 24,* (1-6), 359-376. New York, New York: Academic Press. TIC: 238507.

168480 Nordstrom, D.K. and Munoz, J.L. 1994. *Geochemical Thermodynamics.* 2nd Edition. Boston, Massachusetts: Blackwell Scientific Publications. TIC: 255853.

153965 Nordstrom, D.K. and Munoz, J.L. 1986. *Geochemical Thermodynamics.* Palo Alto, California: Blackwell Scientific Publications. TIC: 208228.

163274 NRC (U.S. Nuclear Regulatory Commission) 2003. *Yucca Mountain Review Plan, Final Report.* NUREG-1804, Rev. 2. Washington, D.C.: U.S. Nuclear Regulatory Commission, Office of Nuclear Material Safety and Safeguards. TIC: 254568.

151244 Nriagu, J.O. 1972. "Lead Orthophosphates. I. Solubility and Hydroloysis of Secondary Lead Orthophosphate." *Iorganic Chemistry, 11,* (10), 2499-2503. Easton, Pennsylvania: American Chemical Society. TIC: 248479.

178321 Nriagu, J.O. 1975. “Thermochemical Approximations for Clay Minerals.” *American Mineralogist, 60,* (9 and 10), 834-839. Washington, D.C.: Mineralogical Society of America. TIC: 258820.

113277 O'Hare, P.A.G.; Lewis, B.M.; and Nguyen, S.N. 1988. "Thermochemistry of Uranium Compounds, XVII. Standard Molar Enthalpy of Formation at 298.15 K of Dehydrated Schoepite U03.0.9H2O. Thermodynamics of (Schoepite + Dehydrated Schoepite + Water)." *Journal of Chemical Thermodynamics, 20,* 1287-1296. New York, New York: Academic Press. TIC: 246154.

159027 OECD (Organisation for Economic Co-operation and Development, Nuclear Energy Agency) 2001. *Chemical Thermodynamics of Neptunium and Plutonium.* Volume 4 of *Chemical Thermodynamics.* New York, New York: Elsevier. TIC: 209037.

172353 Ogorodova, L.P.; Kiseleva, I.A.; Mel'chakova, L.V.; and Belitskii, I.A. 2002. "Thermodynamic Properties of Calcium and Potassium Chabazites." *Geochemistry International, 40,* (5), 466-471. Moscow, Russia: MAIK Nauka/Interperiodica. TIC: 256753.

172005 Ogorodova, L.P.; Mel'chakova, L.V.; Kiseleva, I.A.; and Belitskii, I.A. 2003. "Thermodynamic Properties of Natural Zeolites of the Gismondine-Harronite Group." *Russian Journal of Physical Chemistry, 77,* (9), 1543-1545. Moscow, Russia: MAIK Nauka/Interperiodica. TIC: 256674.

177640 Olin, A.; Noläng, B.; Öhman, L-O.; Osadchii, E.G.; and Rosén, E. 2005. *Chemical Thermodynamics of Selenium.* Mompean, F.J.; Perrone, J.; and Illemassène, M., eds. Chemical Thermodynamics 7. Amsterdam, The Netherlands: Elsevier. TIC: 257920.

150834 Östhols, E.; Bruno, J.; and Grenthe, I. 1994. "On The Influence of Carbonate on Mineral Dissolution: III. The Solubility of Microcrystalline ThO2 in CO2-H2O Media." *Geochimica et Cosmochimica Acta, 58,* (2), 613-623. New York, New York: Pergamon. TIC: 245115.

168010 Parker, V.B. and Khodakovskii, I.L. 1995. "Thermodynamic Properties of the Aqueous Ions (2+ and 3+) of Iron and the Key Compounds of Iron." *Journal of Physical and Chemical Reference Data, 24,* (5), 1699-1745. Washington, D.C.: American Chemical Society. TIC: 255714.

157910 Pérez, I.; Casas, I.; Martín, M.; and Bruno, J. 2000. "The Thermodynamics and Kinetics of Uranophane Dissolution in Bicarbonate Test Solutions." *Geochimica et Cosmochimica Acta, 64,* (4), 603-608. New York, New York: Elsevier. TIC: 250919.

100812 Perez, I.; Casas, I.; Torrero, M.E.; Cera, E.; Duro, L.; and Bruno, J. 1997. "Dissolution Studies of Soddyite as a Long-Term Analogue of the Oxidative Alteration of the Spent Nuclear Fuel Matrix." *Scientific Basis for Nuclear Waste Management XX, Symposium held December 2-6, 1996, Boston, Massachusetts.* Gray, W.J. and Triay I.R., eds. *465,* 565-572. Pittsburgh, Pennsylvania: Materials Research Society. TIC: 238884.

152703 Perkins, R.B. and Palmer, C.D. 1999. "Solubility of Ettringite $(Ca_6[Al(OH)_6]_2(SO_4)_3 \times 26H_2O)$ at 5–75°C." *Geochimica et Cosmochimica Acta, 63,* (13/14), 1969-1980. New York, New York: Pergamon Press. TIC: 248983.

153349 Perkins, R.B. and Palmer, C.D. 2000. "Solubility of Ca6[Al(OH)6]2(CrO4)3 . 26H2O, the Chromate Analog of Ettringite; 5-75°C." *Applied Geochemistry, 15,* 1203-1218. New York, New York: Pergamon Press. TIC: 248980.

172359 Pialoux, A. and Touzelin, B. 1998. "Etude du Système U-Ca-O par Diffractométrie de Rayons X à Haute Température." *Journal of Nuclear Materials, 255,* 14-25. New York, New York: Elsevier. TIC: 256724.

151737 Plummer, L.N. and Busenberg, E. 1982. "The Solubilities of Calcite, Aragonite and Vaterite in CO2-H20 Solutions Between 0 and 90°C, and an Evaluation of the Aqueous Model for the System CaCO3-CO2-H2O." *Geochimica et Cosmochimica Acta, 46,* (6), 1011-1040. Elmsford, New York: Pergamon Press. TIC: 248743.

159204 Puigdomenech I.; Rard, J.A.; Plyasunov, A.V.; and Grenthe, I. 1997. "Temperature Corrections to Thermodynamic Data and Enthalpy Calculations." Chapter X of *Modelling in Aquatic Chemistry.* Grenthe, I. and Puigdomenech, I., eds. Paris, France: Organisation for Economic Co-Operation and Development, Nuclear Energy Agency. TIC: 250748.

159205 Puigdomènech, I.; Rard, J.A.; Plyasunov, A.V.; and Grenthe, I. 1999. *Temperature Corrections to Thermodynamic Data and Enthalpy Calculations.* TDB-4. Issy-les-Moulineaux, France: Organization for Economic Co-Operation and Development, Nuclear Energy Agency. TIC: 252917.

168155 Rai, D.; Felmy, A.R.; Hess, N.J.; LeGore, V.L.; and McCready, D.E. 2002. "Thermodynamics of the U(VI)-$Ca2^{+}$-Cl^{-}-OH^{-}-H_2O System: Solubility Product of Becquerelite." *Radiochimica Acta, 90,* (9-11), 495-503. München, Germany: Oldenbourg Wissenschaftsverlag. TIC: 255830.

163369 Rai, D.; Sass, B.M.; and Moore, D.A. 1987. "Chromium(III) Hydrolysis Constants and Solubility of Chromium(III) Hydroxide." *Inorganic Chemistry, 26,* (3), 345-349. Washington, D.C.: American Chemical Society. TIC: 254060.

179582 Rai, D.; Moore, D.A.; Hess, N.J.; Rao, L.; and Clark, S.B. 2004. "Chromium(III) Hydroxide Solubility in the Aqueous Na^+-OH^--$H_2PO^-_4$-HPO^{2-}_4-PO^{3-}_4-H_2O System: A Thermodynamic Model." Journal of Solution Chemistry, 33, (10), 1213-1242. New York, New York: Springer Science + Business Media. TIC: 259197.

181002 Rai, D.; Xia, Y.; Rao, L.; Hess, N.J.; Felmy, A.R.; Moore, D.A.; and McCready, D.E. 2005. "Solubility of $(UO_2)_3(PO_4)_2 \cdot 4H_2O$ in H^+-Na^+-OH^--$H_2PO^{2-}_4$-PO^{3-}_4-H_2O and its Comparison to the Analogous PuO^{2+}_2 System." *Journal of Solution Chemistry, 34,* (4), 469-498. New York, New York: Springer Science + Business Media. TIC: 259414.

172416 Ralph, J. [n.d.]. "Cejkaite." *Cejkaite Mineral Data.* Croydon, Surrey, England: Mindat.org. Accessed October 26, 2004. TIC: 256690. URL: http://www.mindat.org/min-7105.html

159207 Ransom, B. and Helgeson, H.C. 1994. "Estimation of the Standard Molal Heat Capacities, Entropies, and Volumes of 2:1 Clay Minerals." *Geochimica et Cosmochimica Acta, 58,* (21), 4537-4547. New York, New York: Elsevier. TIC: 252610.

178805 Rard, J.A. 2007. "Fwd: Re: Phosphates" E-mail from J. Rard to W. Mitcheltree, January 31, 2007. ACC: LLR.20070213.0101.

157912 Rard, J.A.; Rand, M.H.; Anderegg, G.; and Wanner, H. 1999. *Chemical Thermodynamics of Technetium.* Sandino, M.C.A., and Östhols, E., eds. Chemical Thermodynamics 3. Amsterdam, The Netherlands: Elsevier. TIC: 247228.

100821 Reardon, E.J. 1990. "An Ion Interaction Model for the Determination of Chemical Equilibria in Cement Water Systems." *Cement and Concrete Research, 20,* 175-192. Elmsford, New York: Pergamon Press. TIC: 239801.

100822 Reardon, E.J. 1992. "Problems and Approaches to the Prediction of the Chemical Composition in Cement/Water Systems." *Waste Management, 12,* 221-239. New York, New York: Pergamon Press. TIC: 236730.

101709 Rimstidt, J.D. 1997. "Quartz Solubility at Low Temperatures." *Geochimica et Cosmochimica Acta, 61,* (13), 2553-2558. New York, New York: Pergamon Press. TIC: 239020.

107105 Roberts, W.L.; Campbell, T.J.; and Rapp, G.R., Jr. 1990. *Encyclopedia of Minerals.* 2nd Edition. New York, New York: Van Nostrand Reinhold. TIC: 242976.

153683 Robie, R.A. and Hemingway, B.S. 1995. Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (10^5 Pascals) Pressure and at Higher Temperatures. Bulletin 2131. Reston, Virginia: U.S. Geological Survey. TIC: 249441.

179157 Robie, R.A.; Hemingway, B.S.; and Fisher, J.R. 1978. *Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (10^5 Pascals) Pressure and at Higher Temperatures.* Geological Survey Bulletin 1452. Washington, D.C.: U.S. Government Printing Office. ACC: LLR.20070418.0031.

107109 Robie, R.A.; Hemingway, B.S.; and Fisher, J.R. 1979. Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (10^5 Pascals) Pressure and at Higher Temperatures. U.S. Geological Survey Bulletin 1452. Washington, D.C.: U.S. Government Printing Office. ACC: NNA.19900702.0002.

178624 Rossini, F.D.; Wagman, D.D.; Evans, W.H.; Levine, S.; and Jaffe, I. 1952. *Selected Values of Chemical Thermodynamic Properties.* Circular of the National Bureau of Standards 500. Washington, D.C.: United States Government Printing Office. ACC: MOL.20061206.0146.

113360 Sandino, M.C.A. and Grambow, B. 1994. "Solubility Equilibria in the U(VI)-Ca-K-Cl-H2O System: Transformation of Schoepite into Becquerelite and Compreignacite." *Radiochimica Acta, 66/67,* 37-43. Munich, Germany: R. Oldenbourg Verlag. TIC: 246117.

119581 Sarkar, A.K.; Barnes, M.W.; and Roy, D.M. 1982. Longevity of Borehole and Shaft Sealing Materials: Thermodynamic Properties of Cements and Related Phases Applied to Repository Sealing. ONWI-201. Columbus, Ohio: Battelle Memorial Institute, Office of Nuclear Waste Isolation. TIC: 248672.

173091 Sattonnay, G.; Ardois, C.; Lucchini, J.F.; Barthe, M.F.; Garrido, F.; and Gosset, D. 2001. "Alpha-Radiolysis Effects on UO_2 Alteration in Water." *Journal of Nuclear Materials, 288,* 11-19. New York, New York: Elsevier. TIC: 256824.

178844 Schlesinger, M.E. 2002. "The Thermodynamic Properties of Phosphorus and Solid Binary Phosphides." *Chemical Reviews, 102,* (11), 4267-4301. Washington, D.C.: American Chemical Society. TIC: 259091.

178842 Schumm, R.H.; Prosen, E.J.; and Wagman, D.D. 1974. "Enthalpy of Formation of Phosphorus Pentachloride; Derivation of the Enthalpy of Formation of Aqueous Orthophosphoric Acid.:" *Journal of Research of the National Bureau of Standards - A Physics and Chemistry, 78A,* (3), 375-386. Washington, D.C.: U.S. Department of Commerce National Bureau Standards. ACC: MOL.20061205.0039.

177245 Séby, F.; Potin-Gautier, M.; Giffaut, E.; and Donard, O.F.X. 2001. “A Critical Review of Thermodynamic Data for Inorganic Tin Species.” *Geochimica et Cosmochimica Acta, 65,* (18), 3041-3053. New York, New York: Pergamon. TIC: 258461.

172386 Shannon, R.D. and Calvo, C. 1973. “Crystal Structure of $Cu_5V_2O_{10}$.” *Acta Crystallographica, B29,* 1338-1345. Copenhagen, Denmark: Munksgaard. TIC: 256737.

179396 Sharmasarkar, S.; Vance, G.F.; and Cassel-Sharmasarkar, F. 1998. “Analysis and Speciation of Selenium Ions in Mine Environments.” *Environmental Geology, 34,* (1), 31-38. New York, New York: Springer-Verlag. TIC: 259072.

158028 Shaw, S.; Henderson, C.M.B.; and Komanschek, B.U. 2000. “Dehydration/Recrystallization Mechanisms, Energetics, and Kinetics of Hydrated Calcium Silicate Minerals: An in Situ TGA/DSC and Synchrotron Radiation SAXS/WAXS Study.” *Chemical Geology, 167,* (1-2), 141-159. New York, New York: Elsevier. TIC: 251588.

144817 Shock, E.L. and Helgeson, H.C. 1988. “Calculation of the Thermodynamic and Transport Properties of Aqueous Species at High Pressures and Temperatures: Correlation Algorithms for Ionic Species and Equation of State Predictions to 5 kb and 1000°C.” *Geochimica Cosmochimica Acta, 52,* (8), 2009-2016. New York, New York: Pergamon Press. TIC: 247203.

150770 Shock, E.L.; Sassani, D.C.; and Betz, H. 1997. “Uranium in Geologic Fluids: Estimates of Standard Partial Molal Properties, Oxidation Potentials, and Hydrolysis Constants at High Temperatures and Pressures.” *Geochimica et Cosmochimica Acta, 61,* (20), 4245-4266. New York, New York: Elsevier. TIC: 248305.

127953 Shock, E.L.; Sassani, D.C.; Willis, M.; and Sverjensky, D.A. 1997. “Inorganic Species in Geologic Fluids: Correlations Among Standard Molal Thermodynamic Properties of Aqueous Ions and Hydroxide Complexes.” *Geochimica et Cosmochimica Acta, 61,* (5), 907-950. New York, New York: Pergamon Press. TIC: 246451.

180793 Shoemaker, G.L.; Anderson, J.B.; Kostiner, E. 1977. "Copper(II) Phosphate." *Acta Crystallographica, 33,* 2969-2972. Copenhagen, Denmark: Munksgaard. TIC: 252225.

102087 Silva, R.J.; Bidoglio, G.; Rand, M.H.; Robouch, P.B.; Wanner, H.; and Puigdomenech, I. 1995. *Chemical Thermodynamics of Americium.* Volume 2 of *Chemical Thermodynamics.* Amsterdam, The Netherlands: Elsevier. TIC: 237106.

127382 Smith, R.M. and Martell, A.E. 1976. *Inorganic Complexes.* Volume 4 of *Critical Stability Constants.* New York, New York: Plenum Press. TIC: 224070.

177411 SNL 2007. *In-Drift Precipitates/Salts Model.* ANL-EBS-MD-000045 REV 03. Las Vegas, Nevada: Bechtel SAIC Company. ACC: DOC.20070306.0037.

103804 Spahiu, K. and Bruno, J. 1995. *A Selected Thermodynamic Database for REE to be Used in HLNW Performance Assessment Exercises.* SKB TR-95-35. Stockholm, Sweden: Svensk Kärnbränsleförsörjning A.B. TIC: 225493.

180749 Spencer, P.J. 1981. "Thermochemical Properties." In *Hafnium: Physico-Chemical Properties of its Componds and Alloys,* Chapter 1 of *Atomic Energy Review, Special Issue No. 8.* Vienna, Austria: International Atomic Energy Agency. TIC: 259402.

159208 Stefánsson, A. 2001. "Dissolution of Primary Minerals of Basalt in Natural Waters I. Calculation of Mineral Solubilities from 0°C to 350°C." *Chemical Geology, 172,* (3-4), 225-250. New York, New York: Elsevier. TIC: 250507.

161956 Steinborn, T.L.; Wolery, T.J.; Alcorn, S.R.; Arthur, S.E.; Bernot, P.A.; Brady, P.V.; Chen, Y.; Domski, P.S.; Jolley, D.M.; Metcalf, R.C.; and Thomas, E. 2003. *Data Qualification: Update and Revision of the Geochemical Thermodynamic Database, Data0.ymp.* TDR-EBS-MD-000022 REV 00. Las Vegas, Nevada: Bechtel SAIC Company. ACC: DOC.20030331.0003.

151259 Strunz, H. and Tennyson, C. 1982. "Symmetry and Twinning in Boltwoodite." *Soviet Physics Crystallography, 26,* (6), 732-735. New York, New York: American Institute of Physics. TIC: 248486.

100829 Stumm, W. and Morgan, J.J. 1981. *Aquatic Chemistry, An Introduction Emphasizing Chemical Equilibria in Natural Waters.* 2nd Edition. New York, New York: John Wiley & Sons. TIC: 208448.

125332 Stumm, W. and Morgan, J.J. 1996. *Aquatic Chemistry, Chemical Equilibria and Rates in Natural Waters.* 3rd Edition. New York, New York: John Wiley & Sons. TIC: 246296.

159209 Tardy, Y. and Garrels, R.M. 1974. "A Method of Estimating the Gibbs Energies of Formation of Layer Silicates." *Geochimica et Cosmochimica Acta, 38,* (7), 1101-1116. New York, New York: Pergamon Press. TIC: 252611.

178272 Tardy, Y. and Garrels, R.M. 1976. “Prediction of Gibbs Energies of Formation — I. Relationships Among Gibbs Energies of Formation of Hydroxides, Oxides and Aqueous Ions.” *Geochimica et Cosmochimica Acta, 40,* 1051-1056. Oxford, New York: Pergamon Press. TIC: 258801.

178273 Tardy, Y. and Garrels, R.M. 1977. “Prediction of Gibbs Energies of Formation of Compunds from the Elements — II. Monovalent and Divalent Metal Silicates.” *Geochimica et Cosmochimica Acta, 41,* 87-92. Oxford, New York: Pergamon Press. TIC: 258802.

120495 Taylor, H.F.W. 1990. *Cement Chemistry.* San Diego, California: Academic Press Limited. TIC: 243267.

153213 Titley, S.R. 1963. "Some Behavioral Aspects of Molybdenum in the Supergene Environment." *Transactions of the Society of Mining Engineers, 226,* 199-204. New York, New York: Society of Mining Engineers of AIME. TIC: 249114.

181154 Titley, S.R. 1964. "Authors' Reply: S.R. Titley's Reply to Do Discussion by Professor Paul L. Cloke on "Some Behavorial Aspects of Molybdenum in the Supergene Environment." *American Institute of Mining, Metallurgical, and Petroleum Engineers (AIME),* 39-40. Dallas, TX: American Institute of Mining, Metallurgical, and Petroleum Engineers (AIME).

155334 Towe, K.M. and Bradley, W.F. 1967. “Mineralogical Constitution of Colloidal 'Hydrous Ferric Oxides'.” *Journal of Colloid and Interface Science, 24,* 384-392. New York, New York: Academic Press. TIC: 250230.

159210 Triolo, R.; Grigera, J.R.; and Blum, L. 1976. “Simple Electrolytes in the Mean Spherical Approximation.” *Journal of Physical Chemistry, 80,* (17), 1858-1861. Washington, D.C.: American Chemical Society. TIC: 253397.

101496 Vaniman D.T. and Bish, D.L. 1995. “The Importance of Zeolites in the Potential High-Level Radioactive Waste Repository at Yucca Mountain, Nevada.” *Natural Zeolites `93: Occurrence, Properties, Use, Proceedings of the 4th International Conference on the Occurrence, Properties, and Utilization of Natural Zeolites, June 20-28, 1993, Boise, Idaho.* Ming, D.W. and Mumpton, F.A., eds. Pages 533-546. Brockport, New York: International Committee on Natural Zeolites. TIC: 243086.

150836 Vasil'ev, V.P.; Vorobe.ev, P.N.; and Khodakovskii, I.L. 1974. “Standard Free Energies of Formation of Titanium Hydroxo-Complexes and of the Ti4+ Ion in Aqueous Solution.” *Translated from: Russian Journal of Inorganic Chemistry, 19,* (10), 1481-1483. London, England: Royal Society of Chemistry. TIC: 248330.

101407 Viani, B.E. and Bruton, C.J. 1992. *Modeling Fluid-Rock Interaction at Yucca Mountain, Nevada: A Progress Report.* UCRL-ID-109921. Livermore, California: Lawrence Livermore National Laboratory. ACC: NNA.19920805.0002.

159213 Vieillard, P. 1994. "Prediction of Enthalpy of Formation Based on Refined Crystal Structures of Multisite Compounds: Part 1. Theories and Examples." *Geochimica et Cosmochimica Acta, 58,* (19), 4049-4063. New York, New York: Elsevier. TIC: 252614.

159214 Vieillard, P. 1994. "Prediction of Enthalpy of Formation Based on Refined Crystal Structures of Multisite Compounds: Part 2. Application to Minerals Belonging to the System Li_2O-Na_2O-K_2O-BeO-MgO-CaO-MnO-FeO-Fe_2O_3-Al_2O_3-SiO_2-H_2O. Results and Discussion." *Geochimica et Cosmochimica Acta, 58,* (19), 4065-4107. New York, New York: Elsevier. TIC: 252615.

172320 Vieillard, P. 1995. "Estimation of Enthalpy of Formation of Some Zeolites from their Refined Crystal Structures." *Zeolites, 15,* 202-212. New York, New York: Elsevier. TIC: 256712.

171586 Vieillard, P. 2000. "A New Method for the Prediction of Gibbs Free Energies of Formation of Hydrated Clay Minerals Based on the Electronegativity Scale." *Clay and Clay Minerals, 48,* (4), 459-473. Aurora, Colorado: Clays Mineral Society. TIC: 256527.

120508 Vieillard, P. and Rassineux, F. 1992. "Thermodynamic and Geochemical Modelling of the Alteration of Two Cement Matrices." *Applied Geochemistry, Geochemistry of Radioactive Waste Disposal: A French Contribution, Supplemental Issue No. 1,* 125-136. New York, New York: Pergamon Press. TIC: 246918.

178821 Vieillard, P. and Tardy, Y. 1998. "Estimation of Enthalpies of Formation of Minerals Based on Their Refined Crystal Structures." *American Journal of Science, 288,* (10), 997-1040. New Haven, Connecticut: Yale University, Kline Geology Laboratory. TIC: 259085.

113433 Vochten, R. and Van Haverbeke, L. 1990. "Transformation of Schoepite into the Uranyl Oxide Hydrates: Becquerelite, Billietite and Wölsendorfite." *Mineralogy and Petrology, 43,* 65-72. New York, New York: Springer Verlag. TIC: 246060.

178625 Wagman, D.D.; Evans, W.H.; Parker, V.B.; Halow, I.; Bailey, S.M.; and Schumm, R.H. 1968. "Phosphorus." Table 19 of *Selected Values of Chemical Thermodynamic Properties.* Technical Note 270-3. Pages 84-94. Washington, D.C.: United States Government Printing Office. ACC: MOL.20061206.0148.

159216 Wagman, D.D.; Evans, W.H.; Parker, V.B.; Schumm, R.H.; Halow, I.; Bailey, S.M.; Churney, K.L.; and Nuttall, R.L. 1982. "The NBS Tables of Chemical Thermodynamic Properties, Selected Values for Inorganic and C_1 and C_2 Organic Substances in SI Units." *Journal of Physical and Chemical Reference Data, 11,* (Supplement No. 2), 2-276 - 2-282. Washington, D.C.: American Chemical Society. TIC: 239715.

179315 Wagman, D.D.; Evans, W.H.; Parker, V.B.; Schumm, R.H.; Halow, I.; Bailey, S.M.; Churney, K.L.; and Nuttall, R.L. 1989. "Erratum: The NBS Tables of Chemical Thermodynamic Properties, Selected Values for Inorganic and C_1 and C_2 Organic Substances in SI Units." *Journal of Physical and Chemical Reference Data, 18,* (4), 2-276 - 2-282, 1807-1812. Washington, D.C.: American Chemical Society. TIC: 239715; 259123.

133240 Walther, J.V. and Helgeson, H.C. 1977. "Calculation of the Thermodynamic Properties of Aqueous Silica and the Solubility of Quartz and Its Polymorphs at High Pressures and Temperatures." *American Journal of Science, 277,* 1315-1351. New Haven, Connecticut: Yale University, Kline Geology Laboratory. TIC: 223171.

159222 Wanner, H. and Östhols, E. 1999. *Guidelines for the Assignment of Uncertainties.* TDB-3. Issy-les-Moulineaux, France: Organization for Economic Co-operation and Development, Nuclear Energy Agency. TIC: 253366.

102865 Weast, R.C. and Astle, M.J., eds. 1979. *CRC Handbook of Chemistry and Physics.* 60th Edition. 2nd Printing 1980. Boca Raton, Florida: CRC Press. TIC: 245312.

100833 Weast, R.C. and Astle, M.J., eds. 1981. *CRC Handbook of Chemistry and Physics.* 62nd Edition. Boca Raton, Florida: CRC Press. TIC: 240722.

162148 Wesolowski, D.J. 1992. "Aluminum Speciation and Equilibria in Aqueous Solution: I. The Solubility of Gibbsite in the System Na-K-Cl-OH-$Al(OH)_4$ from 1 to 100°C." *Geochimica et Cosmochimica Acta, 56,* (3), 1065-1091. New York, New York: Pergamon Press. TIC: 253946.

178567 Westrich, H.R. and Navrotsky, A. 1981. "Some Thermodynamic Properties of Fluorapatite, Fluorpargasite, and Fluoraphlogopite." *American Journal of Science, 281,* 1091-1103. New Haven, Connecticut: Yale University, Kline Geology Laboratory. TIC: 258922.

172351 Wilkin, R.T. and Barnes, H.L. 1998. "Solubility and Stability of Zeolites in Aqueous Solutions: I. Analcime, Na-, and K-Clinoptilolite." *American Mineralogist, 83,* (7-8), 746-761. Washington, D.C.: Mineralogical Society of America. TIC: 256734.

113473 Wilson, C.N. 1988. "Summary of Results from the Series 2 and Series 3 NNWSI Bare Fuel Dissolution Tests." *Scientific Basis for Nuclear Waste Management XI, Symposium held November 30-December 3, 1987, Boston, Massachusetts.* Apted, M.J. and Westerman, R.E., eds. *112,* 473-483. Pittsburgh, Pennsylvania: Materials Research Society. TIC: 203662.

151346 Wolery, T.J. 1978. Some Chemical Aspects of Hydrothermal Processes at Mid-Oceanic Ridges - A Theoretical Study. I. Basalt-Sea Water Reaction and Chemical Cycling Between the Oceanic Crust and the Oceans. II. Calculation of Chemical Equilibrium Between Aqueous Solutions and Minerals. Ph.D. dissertation. Evanston, Illinois: Northwestern University. TIC: 219640.

159223 Wolery, T.J. 1990. "On the Thermodynamic Framework of Solutions (with Special Reference to Aqueous Electrolyte Solutions)." *American Journal of Science, 290,* (3), 296-320. New Haven, Connecticut: Yale University, Kline Geology Laboratory. TIC: 252904.

100836 Wolery, T.J. 1992. EQ3NR, A Computer Program for Geochemical Aqueous Speciation-Solubility Calculations: Theoretical Manual, User's Guide, and Related Documentation (Version 7.0). UCRL-MA-110662 PT III. Livermore, California: Lawrence Livermore National Laboratory. ACC: MOL.19980717.0626.

162340 Wollast, R.; Mackenzie, F.T.; and Bricker, O.P. 1968. "Experimental Precipitation and Genesis of Sepiolite at Earth-Surface Conditions." *American Mineralogist, 53,* 1645-1662. Washington, D.C.: Mineralogical Society of America. TIC: 253980.

100493 Wronkiewicz, D.J.; Bates, J.K.; Gerding, T.J.; Veleckis, E.; and Tani, B.S. 1992. "Uranium Release and Secondary Phase Formation During Unsaturated Testing of UO2 at 90°C." *Journal of Nuclear Materials, 190,* 107-127. Amsterdam, The Netherlands: North-Holland Publishing Company. TIC: 236558.

102047 Wronkiewicz, D.J.; Bates, J.K.; Wolf, S.F.; and Buck, E.C. 1996. "Ten-Year Results from Unsaturated Drip Tests with UO_2 at 90°C: Implications for the Corrosion of Spent Nuclear Fuel." *Journal of Nuclear Materials, 238,* (1), 78-95. Amsterdam, The Netherlands: North-Holland. TIC: 243361.

172325 Ziemniak, S.E.; Jones, M.E.; and Combs, K.E.S. 1993. "Solubility Behavior of Titanium(IV) Oxide in Alkaline Media at Elevated Temperatures." *Journal of Solution Chemistry, 22,* (7), 601-623. New York, New York: Plenum Press. TIC: 256710.

8.2 CODES, STANDARDS, REGULATIONS, AND PROCEDURES

10 CFR 63. 2006. Energy: Disposal of High-Level Radioactive Wastes in a Geologic Repository at Yucca Mountain, Nevada. Internet Accessible.

AP-SIII.2Q, Rev. 1, ICN 2. *Qualification of Unqualified Data.* Washington, D.C.: U.S. Department of Energy, Office of Civilian Radioactive Waste Management. ACC: DOC.20040127.0008. Historical reference

IM-PRO-003, Rev. 2, ICN 0. Software Management. Washington, D.C.: U.S. Department of Energy, Office of Civilian Radioactive Waste Management. ACC: DOC.20070228.0002.

LS-PRO-0203, Rev. 2, ICN 0. *Q-List and Classification of Structures, Systems, and Components*. Washington, D.C.: U.S. Department of Energy, Office of Civilian Radioactive Waste Management. ACC: DOC.20060927.0016.

SCI-PRO-001, Rev 2, ICN 0. *Qualification of Unqualified Data.* Washington, D.C.: U.S. Department of Energy, Office of Civilian Radioactive Waste Management. ACC: DOC.20070522.0016.

SCI-PRO-005, Rev. 3, ICN 0. *Scientific Analyses and Calculations.* Washington, D.C.: U.S. Department of Energy, Office of Civilian Radioactive Waste Management. ACC: DOC.20070531.0004.

8.3 SOURCE DATA, LISTED BY DATA TRACKING NUMBER

152576 MO0009THRMODYN.001. Input Transmittal for Thermodynamic Data Input Files for Geochemical Calculations. Submittal date: 09/20/2000.

161791 MO0106MWDTDG01.035. Model Warehouse Data for the Development of Temperature Dependant GIBBS Free Energys for Selected Half Reactions Involved in Microbial Metabolism. Submittal date: 06/18/2001.

161756 MO0302SPATHDYN.000. Thermodynamic Data Input Files - Data0.YMP.R2. Submittal date: 02/05/2003.

161886 MO0302SPATHDYN.001. Thermodynamic Data Supporting Spreadsheet Files - Data0.YMP.R2. Submittal date: 02/05/2003.

162278 MO0303SPASPEQ2.000. Thermodynamic Datafile SPEQ02.DAT. Submittal date: 03/17/2003.

167800 MO0312SPATDMIF.000. Thermodynamic Data Input Files - Data0.YMP.R3. Submittal date: 12/22/2003.

162572 SN0302T0510102.002. Pitzer Thermodynamic Database (data0.ypf.r0, Formerly data0.ypf, Revision 1). Submittal date: 02/06/2003.

179388 SN0504T0502205.008. Ammonium Pitzer Database Additions (DATA0.YPF.R2) and Binary File (DATA1.YP2). Submittal date: 04/29/2005.

179067 SN0609T0502404.012. Pitzer Thermodynamic Database (DATA0.YP2). Submittal date: 09/28/2006.

8.4 OUTPUT DATA, LISTED BY DATA TRACKING NUMBER

SN0410T0510404.002. Thermodynamic Database Input File for EQ3/6 - DATA0.YMP.R4. Submittal date: 11/01/2004.

SN0410T0510404.001. Corrections to Errors in the DATA0.YMP.R2 Thermodynamic Database. Submittal date: 11/01/2004.

SN0612T0502404.014. Thermodynamic Database Input File for EQ3/6 - Data0.YMP.R5. Submittal date: 12/15/2006.

SN0702T0502404.015. Supporting Spreadsheets and Data Files for Thermodynamic Database Input File for EQ3/6 - Data0.YMP.R5 Submittial date: 02/09/2007.

8.5 SOFWARE CODES

162228 EQ3/6 V. 8.0. 2003. WINDOWS 2000, WIN NT 4.0, WIN 98, WIN 95. STN: 10813-8.0-00.

153218 Software Code: SUPCRT92 VV1.0. 1999. PC w/Windows OS and MAC w/MAC OS. 10058-1.0-00.

INTENTIONALLY LEFT BLANK

APPENDIX A

DISCREPANCIES IN THERMODYNAMIC DATA FOR KEY AQUEOUS SPECIES

INTENTIONALLY LEFT BLANK

Note: This appendix is a revised version of a white paper entitled *Discrepancies in Key Thermodynamic Data for the Fundamental Aqueous Species* by Thomas J. Wolery, dated September 29, 2005. The phosphate key data discrepancy that was noted was later incorporated into CR 6731.

Thermochemical data for any database that addresses aqueous solutions include the standard Gibbs energies of formation, enthalpies of formation, and entropies of the key aqueous species that represent the common oxidation states of the chemical elements. These key species include simple ions such as Na^+ and Cl^-, oxy-ions and hydroxy-ions such as UO_2^{2+} and HCO_3^-, and electrically neutral species such as $SiO_2(aq)$. Three distinct, influential sets of recommended key data for such species are presently in common use:

(1) *SUPCRT92*: As represented in the data files slop98.dat, sprons98.dat, and speq02.dat. The files slop98.dat and sprons98.dat are nearly identical; slop98.dat is in DTN: MO0106MWDTDG01.035 [DIRS 161791]; sprons98.dat and speq02.dat are in DTN: MO0009THRMODYN.001 [DIRS 152576], in the folder *\cd\SUPCRT_runs_TJW\SUPCRT_datafiles*. Differences among these three files do not affect any key aqueous species to be addressed in this appendix.

(2) *NIST89*: *The NBS Tables of Chemical Thermodynamic Properties, Selected Values for Inorganic and* C_1 *and* C_2 *Organic Substances in SI Units* (Wagman et al. 1982 [DIRS 159216]; Wagman et al. 1989 [DIRS 179315])

(3) *CODATA89*: *CODATA Key Values for Thermodynamics* (Cox et al. 1989 [DIRS 150874]).

The dilute systems thermochemical databases data0.ymp.R2 and data0.ymp.R4 (DTN: MO0302SPATHDYN.000 [DIRS 161756] and Output DTN: SN0410T0510404.002) mainly use the *SUPCRT92* data for key species. Some key aqueous species are not represented in the *SUPCRT92* set. These are taken from other sources, primarily volumes in the multi-volume *Chemical Thermodynamics* series sponsored by the Nuclear Energy Agency (NEA) of the Organisation for Economic Co-operation and Development (OECD) (e.g., volume 2, *Chemical Thermodynamics of Americium*, Silva et al. 1995 [DIRS 102087]).

It might be assumed that the thermochemical data for key aqueous species differs not at all or to a negligible degree among the *SUPCRT92*, *NIST89*, and *CODATA89* datasets. The purpose of this appendix is to test that assumption. It is noted that the OECD/NEA series *Chemical Thermodynamics* has followed consistency with *CODATA89* since the publication of volume 1, *Chemical Thermodynamics of Uranium* (Grenthe et al. 1992 [DIRS 101671]).

Key thermodynamic data for a set of select, fundamental species underpin any thermodynamic database (cf. Nordstrom and Munoz 1994 [DIRS 168480]; Garrels and Christ 1990 [DIRS 144877]). These key data for any such database used to address aqueous solutions include the standard Gibbs energies of formation, enthalpies of formation, and entropies of the most basic aqueous solute species or referred in the report as "ions". Examples are simple ions including Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Cl^-, and F^-; oxy-ions and hydroxy-ions including UO_2^{2+}, NpO_2^+, SO_4^{2-}, HCO_3^-, and HPO_4^{2-}; and compositionally similar but electrically neutral species including SiO_2(aq) and $Ti(OH)_4$(aq). In geochemical modeling parlance, such species are often referred to as "basis" or "master" species (e.g., Wolery, 1992 [DIRS 100836]), because they are used as "building blocks" in constructing reactions for other species. In thermodynamic property measurement, it is often a property of the reaction that is actually measured. The corresponding property of a non-basis species is often then extracted using a set of adopted values for the corresponding properties of these basis species. In the construction of thermodynamic databases, reaction properties are sometimes computed from adopted values of the corresponding properties of the species appearing in the desired reaction. That reaction does not necessarily match any reaction whose properties were measured to obtain any of these species properties.

It would be reasonable to surmise that the thermodynamic properties of the basic aqueous solute species would in large part be well established, for example by an organization such as the National Institute of Standards and Technology (NIST) or by a succession of published technical results converging to an agreed upon set of values with small uncertainties. Unfortunately that is not the case. At least three distinct sets of key data for such species are presently in common use; these will be referred to as *CODATA89*, *NIST89*, and *SUPCRT92*. The present YMP thermodynamic database (e.g., data0.ymp.R4, Output DTN: SN0410T0510404.002) is founded on *SUPCRT92*. However, *CODATA89* and *NIST89* are also influential. The differences among these data sets for key species in common appear to have received little previous attention. These differences will now be examined in this appendix. Most of the attention will focus on differences in values for the standard Gibbs energies of formation.

CODATA89. CODATA (Committee on Data for Science and Technology) is an interdisciplinary Scientific Committee of the International Council for Science (ICSU). Its purpose is to improve the quality, reliability, management and accessibility of data of importance to all fields of science and technology. In the 1970s and 1980s, the CODATA Task Group published a series of papers giving and updating recommendations for key thermodynamic data (including for the basic aqueous ions). These reports had great influence on geochemical and other thermodynamic databases. The series culminated with a book by Cox et al. (1989 [DIRS 150874]) entitled *CODATA Key Values for Thermodynamics*. This book was CODATA's last word on the subject. In the present report, this key data set will be referred to as *CODATA89*. *CODATA89* was adopted by the NEA (e.g., volume 1, *Chemical Thermodynamics of Uranium*, Grenthe et al. 1992 [DIRS 101671]) as part of the "selected auxiliary data" for its recommendations of thermodynamic data for species of radionuclide elements. Cox et al. (1989 [DIRS 150874]) do not give the standard Gibbs energies of formation, only the standard enthalpies of formation and the standard entropies, along with stated uncertainties for these quantities (these data are only for 298.15 K). Together with data for the entropies of the elements in their reference forms (which Cox et al. 1989 [DIRS 150874] also give, one may calculate the equivalent *CODATA89* standard Gibbs energies of formation (the OECD/NEA volumes include such calculated data in their tables of auxiliary data).

Table A-1 shows the relevant thermodynamic data of key aqueous species for *CODATA89*, along with the associated uncertainty values. The standard Gibbs energies of formation are calculated from the corresponding enthalpies of formation and entropies using standard thermodynamic relations (Output DTN: SN0702T0502404.015, folder: *\Key Data Comparison*, spreadsheet: *Thermo_data_ions_intercomparison.xls*, worksheet: "CODATA"). The given uncertainties are "worst case" results based on the uncertainties in the standard enthalpies of formation, the standard entropies, and the entropies of the chemical elements in their stable reference states. Note that in the best cases, the uncertainties in the Gibbs energies are a few tenths of a kJ, in the worst cases, about 1-4.5 kJ. The single worst case here is for the aluminum ion (Al^{3+}). Note that uncertainties > 1 kJ are associated with some of the more common and important species (e.g., Ca^{2+}, Cu^{2+}, Mg^{2+}, and UO_2^{2+}). *CODATA89* is the only one of the three key data sets to be discussed in this report which gives explicit uncertainties.

Table A-1. *CODATA89* Data Summary

Species	ΔG_f^o J/mol	ΔG_f^o ± J/mol	ΔH_f^o J/mol	ΔH_f^o ± J/mol	S^o J/mol-K	S^o ± J/mol-K
Ag^+	77096.0	259.3	105790.0	80.0	73.450	0.400
Al^{3+}	−491507.0	4512.7	−538400.0	1500.0	−325.000	10.000
Br^-	−103850.5	254.8	−121410.0	150.0	82.550	0.200
CO_3^{2-}	−527899.8	581.1	−675230.0	250.0	−50.000	1.000
Ca^{2+}	−552806.2	1418.3	−543000.0	1000.0	−56.200	1.000
Cd^{2+}	−77732.8	1092.8	−75920.0	600.0	−72.800	1.500
Cl^-	−131218.4	161.6	−167080.0	100.0	56.600	0.200
ClO_4^-	−7890.5	852.1	−128100.0	400.0	184.000	1.500
Cs^+	−291455.4	768.8	−258000.0	500.0	132.100	0.500
Cu^{2+}	65040.1	2217.3	64900.0	1000.0	−98.000	4.000
F^-	−281523.3	889.7	−335350.0	650.0	−13.800	0.800
H^+	0.0	0.0	0.0	0.0	0.000	0.000
HCO_3^-	−586845.2	382.0	−689930.0	200.0	98.400	0.500
HPO_4^{2-}	−1095985.5	2026.1	−1299000.0	1500.0	−33.500	1.500
HS^-	12243.1	3006.6	−16300.0	1500.0	67.000	5.000
HSO_4^-	−755315.1	1018.8	−886900.0	1000.0	131.700	3.000
$H_2PO_4^-$	−1137152.4	2026.1	−1302600.0	1500.0	92.500	1.500
Hg^{2+}	164667.4	475.2	170210.0	200.0	−36.190	0.800
Hg_2^{2+}	153566.5	811.0	166870.0	500.0	65.740	0.800
I^-	−51723.4	184.6	−56780.0	50.0	106.450	0.300
K^+	−282509.6	199.7	−252140.0	80.0	101.200	0.200
Li^+	−292918.3	184.8	−278470.0	80.0	12.240	0.150
Mg^{2+}	−455375.1	1823.3	−467000.0	600.0	−137.000	4.000
NH_4^+	−79397.9	371.2	−133260.0	250.0	111.170	0.400
NO_3^-	−110794.3	522.5	−206850.0	400.0	146.700	0.400
Na^+	−261952.9	164.8	−240340.0	60.0	58.450	0.150
OH^-	−157219.9	101.3	−230015.0	40.0	−10.900	0.200
Pb^{2+}	−24237.9	638.5	920.0	250.0	18.500	1.000
Rb^+	−284008.9	264.4	−251120.0	100.0	121.750	0.250
SO_4^{2-}	−744004.5	538.0	−909340.0	400.0	18.500	0.400

Table A-1. *CODATA89* Data Summary (Continued)

Species	ΔG_f^o J/mol	ΔG_f^o ± J/mol	ΔH_f^o J/mol	ΔH_f^o ± J/mol	S^o J/mol-K	S^o ± J/mol-K
Sn^{2+}	−27623.8	2217.3	−8900.0	1000.0	−16.700	4.000
UO_2^{2+}	−952550.7	2456.5	−1019000.0	1500.0	−98.200	3.000
Zn^{2+}	−147203.4	394.7	−153390.0	200.0	−109.800	0.500

Source: Output DTN: SN0702T0502404.015, folder: *\Key Data Comparison*, workbook: *Thermo_data_ions_intercomparison.xls*, worksheet: "CODATA."

NOTE: The standard Gibbs energies of formation and the corresponding uncertainties were calculated using data provided by the source. The calculated uncertainty in the Gibbs energy is a worst-case upper bound based on the uncertainties given by the source for the standard enthalpy of formation, the standard entropy, and the standard entropies of the chemical elements in their reference states.

NIST89. An alternative set of values for thermodynamic data of key aqueous species are given by what will be referred to in this appendix as *NIST89* (Wagman et al. 1982 [DIRS 159216]; Wagman et al. 1989 [DIRS 179315]). This is a product of the National Institute of Standards and Technology (NIST, formerly the National Bureau of Standards, and NBS). The two Wagman et al. reports were products of the old National Bureau of Standards. The scope of the data in these reports is extensive, covering many chemical elements and their species, solid and aqueous. Although the 1982 report is widely referenced and generally considered a trustworthy source of data, it is often criticized because with little exception there is no published record of the derivation of the data or explanation of how it is that these particular data came to be recommended instead of possible alternatives. The 1989 "erratum" contains a large number of corrections, but offers little additional insight. The two reports are actually the culmination of a long series of reports by Wagman and other NBS researchers; they supersede the older reports in the series. The series itself has been widely recognized and used in geochemistry and in other fields.

Table A-2 summarizes the *NIST89* data for key species matching those in A-1. Note that uncertainties are not provided, only recommended values for the standard thermodynamic quantities.

Table A-2. *NIST89* Data Summary

Species	ΔG^o_f J/mol	ΔH^o_f J/mol	S^o J/mol-K
Ag^+	77107.0	105579.0	72.680
Al^{3+}	−485000.0	−531000.0	−321.700
Br^-	−103960.0	−121550.0	82.400
CO_3^{2-}	−527810.0	−677140.0	−56.900
Ca^{2+}	−553580.0	−542830.0	−53.100
Cd^{2+}	−77612.0	−75900.0	−73.200
Cl^-	−131228.0	−167159.0	56.500
ClO_4^-	−8520.0	−129330.0	182.000
Cs^+	−292020.0	−258280.0	133.050
Cu^{2+}	65490.0	64770.0	−99.600

Table A-2. *NIST89* Data Summary (Continued)

Species	ΔG^o_f J/mol	ΔH^o_f J/mol	S^o J/mol-K
F^-	−278790.0	−332630.0	−13.800
H^+	0.0	0.0	0.000
HCO_3^-	−586770.0	−691990.0	91.200
HPO_4^{2-}	−1089150.0	−1292140.0	−33.500
HS^-	12080.0	−17600.0	62.800
HSO_4^-	−755910.0	−887340.0	131.800
$H_2PO_4^-$	−1130280.0	−1296290.0	90.400
Hg^{2+}	164400.0	171100.0	−32.200
Hg_2^{2+}	153520.0	172400.0	84.500
I^-	−51570.0	−55190.0	111.300
K^+	−283270.0	−252380.0	102.500
Li^+	−293310.0	−278490.0	13.400
Mg^{2+}	−454800.0	−466850.0	−138.100
NH_4^+	−79310.0	−132510.0	113.400
NO_3^-	−111250.0	−207360.0	146.400
Na^+	−261905.0	−240120.0	59.000
OH^-	−157244.0	−229994.0	−10.750
Pb^{2+}	−24430.0	−1700.0	10.500
Rb^+	−283980.0	−251170.0	121.500
SO_4^{2-}	−744530.0	−909270.0	20.100
Sn^{2+}	—	—	—
UO_2^{2+}	−953500.0	−1019600.0	−97.500
Zn^{2+}	−147060.0	−153890.0	−112.100

Source: Output DTN: SN0702T0502404.015, folder: *\Key Data Comparison*, spreadsheet: *Thermo_data_ions_intercomparison.xls*, worksheet: "NIST89."

NOTE: Species shown match those in Table A-1.

Table A-3 provides direct comparison of Gibbs energies for *CODATA89* vs. *NIST89*. Note the particularly large magnitudes of discrepancies for Al^{3+} (6.5 kJ/mol), HPO_4^{2-}(6.8 kJ/mol), $H_2PO_4^-$(6.9 kJ/mol), and F^- (2.7 kJ/mol). The magnitude of the discrepancy for UO_2^{2+} is also rather high, just under 1 kJ/mol. Otherwise, the general range of discrepancies appears to be not unreasonable, especially in comparison with the worst-case uncertainties shown in Table A-1 for *CODATA89* data. The larger discrepancies are surprising. D.D. Wagman was a principal author of both *CODATA89* (second author of Cox et al. 1989 [DIRS 150874]) and *NIST89* (first author of Wagman et al. 1982 [DIRS 159216] and Wagman et al. 1989 [DIRS 179315]). Cox et al. (1989 [DIRS 150874]) and the later paper by Wagman et al. (1989 [DIRS 179315]) are essentially contemporaneous. One might therefore expect that a comparison of key data from the two sets would yield few if any discrepancies, and certainly no large ones. However, neither Cox et al. (1989 [DIRS 150874]) nor Wagman et al. (1989 [DIRS 179315]) address these discrepancies.

Table A-3. Comparison of 298.15 K Values of the Standard Gibbs Energies of Formation (ΔG_f^o J/mol) of Key Aqueous Species, *CODATA89* vs. *NIST89*

Species	***CODATA89***	***NIST89***	**Discrepancy**
Ag^+	77096.0	77107.0	−11.0
Al^{3+}	−491507.0	−485000.0	**−6507.0**
$Br^−$	−103850.5	−103960.0	109.5
$CO_3^{2−}$	−527899.8	−527810.0	−89.8
Ca^{2+}	−552806.2	−553580.0	**773.8**
Cd^{2+}	−77732.8	−77612.0	−120.8
$Cl^−$	−131218.4	−131228.0	9.6
$ClO_4^−$	−7890.5	−8520.0	**629.5**
Cs^+	−291455.4	−292020.0	**564.6**
Cu^{2+}	65040.1	65490.0	−449.9
$F^−$	−281523.3	−278790.0	**−2733.3**
H^+	0.0	0.0	0.0
$HCO_3^−$	−586845.2	−586770.0	−75.2
$HPO_4^{2−}$	−1095985.5	−1089150.0	**−6835.5**
$HS^−$	12243.1	12080.0	163.1
$HSO_4^−$	−755315.1	−755910.0	**594.9**
$H_2PO_4^−$	−1137152.4	−1130280.0	**−6872.4**
Hg^{2+}	164667.4	164400.0	267.4
Hg_2^{2+}	153566.5	153520.0	46.5
$I^−$	−51723.4	−51570.0	−153.4
K^+	−282509.6	−283270.0	**760.4**
Li^+	−292918.3	−293310.0	391.7
Mg^{2+}	−455375.1	−454800.0	**−575.1**
NH_4^+	−79397.9	−79310.0	−87.9
$NO_3^−$	−110794.3	−111250.0	455.7
Na^+	−261952.9	−261905.0	−47.9
$OH^−$	−157219.9	−157244.0	24.1
Pb^{2+}	−24237.9	−24430.0	192.1
Rb^+	−284008.9	−283980.0	−28.9
$SO_4^{2−}$	−744004.5	−744530.0	**525.5**
Sn^{2+}	−27623.8	—	—
UO_2^{2+}	−952550.7	−953500.0	**949.3**
Zn^{2+}	−147203.4	−147060.0	−143.4

Source: Output DTN: SN0702T0502404.015, folder: *Key Data Comparison*, spreadsheet: *Thermo_data_ions_intercomparison.xls*, worksheet: “NIST89 vs. SUPCRT92.”

NOTE: Species shown match those in previous tables. Discrepancies of magnitude greater than 1,000 J/mol are shown using red bold font; lesser discrepancies with magnitude greater than 500 J/mol are shown in blue bold font.

SUPCRT92. SUPCRT92 is actually the name of a computer program (Johnson et al. 1992 [DIRS 101632]) for making certain types of thermodynamic calculations. As used in this report, *SUPCRT92* refers to the associated data files *slop98.dat*, *sprons98.dat*, and *speq02.dat*. The file *slop98.dat* is in DTN: MO0106MWDTDG01.035 [DIRS 161791]; *sprons98.dat* and *speq02.dat* are in folder *\cd\SUPCRT_runs_TJW\SUPCRT_datafiles* of DTN: MO0009THRMODYN.001 [DIRS 152576]. The files *slop98.dat* and *sprons98.dat* are nearly identical. They differ only in that the latter corrects a sign error in the Gibbs energy of formation of the non-key aqueous species $AuCl_4^-$. The file *speq02.dat* has very slightly different data for the mineral quartz (SiO_2) and notably different data for the key aqueous species SiO_2(aq), reflecting a change to the "Rimstidt" paradigm from the older "Fournier" paradigm (see Section 6.1.5).

The *SUPCRT92* database is a product of geochemists, with origins tracing to the University of California at Berkeley laboratory of Harold C. Helgeson (e.g., Helgeson et al. 1978 [DIRS 101596]; Helgeson and Kirkham 1974 [DIRS 157904];) and tracing through a succession of subsequent papers mainly by Helgeson, his students, and their students (e.g., Shock and Helgeson 1988 [DIRS 144817]; Shock et al. 1997 [DIRS 150770]; and Shock et al. 1997 [DIRS 127953])). *CODATA89* and *NIST89* basically reflect work up to 1989, while *SUPCRT92* (despite the "92") in part reflects more recent work.

Table A-4 summarizes the *SUPCRT92* data for key species matching those in Tables A-1 (*CODATA89*) and A-2 (*NIST89*). Note that uncertainties are again not provided (as was the case for the *NIST89* data).

Table A-4. *SUPCRT92* Data Summary

Species	**ΔG^o_f J/mol**	**ΔH^o_f J/mol**	**S^o J/mol-K**
Ag^+	77098.6	105750.6	73.4
Al^{3+}	−483708.1	−530673.5	−325.1
Br^-	−104056.1	−121503.4	82.8
CO_3^{2-}	−527983.1	−675234.8	−50.0
Ca^{2+}	−552790.1	−543083.2	−56.5
Cd^{2+}	−77655.0	−75897.8	−72.8
Cl^-	−131289.7	−167079.7	56.7
ClO_4^-	−8535.4	−129327.4	182.0
Cs^+	−291666.6	−258027.3	132.8
Cu^{2+}	65584.2	65688.8	−97.1
F^-	−281750.6	−335347.6	−13.2
H^+	0.0	0.0	0.0
HCO_3^-	−586939.9	−689933.2	98.4
HPO_4^{2-}	−1089137.0	−1292082.0	−33.5
HS^-	11966.2	−16108.4	68.2
HSO_4^-	−755755.9	−889100.0	125.5
$H_2PO_4^-$	−1130265.8	−1296286.9	90.4
Hg^{2+}	164682.2	170163.3	−36.3
Hg_2^{2+}	153594.6	166857.9	65.7
I^-	−51923.4	−56902.4	106.7
K^+	−282461.8	−252169.7	101.0

Table A-4. *SUPCRT92* Data Summary (Continued)

Species	**ΔG^o_f J/mol**	**ΔH^o_f J/mol**	**S^o J/mol-K**
Li^+	−292599.7	−278453.6	11.3
Mg^{2+}	−453984.9	−465959.5	−138.1
NH_4^+	−79454.2	−133260.4	111.2
NO_3^-	−110905.3	−206810.9	146.9
Na^+	−261880.7	−240299.7	58.4
OH^-	−157297.5	−230023.8	−10.7
Pb^{2+}	−23890.6	920.5	17.6
Rb^+	−283675.2	−251123.7	120.5
SO_4^{2-}	−744459.1	−909601.6	18.8
Sn^{2+}	−27488.9	−8786.4	−16.7
UO_2^{2+}	−952613.1	−1019013.2	−98.3
Zn^{2+}	−147276.8	−153385.4	−109.6

Source: Output DTN: SN0702T0502404.015, folder: *\Key Data Comparison*, spreadsheet: *Thermo_data_ions_intercomparison.xls*, worksheet: "SUPCRT92."

NOTE: Species shown match those in previous tables. Values from the cited source are in calorie units (e.g., cal/mol, cal/mol-K). They have been converted to Joule units.

Table A-5 provides a direct comparison of Gibbs energies for *CODATA89* vs. *SUPCRT92*. Note the particularly large magnitudes of the discrepancies for Al^{3+} (7.8 kJ/mol), HPO_4^{2-} (6.8 kJ/mol), $H_2PO_4^-$ (6.9 kJ/mol), and Mg^{2+} (1.4 kJ/mol). Note that the extreme discrepancies for Al^{3+}, HPO_4^{2-}, and $H_2PO_4^-$ basically match those obtained when comparing *NIST89* with *CODATA89*.

Table A-5. Comparison of 298.15 K Values of the Standard Gibbs Energies of Formation (ΔG^o_f J/mol) of Key Aqueous Species, *CODATA89* vs. *SUPCRT92*

Species	***CODATA89***	***SUPCRT92***	**Discrepancy**
Ag^+	77096.0	77098.6	−2.5
Al^{3+}	−491507.0	−483708.1	**−7798.9**
Br^-	−103850.5	−104056.1	205.6
CO_3^{2-}	−527899.8	−527983.1	83.4
Ca^{2+}	−552806.2	−552790.1	−16.1
Cd^{2+}	−77732.8	−77655.0	−77.7
Cl^-	−131218.4	−131289.7	71.4
ClO_4^-	−7890.5	−8535.4	**644.8**
Cs^+	−291455.4	−291666.6	211.2
Cu^{2+}	65040.1	65584.2	**−544.1**
F^-	−281523.3	−281750.6	227.2
H^+	0.0	0.0	0.0
HCO_3^-	−586845.2	−586939.9	94.7
HPO_4^{2-}	−1095985.5	−1089137.0	**−6848.5**
HS^-	12243.1	11966.2	276.9

Table A-5 Comparison of 298.15 K Values of the Standard Gibbs Energies of Formation (ΔG^o_f J/mol) of Key Aqueous Species, *CODATA89* vs. *SUPCRT92* (Continued)

Species	***CODATA89***	***SUPCRT92***	**Discrepancy**
HSO_4^-	−755315.1	−755755.9	440.8
$H_2PO_4^-$	−1137152.4	−1130265.8	**−6886.6**
Hg^{2+}	164667.4	164682.2	−14.8
Hg_2^{2+}	153566.5	153594.6	−28.1
I^-	−51723.4	−51923.4	200.1
K^+	−282509.6	−282461.8	−47.7
Li^+	−292918.3	−292599.7	−318.7
Mg^{2+}	−455375.1	−453984.9	**−1390.2**
NH_4^+	−79397.9	−79454.2	56.3
NO_3^-	−110794.3	−110905.3	111.0
Na^+	−261952.9	−261880.7	−72.1
OH^-	−157219.9	−157297.5	77.6
Pb^{2+}	−24237.9	−23890.6	−347.3
Rb^+	−284008.9	−283675.2	−333.7
SO_4^{2-}	−744004.5	−744459.1	454.6
Sn^{2+}	−27623.8	−27488.9	−134.9
UO_2^{2+}	−952550.7	−952613.1	62.4
Zn^{2+}	−147203.4	−147276.8	73.4

Source: Output DTN: SN0702T0502404.015, folder: *Key Data Comparison*, spreadsheet: *Thermo_data_ions_intercomparison.xls*, worksheet: "CODATA vs. SUPCRT92."

NOTE: Species shown match those in previous tables. Discrepancies of magnitude greater than 1000 J/mol are shown using red bold font; lesser discrepancies with magnitude greater than 500 J/mol are shown in blue bold font.

Table A-6 provides a direct comparison of Gibbs energies for *SUPCRT92* vs. *NIST89*. Note the largest discrepancies are smaller than for either of these data sets vs. *CODATA89*. The magnitude of the discrepancy for Al^{3+} is large, but notably smaller (1.3 kJ/mol) than in the previous comparisons. The largest magnitude of a discrepancy is for F^- (3.0 kJ/mol). The discrepancies for HPO_4^{2-} and $H_2PO_4^-$ are trivial. It is likely that these values only differ due to conversion between calorie and joule units, and a small degree of rounding.

Table A-6. Comparison of 298.15 K Values of the Standard Gibbs Energies of Formation (ΔG^o_f J/mol) of Key Aqueous Species, *NIST89* vs. *SUPCRT92*

Species	***NIST89***	***SUPCRT92***	**Discrepancy**
Ag^+	77107.0	77098.6	8.4
Al^{3+}	−485000.0	−483708.1	**−1291.9**
Br^-	−103960.0	−104056.1	96.1
CO_3^{2-}	−527810.0	−527983.1	173.1
Ca^{2+}	−553580.0	−552790.1	**−789.9**
Cd^{2+}	−77612.0	−77655.0	43.0
Cl^-	−131228.0	−131289.7	61.7
ClO_4^-	−8520.0	−8535.4	15.4
Cs^+	−292020.0	−291666.6	−353.4
Cu^{2+}	65490.0	65584.2	−94.2
F^-	−278790.0	−281750.6	**2960.6**
H^+	0.0	0.0	0.0
HCO_3^-	−586770.0	−586939.9	169.9
HPO_4^{2-}	−1089150.0	−1089137.0	−13.0
HS^-	12080.0	11966.2	113.8
HSO_4^-	−755910.0	−755755.9	−154.1
$H_2PO_4^-$	−1130280.0	−1130265.8	−14.2
Hg^{2+}	164400.0	164682.2	−282.2
Hg_2^{2+}	153520.0	153594.6	−74.6
I^-	−51570.0	−51923.4	353.4
K^+	−283270.0	−282461.8	**−808.2**
Li^+	−293310.0	−292599.7	**−710.3**
Mg^{2+}	−454800.0	−453984.9	**−815.1**
NH_4^+	−79310.0	−79454.2	144.2
NO_3^-	−111250.0	−110905.3	−344.7
Na^+	−261905.0	−261880.7	−24.3
OH^-	−157244.0	−157297.5	53.5
Pb^{2+}	−24430.0	−23890.6	**−539.4**
Rb^+	−283980.0	−283675.2	−304.8
SO_4^{2-}	−744530.0	−744459.1	−70.9
Sn^{2+}	—	−27488.9	—
UO_2^{2+}	−953500.0	−952613.1	**−886.9**
Zn^{2+}	−147060.0	−147276.8	216.8

Source: Output DTN: SN0702T0502404.015, folder: *Key Data Comparison*, spreadsheet: *Thermo_data_ions_intercomparison.xls*, worksheet: “NIST89 vs. SUPCRT92.”

NOTE: Species shown match those in previous tables. Discrepancies of magnitude greater than 1000 J/mol are shown using red bold font; lesser discrepancies with magnitude greater than 500 J/mol are shown in blue bold font.

SUPCRT92 and *NIST89* agree better with each other than with *CODATA89*, at least when considering the extreme discrepancies. In particular, the Gibbs energy values of *CODATA89* of Al^{3+}, HPO_4^{2-}, and $H_2PO_4^-$ are quite different from those of *SUPCRT92* and *NIST89*. The thermodynamic properties of the aluminum ion are now more the hands of geochemists and engineers (e.g., Wesolowski 1992 [DIRS 162148]; Bourcier et al., 1993 [DIRS 149834]) than of the more traditional thermodynamicists (who tend to avoid solubility data). It is unlikely that anyone conducting a detailed examination of the discrepancies noted here for Al^{3+} would fail to quickly reject the *CODATA89* data for this ion.

The data recommended by *CODATA89* (and the OCED/NEA volumes) on the one hand and those by *NIST89* (and *SUPCRT92*) on the other for HPO_4^{2-} and $H_2PO_4^-$ are highly discrepant. Although these ions are of significance in geochemistry, they have not received the same attention as the aluminum ion. Cox et al. (1989 [DIRS 150874]) provide brief notes on the origin of the *CODATA89* data. They do not discuss why their recommendations for these species differ from those recommended by *NIST89*, nor do they note that such differences exist. Wagman et al. (1982 [DIRS 159216]) and Wagman et al. (1989 [DIRS 179315]) give no specific information regarding the origin of the *NIST89* number for these species. Nor do they discuss or note differences with other sources. The discrepancies in the recommended data for these two key phosphate species is problematic for thermochemical databases such as those in the data0.ymp.R* series that attempt broad coverage of phosphate compounds and species. Data for various compounds and species must be gathered from different sources in the literature. Some sources may be consistent with *CODATA89*, that from others with *NIST89*, and in some remaining cases there may be mixed or unknown consistency.

The thermochemical databases in the data0.ymp.R* series from R0 (Steinborn et al. (2003 [DIRS 161956]) through R4 (Rev. 00 of the present analysis report) adopted data for solids and aqueous complexes of many radionuclide elements from the then-available NEA recommendations (e.g., Grenthe et al. 1992 [DIRS 101671]). A number of those solids and aqueous complexes involve phosphate [e.g., for uranium, from Grenthe et al. 1992 [DIRS 101671], p. 44-45: $(UO_2)_3(PO_4)_2(cr)$, $UO_2HPO_4.4H_2O(cr)$, $U(HPO_4)_2.4H_2O(cr)$, $UO_2HPO_4(aq)$, $UO_2H_2PO_4^+$, and $UO_2(HPO_4)_2(aq)$]. However, those data0.ymp.R* databases used the *SUPCRT92* data for the species HPO_4^{2-} and $H_2PO_4^-$. Because the NEA (e.g., Grenthe et al. 1992 [DIRS 101671]) adopted the *CODATA89* recommendations for these ions (HPO_4^{2-} is the phosphate basis species used in the data0.ymp.R* series), the resulting data0.ymp.R* results contain an inconsistency of ~6.8 kJ/mol per HPO_4^{2-} in each reaction. The first step in resolving this inconsistency is to determine which values should actually be used for the standard Gibbs energies of HPO_4^{2-} and $H_2PO_4^-$. This will be addressed in Appendix B.

The three data sets (*CODATA89*, *NIST89*, and *SUPCRT92*) exhibit a significant number of lesser discrepancies when any two data sets are compared. These are much less problematic. The low magnitude discrepancies up to about 200-300 J/mol are comparable to minimal uncertainties as suggested by the uncertainties for the *CODATA89* dataset (Table A-1). At this level, the important thing is to choose a set of data and apply it consistently. Small ad hoc adjustments within this uncertainty level are justified to reconcile conflicting thermodynamic data (e.g., solubility vs. calorimetry). If the consequences of discrepancies at this level were problematic, then the means would exist to extract more accurate values (with reduced uncertainty).

Species for which the Gibbs energies discrepancies lie between these levels (there are a number of examples in the approximate range 500-1000 J/mol in Tables A-3, A-5, and A-6) are more problematical in that in certain applications just using a consistent set of data might suffice, whereas in other applications it might not.

In dealing with a reaction, errors or discrepancies in standard Gibbs energies of formation affect the Gibbs energy of reaction (ΔG_r^o) in a linear fashion:

$$\Delta G_r^o = \sum_i \nu_{ir} \Delta G_{f,i}^o \qquad \text{(Eq. A-1)}$$

where ν_{ir} is the reaction coefficient of the *i*-th species in reaction *r*. This is in turn related to the equilibrium constant (log K) by:

$$\Delta G_r^o = -2.3026 RT \log K \qquad \text{(Eq. A-2)}$$

where 2.3026 is an approximation representing ln(10), *R* is the gas constant (8.31441 J/mol-K; Weast and Astle 1981 [DIRS 100833], p. F-203) and T is the absolute temperature. For purposes of the following discussion, on a temperature of 25°C (298.15 K) will be considered. Consider a reaction for the dissociation of an aqueous complex or the dissolution of a solid. The effect of incrementing the Gibbs energy of reaction on the equilibrium constant (log K) and on the concentration of a species whose reaction coefficient is 1, with the concentrations of all other species held constant, and the activity coefficients of all other species held constant, is given in Table A-7 for increments ranging from -7000 J/mol to +7000 J/mol. These conditions would apply for the case of AgCl solid (a sparingly soluble salt) in a solution of say 0.1 molal NaCl. The Cl^- and the activity coefficients would be essentially fixed by the specified concentration of NaCl, and the table would then describe the effect of the Gibbs energy of reaction increments on the concentration of the Ag^+ ion. These increments could be due to increments in the Gibbs energies of formation of any or all of Ag^+, Cl^-, or the AgCl solid. A decrement of 100 J/mol would increase the concentration of Ag^+ by 4.12%; an increment of the same magnitude would lower it by 3.95%. A decrement of 800 J/mol would increase it by 38.09%, whereas an increment of the same magnitude would decrease it by 27.58%. It therefore becomes clear that calculated concentrations (solubilities) can be very sensitive to discrepancies in standard Gibbs energies that exist among currently available data sets.

The effect discussed above can be worse in modeling the solubilities of highly soluble salts. In that case, the salts themselves generally determine the "ionic medium" and thus the activity coefficients. The effect on calculated concentrations by a decrement or increment in the assumed standard Gibbs energy of reaction cannot assume that the activity coefficients are constant. The results are may be catastrophic in that a decrement may increase the solubility, which increases the concentrations, but which may lower the activity coefficients such that the activities themselves may decrease and thus require a still higher solubility (this behavior depends on the activity coefficient behavior). This may impose a critical value of the standard Gibbs energy of reaction at which the solubility is no longer finite.

Table A-7. Effect at 298.15 K of Incrementing the Gibbs Energy of Reaction on the Associated Equilibrium Constant and the Effect on Concentration of a Single Aqueous Species, Whose Reaction Coefficient Is 1, for the Case of Fixed Concentrations of All Other Species in the Reaction and Assuming That Activity Coefficients of All Species Are Fixed

$\Delta(\Delta G_r^o)$ J/mol	Δ(log K)	Concentration Ratio	Δ(Concentration) %
−7000	1.2264	16.840	1584.05
−5000	0.8760	7.516	651.57
−3000	0.5256	3.354	235.41
−2000	0.3504	2.241	124.07
−1000	0.1752	1.497	49.69
−800	0.1402	1.381	38.09
−500	0.0876	1.223	22.35
−300	0.0526	1.129	12.86
−200	0.0350	1.084	8.40
−100	0.0175	1.041	4.12
−50	0.0088	1.020	2.04
0	0.0000	1.000	0.00
50	−0.0088	0.980	−2.00
100	−0.0175	0.960	−3.95
200	−0.0350	0.922	−7.75
300	−0.0526	0.886	−11.40
500	−0.0876	0.817	−18.27
800	−0.1402	0.724	−27.58
1000	−0.1752	0.668	−33.20
2000	−0.3504	0.446	−55.37
3000	−0.5256	0.298	−70.19
5000	−0.8760	0.133	−86.69
7000	−1.2264	0.059	−94.06

Source: Output DTN: SN0702T0502404.015, folder: *\Key Data Comparison*, workbook: *DepLogKonDelG.xls*.

The following conclusions can be drawn. There are a large number of discrepancies among the *CODATA89*, *NIST89*, and *SUPCRT92* datasets. These range in magnitude from small to large, the smaller ones being within the likely uncertainties. Uncertainties and discrepancies at the 500 J/mol level or higher lead to relatively high uncertainty in calculated solubilities. The discrepancies in the data for HPO_4^{2-} and $H_2PO_4^-$ between the *CODATA89* data set on the one hand and the *NIST89* and *SUPCRT92* data sets on the other are quite large (6.7 to 6.8 kJ/mol), indicating a serious error that at least one source. Appendix B provides an evaluation and resolution for the phosphate discrepancies. Other discrepancies described in this appendix are merely noted; no attempt is made to resolve them.

Since the issuance of the *NIST89* and *CODATA89* datasets, there has been relatively little work to resolve, let along recognize, the discrepancies in the standard thermodynamic data for key aqueous specie, or to reduce the larger uncertainties. In particular, the sanctioning bodies such as NIST and CODATA appear to have largely abandoned work in this area. Subsequent efforts by various investigators have focused on a relative handful of key aqueous species. As noted previously, the problem of data for the Al^{3+} ion has been more recently addressed (e.g., Wesolowski 1992 [DIRS 162148]; Bourcier et al., 1993 [DIRS 149834]). The data for $SiO_2(aq)$ have recently been changed in the switch from the "Fournier" paradigm to the "Rimstidt" paradigm (Section 6.1.5).   Also, Parker and Khodakovskii (1995 [DIRS 168010]) have made a an effort to constrain the standard Gibbs energies of Fe^{2+} and Fe^{3+}, key geochemical species that are not reflected in the tables in the present report due to their having been ignored by *CODATA89*.

APPENDIX B

THERMOCHEMICAL PROPERTIES OF KEY SPECIES OF PHOSPHORUS

INTENTIONALLY LEFT BLANK

Appendix A of this analysis report noted a significant discrepancy between the CODATA recommendations (Cox et al. 1989 [DIRS 150874]) and the “NBS tables” (Wagman et al. 1982 [DIRS 159216]) for the thermochemical properties of the key phosphate species $H_2PO_4^-$ and HPO_4^{2-}. The latter work is still commonly referred to as the NBS tables, although NBS (National Bureau of Standards) is now NIST (National Institute of Standards and Technology). An erratum appeared some years later (Wagman et al. 1989 [DIRS 179315]). The original tables and the erratum are collectively referred to in Appendix A as the *NIST89* data set, which also refers to the CODATA work as *CODATA89*. As was noted in Appendix A, various subsequent works have adopted one or the other set of data for these two key phosphate species. The purpose of the present appendix is to provide an evaluation of the data and a recommendation of which set of key phosphate data should be used in thermochemical database development. Some of the literature uses obsolete calorie units. These will be here converted to Joule units (1 calorie = 4.1840 Joule; Weast and Astle 1981 [DIRS 100833], p. F-304).

The aqueous chemistry of phosphorus is dominated by P(V); it is nevertheless still quite complicated. Orthophosphoric acid, H_3PO_4, has three acidic protons and can thus exist as H_3PO_4(aq), $H_2PO_4^-$, HPO_4^{2-}, or PO_4^{3-}, depending on concentration, pH, and temperature. Polymeric forms of the phosphate ion are also encountered including the pyrophosphate ion $P_2O_7^{4-}$ and its hydrolyzed forms, the triphosphate ion $P_3O_{10}^{5-}$ and its hydrolyzed forms, and higher-order polymers. Aqueous species containing phosphorus in lower valence states are encountered under anaerobic conditions. These include the orthophosphite ion PO_3^{3-} and its hydrolyzed forms and the phosphite ion PO_2^{3-} and its hydrolyzed forms. Because of this multiplicity of aqueous species, the characterization of the chemical thermodynamic properties of phosphorus is more difficult than for many other elements.

Rossini et al. (1952 [DIRS 178624]) in the National Bureau of Standard’s “Circular 500” summarized the results of previous evaluations of the thermodynamic properties of pure compounds and aqueous species of phosphorus. This evaluation mainly consisted of values of the standard enthalpy of formation $\Delta_f H_m^o$, and in some cases, Gibbs energies of formation, $\Delta_f G_m^o$, standard molar entropies, S_m^o, and molar heat capacities, $C_{p,m}^o$. These tables were subsequently extended and updated by groups of elements in the Technical Note 270 series (e.g., Wagman et al. 1968 [DIRS 178625]). All of the Technical Note 270 series of reports were later combined, with minor corrections, and converted from units of calories to joules (Wagman et al. 1982 [DIRS 159216]). The more recent and widely accepted evaluation of standard values of $\Delta_f H_m^o$ and S_m^o {and values of $H°(298.15\text{ K}) - H°(0)$ for pure phases} is the 1989 CODATA evaluation (Cox et al. 1989 [DIRS 150874]). Grenthe et al. (1992 [DIRS 101671]) have calculated values of $\Delta_f G_m^o$ and their uncertainties from the CODATA results and in a few cases gave additional evaluations. The CODATA recommended results for phosphorus are limited to P(cr, white), the aqueous ions $H_2PO_4^-$ and HPO_4^{2-}, and several gas phase species. However, assessed values of $\Delta_f H_m^o$ for P_4O_{10}(cr, hexagonal) and PCl_5(cr) were cited or implied in the CODATA report because they were involved in the thermodynamic cycles used for the evaluations for the properties of the aqueous species, based on measurements by Head and Lewis (1970 [DIRS 178456]) and Schumm et al. (1974 [DIRS 178842]). All of the evaluations described in this paragraph (Rossini et al. 1952 [DIRS 178624]; Wagman et al. 1968 [DIRS 178625]; Wagman et al. 1982 [DIRS 159216]; Cox et al. 1989 [DIRS 150874]; Grenthe et al. 1992 [DIRS 101671] are restricted to 298.15 K.

The NIST-JANAF tables (Chase 1998 [DIRS 157874]) report thermodynamic properties to very high temperatures, which for phosphorus are restricted to P(cr), P(aq), P(g), P_4O_{10}(cr), P_4O_{10}(g), and PCl_5(g). The values of Barin and Platzki (1995 [DIRS 157865]) for P(cr), P(aq), P(g), P_4O_{10}(cr), and P_4O_{10}(g) are essentially identical.

Table B-1 summarizes the values of $\Delta_f H_m^o$, $\Delta_f G_m^o$, and S_m^o of aqueous PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, and H_3PO_4(aq), P(cr, white), P_4O_{10}(cr) and PCl_5(cr) at 298.15 K from these various evaluations (Rossini et al. 1952 [DIRS 178624]; Wagman et al. 1968 [DIRS 178625]; Wagman et al. 1982 [DIRS 159216]; Cox et al. 1989 [DIRS 150874]; Grenthe et al. 1992 [DIRS 101671]; Chase 1998 [DIRS 157874]; Barin and Platzki 1995 [DIRS 157865]). Some differences are expected because the more recent evaluations are based on larger databases that include experimental studies published after the earlier evaluations. In some cases there are large differences, *e.g.*, values of $\Delta_f H_m^o$ vary by 19.7 $kJ \cdot mol^{-1}$ for PCl_5(cr), by 28.5 $kJ \cdot mol^{-1}$ for P_4O_{10}(cr), and by 6.3 to 7.0 $kJ \cdot mol^{-1}$ for the aqueous ions PO_4^{3-}, HPO_4^{2-}, and $H_2PO_4^-$. It is worth noting that, except for PCl_5(cr), the older Circular 500 values of $\Delta_f H_m^o$ and $\Delta_f G_m^o$ (Rossini et al. 1952 [DIRS 178624]), and the more recent CODATA values (Cox et al. 1989 [DIRS 150874]) and the extension by the NEA (e.g., Grenthe et al. 1992 [DIRS 101671]) are generally in good agreement, whereas the later NBS values (Wagman et al. 1968 [DIRS 178625]; Wagman et al. 1982 [DIRS 159216]) are significantly less negative. The value of $\Delta_f G_m^o$ for $H_2PO_4^-$ in the NBS 270 tables (Wagman et al. 1968 [DIRS 178625]) is apparently erroneous and was corrected in the later report (Wagman et al. 1982 [DIRS 159216]).

The Circular 500 (Rossini et al. 1952 [DIRS 178624]) provided a list of references for source papers used for these evaluations but did not give any description of the calculations. In contrast, the NBS 270 reports (Wagman et al. 1968 [DIRS 178625]) and the combined tables (Wagman et al. 1982 [DIRS 159216]) provide no information about the evaluations or source papers for the thermodynamic data. The CODATA evaluations (Cox et al. 1989 [DIRS 150874]) include a list of references and evaluated results for most of the various reactions used in the evaluations. However, the CODATA report does not contain a discussion of the origin of differences between their evaluated thermodynamic values and those given in the earlier evaluations (Rossini et al. 1952 [DIRS 178624]; Wagman et al. 1968 [DIRS 178625]; Wagman et al. 1982 [DIRS 159216]).

Because of these differences in evaluated thermodynamic values among some of these published databases for phosphorus, combining values from different databases runs the risk of introducing significant inconsistencies into thermodynamic modeling calculations. The NBS (Wagman et al. 1982 [DIRS 159216]) and CODATA evaluations (Cox et al. 1989 [DIRS 150874]) are probably the most widely used databases for geochemical modeling calculations (sometimes supplemented by values for additional compounds and aqueous species). In this report we examine the origin of differences between these two databases for compounds and aqueous species of phosphorous that occur in both databases.

Table B-1. Comparison of Published Values of the Standard Molar Enthalpies of Formation ($\Delta_f H_m^\circ$), Gibbs Energies of Formation ($\Delta_f G_m^\circ$), and Standard Molar Entropies (S_m°), of PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, H_3PO_4(aq), P(cr, white), P_4O_{10}(cr) and PCl_5(cr) at 298.15 K (25°C)

Compound or Ion	**Selected Values (1952) [a]**	**NBS 270-3 (1968) [b]**	**NBS Tables (1982) [c]**	**CODATA (1989) [d]**	**CODATA + NEA (1992) [e]**	**JANAF (1998) [f]**
$\Delta_f H_m^\circ$ (kJ·mol^{-1})						
H_3PO_4(aq)	–1293.16 [f]	–1288.34	–1288.34		–1294.12	
$H_2PO_4^-$	–1302.5	–1296.29	–1296.29	–1302.6	–1302.6	
HPO_4^{2-}	–1298.7	–1292.14	–1292.14	–1299.0	–1299.0	
PO_4^{3-}	–1284.1	–1277.4	–1277.4		–1284.4	
P_4O_{10}(cr,hex)	–3012.5	–2984.0	–2984.0	(–3008.4) [g]		–3009.9
PCl_5(cr)	–463.2	–443.5	–443.5	(–443.85) [h]		
P(cr, white)	0	0	0	0	0	0
$\Delta_f G_m^\circ$ (kJ·mol^{-1})						
H_3PO_4(aq)	–1142.65	–1142.65	–1142.54		–1149.367	
$H_2PO_4^-$	–1135.1	–1088.55?	–1130.28		–1137.152	
HPO_4^{2-}	–1094.1	–1089.26	–1089.15		–1095.985	
PO_4^{3-}	–1025.5	–1018.8	–1018.7		–1025.491	
P_4O_{10}(cr,hex)		–2697.8	–2697.7			–2723.3
PCl_5(cr)						
P(cr, white)	0	0	0	0	0	0
S_m° (J·K^{-1}·mol^{-1})						
H_3PO_4(aq)		158.2	158.2		161.912	
$H_2PO_4^-$	89.1	90.4	90.4	92.5	92.5	
HPO_4^{2-}	–36.0	–33.5	–33.5	–33.5	–33.5	
PO_4^{3-}	–218	–222	–222		–220.97	
P_4O_{10}(cr,hex)		228.86	228.86			228.78
PCl_5(cr)						
P(cr, white)	44.35	41.09	41.09	41.09	41.09	41.08

[a] From Rossini et al. (1952 [DIRS 178624]), *Selected Values of Chemical Thermodynamic Properties*. Units of calories were converted to joules using 1 cal = 4.1840 J (Weast and Astle 1981 [DIRS 100833], p. F-304).

[b] From Wagman et al. 1968 [DIRS 178625], Technical Note 270-3; values taken with possibly minor corrections from either Technical note 270-1 or 270-2. Units of calories were converted to joules using 1 cal = 4.1840 J (Weast and Astle 1981 [DIRS 100833], p. F-304).

[c] From Wagman et al. 1982 [DIRS 159216], *The NBS Tables of Chemical Thermodynamic Properties, Selected Values for Inorganic and C_1 and C_2 Organic Substances in SI Units*.

[d] From Cox et al. 1989 [DIRS 150874], *CODATA Key Values for Thermodynamics*.

[e] From Grenthe et al. (1992 [DIRS 101671]). The CODATA Key Values (Cox et al. 1989 [DIRS 150874]) were accepted by these authors and supplemented with calculations of $\Delta_f G_m^\circ$, along with a few additional evaluations.

[f] From Chase 1998 [DIRS 157874], *NIST-JANAF Thermochemical Tables*". The values given by Barin and Platzki 1995 [DIRS 157865], *Thermodynamic Data for Pure Substances*, are essentially identical to the NIST-JANAF values.

[g] This value was not given in the CODATA Key Values but was involved in thermodynamic cycles to obtain $\Delta_f H_m^\circ$ of the various hydrogen phosphate ions. This value was derived in this report; see the discussion in the text.

[h] This value was not given in the CODATA Key Values but was used in thermodynamic cycles to obtain $\Delta_f H_m^\circ$ of the various hydrogen phosphate ions; it was taken from Schumm et al. (1974 [DIRS 178842]).

Differences among values evaluated thermodynamic properties can arise from differences in the derived values of $\Delta_f H_m^o$, $\Delta_f G_m^o$, or S_m^o, or in differences in more than one property. By examining the standard entropies S_m^o listed in Table B-1, it can be seen that the selected S_m^o values from the NBS tables (Wagman et al. 1982 [DIRS 159216]) and the CODATA Key Values (Cox et al. 1989 [DIRS 150874]) are the same or nearly so for the ions and solids, and thus they cannot be the origin of the observed large differences for $\Delta_f H_m^o$ and $\Delta_f G_m^o$.

The enthalpies of formation of the PO_4^{3-}, HPO_4^{2-}, and $H_2PO_4^-$ given in the CODATA tables are described as being derived from enthalpies of formation of 1 mol H_3PO_4 in 100 mol H_2O, $\Delta_f H_m^o$(H_3PO_4 in 100 H_2O, 298.15 K) = –1296.2 ± 1.0 kJ·mol^{-1}, which was reported to be based on the enthalpy of combustion of P(cr) results from Head and Lewis (1970 [DIRS 178456]) to form H_3PO_4 in 40 mol H_2O with appropriate dilution data, and the enthalpy of formation of PCl_5(cr) of Schumm et al. (1974 [DIRS 178842]) together with the enthalpy of hydrolysis of Birley and Skinner (1968 [DIRS 178647]). However, Birley and Skinner's value of $\Delta_f H_m^o$(H_3PO_4 in 100 H_2O, 298.15 K) = –(309.80 ± 0.35)(4.184) = –1296.2 ± 1.5 kJ·mol^{-1} is identical to the CODATA value except for the larger assigned uncertainty. The Head and Lewis (1970 [DIRS 178456]) result, corrected for dilution from 1 mol H_3PO_4 in 40 mol H_2O to 1 mole H_3PO_4 in 100 mol H_2O using the NBS values, is $\Delta_f H_m^o$(H_3PO_4 in 100 H_2O, 298.15 K) = –(1294.3 ± 1.6) – 0.6 = –1294.9 ± 1.6 kJ·mol^{-1}. These calculations imply that the CODATA value of $\Delta_f H_m^o$(H_3PO_4 in 100 H_2O, 298.15 K) = –1296.2 ± 1.0 kJ·mol^{-1} was obtained solely from the PCl_5(cr) data unless there are some additional small but undescribed corrections to the data based on P_4O_{10}(cr) that bring them into exact agreement. Whichever is the case, the CODATA choice of $\Delta_f H_m^o$(H_3PO_4 in 100 H_2O, 298.15 K) yields $\Delta_f H_m^o$(P_4O_{10}, cr, 298.15 K) = –3008.4 kJ·mol^{-1}. This value agrees well with the assessed value of $\Delta_f H_m^o$(P_4O_{10}, cr, 298.15 K) = –3009.9 kJ·mol^{-1} given in the NIST-JANAF tables (Chase 1998 [DIRS 157874]), which is based on the enthalpy of combustion results by Egan and Luff (1964 [DIRS 178626]).

Values of $\Delta_f G_m^o$ for PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, and H_3PO_4(aq) from NBS tables (Wagman et al. 1982 [DIRS 159216]) and those calculated in the NEA review (Grenthe et al. 1992 [DIRS 101671]) from information from the CODATA report (Cox et al. 1989 [DIRS 150874]) are given in Table B-1 and differ by $\Delta(\Delta_f G_m^o)$ = 6.83 ± 0.06 kJ·mol^{-1} where the uncertainty is the 95% confidence limit. This constant difference between the $\Delta_f G_m^o$ values implies that the dissociation constants of orthophosphoric acid used in the NBS evaluation were identical to those described in the CODATA evaluation. If a similar examination of made of the $\Delta_f H_m^o$ values summarized in Table B-1, then $\Delta(\Delta_f H_m^o)$ = 6.5 ± 1.1 kJ·mol^{-1} where the uncertainty is the 95% confidence limit. However, for the enthalpies there is a systematic variation from $\Delta(\Delta_f H_m^o)$ = 7.0 kJ·mol^{-1} for PO_4^{3-}, $\Delta(\Delta_f H_m^o)$ = 6.9 kJ·mol^{-1} for HPO_4^{2-}, $\Delta(\Delta_f H_m^o)$ = 6.3 kJ·mol^{-1} for $H_2PO_4^-$, to $\Delta(\Delta_f H_m^o)$ = 5.8 kJ·mol^{-1} for H_3PO_4(aq). The absence of a constant value for $\Delta(\Delta_f H_m^o)$ implies that the enthalpies of dissociation of the acidic protons of H_3PO_4(aq) used in the NBS evaluations (which are not known) are different from those used in the CODATA evaluations (which are described by Cox et al. 1989 [DIRS 150874]).

Because the $\Delta_f H_m^o$ values for PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, and H_3PO_4(aq) in the CODATA evaluations (Cox et al. 1989 [DIRS 150874]) were based on thermodynamic cycles that include

P_4O_{10}(cr) and PCl_5(cr), it is reasonable to expect that similar thermodynamic cycles were used in the NBS evaluations (Wagman et al. 1968 [DIRS 178625]; Wagman et al. 1982 [DIRS 159216]. However, the values of $\Delta_f H_m^o$(PCl_5, cr, 298.15 K) from the two evaluations are fairly close as shown in Table B-1 and could only account for only a very small fraction of the observed differences for the aqueous species. It is more likely that the observed differences are the result of differences between different sources for the enthalpies of combustion of P(cr) to yield H_3PO_4(aq) that are reflected in the values of $\Delta_f H_m^o$(P_4O_{10}, cr, 298.15 K).

Dissolution of P_4O_{10}(cr) in water yields aqueous solutions of orthophosphoric acid by the reaction:

$$P_4O_{10}(cr) + 6H_2O(aq) \rightarrow 4H_3PO_4(aq) \qquad \text{(B-1)}$$

From the results summarized in Table B-1 for the NBS (Wagman et al. 1982 [DIRS 159216]) and CODATA (Cox et al. 1989 [DIRS 150874]) evaluations, the difference in $\Delta_f H_m^o$(P_4O_{10}, cr, 298.15 K) values yield $\Delta(\Delta_f H_m^o)/4 = 24.4/4 = 6.1$ kJ·mol^{-1}, which is within the uncertainty limits of the value $\Delta(\Delta_f H_m^o) = 6.5 \pm 1.1$ kJ·mol^{-1} derived two paragraphs above for the aqueous species. Similarly, the values of $\Delta_f H_m^o$(H_3PO_4 in 100 H_2O, 298.15 K) in the NBS (Wagman et al. 1982 [DIRS 159216]) and CODATA (Cox et al. 1989 [DIRS 150874]) evaluations yield $\Delta(\Delta_f H_m^o) = 6.79$ kJ·mol^{-1}. The fairly consistent systematic differences observed for $\Delta(\Delta_f H_m^o)$ and $\Delta(\Delta_f G_m^o)$ clearly resulted from the use of inconsistent sets of enthalpies of combustion of P(cr) in the two evaluations.

An examination of all of the source papers cited in the CODATA evaluation identified only one paper that reported $\Delta_f H_m^o$(P_4O_{10}, cr, 298.15 K) = –2984.0 kJ·mol^{-1} that is identical to the value given in the NBS tables (Wagman et al. 1968 [DIRS 178625]; Wagman et al. 1982 [DIRS 159216]). This value, taken from the study of Holmes (1962 [DIRS 178649]), was not used in the CODATA evaluation. Although the detailed calculations and references are not given in the NBS evaluations, Dr. Donald G. Archer of NIST/Gaithersburg was able to locate information that confirms (Archer 2006 [DIRS 178805]) that the paper of Holmes was the source of the NBS value for $\Delta_f H_m^o$(P_4O_{10}, cr, 298.15 K) [21]. As discussed by Head and Lewis (1970 [DIRS 178456]) and Irving and McKerrell (1967 [DIRS 178679]), that result reported by Holmes now appears to be discredited. Head and Lewis (1970 [DIRS 178456]) re-determined the enthalpy of combustion of P(cr) and Irving and McKerrell (1967 [DIRS 178679]) combined their enthalpy of solution of P_4O_{10}(cr) with the enthalpy of combustion results of Egan and Luff (1964 [DIRS 178626]); their consistent results also agree well with that obtained from the enthalpies of formation and hydrolysis of PCl_5(cr) (Schumm et al. 1974 [DIRS 178842]); Birley and Skinner 1968 [DIRS 178647]).

The analysis above implies that the evaluated values of standard thermodynamic properties for PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^{-}$, and H_3PO_4(aq) in the NBS evaluations (Wagman et al. 1968 [DIRS 178625]; Wagman et al. 1982 [DIRS 159216]) are erroneous because of the use of questionable enthalpy of combustion enthalpy data Holmes (1962 [DIRS 178649]) in their evaluation; consequently the corresponding CODATA values (Cox et al. 1989 [DIRS 150874]) appear to be more accurate. Given the information and data now available, the CODATA values should be used in the construction of thermochemical databases, and the NBS (*NIST89*) values should be purged. Because many of the available data for various phosphate species have been derived on the basis of the NBS data, such data will need to be corrected for consistency with the CODATA values.

APPENDIX C

GIBBS ENERGY GRIDS FOR AQUEOUS BASIS SPECIES

INTENTIONALLY LEFT BLANK

Some log K grids are generated directly from a SUPCRT92 data file (e.g., *Speq06.dat*, Output DTN: SN0702T0502404.015, folder: *Speq06_db*) using the SUPCRT92 software (SUPCRT92 V1.0; see Section 3.1.2). This methodology is described in Section 6.1.2. Most other log K grids are obtained by are calculated using the generic template spreadsheets described in Section 6.1.3. That approach is supported by another type of SUPCRT92 calculation (see Sections 6.1.2 and 6.1.3) in which the apparent Gibbs energies of formation of various basis species are calculated on the EQ3/6 temperature grid (0-25-60-100-150-200-250-300°C). The Gibbs energy on this grid is given to the nearest tenth of a Joule/mol, which is well below actual uncertainties that are generally no better than 100 Joule/mol (see Appendix A), but which suffice to avoid certain inconsistencies and which allow smooth interpolation between grid temperatures. In a relatively small number of instances, the SUPCRT92 database lacks the necessary data and the isocoulombic/isopiestic method (Section 6.1.3) is employed instead. This is done for $Ti(OH)_4(aq)$, Sn^{4+}, and the basis species for the actinide elements Am, Np, and Pu.

These Gibbs energy grids are collected on library worksheets named “Basis Species 1,” “Basis Species 2,” etc., a master collection of which is kept in a library workbook whose name has the form *BasisSpeciesLib_j*.xl*s. The most recent version, which was used in constructing data0.ymp.R5 (Output DTN: SN0612T0502404.014), is *BasisSpeciesLib_j_TJW_2p0.xls* (Output DTN: SN0702T0502404.015, folder: *Library Workbooks*). Table C-1 presents the corresponding set of Gibbs energy grids.

Table C-1. Gibbs Energy (Joule/mol) Grids for Aqueous Basis Species

Section A. The following Gibbs energy grids were computed using SUPCRT92.

Species Name	0.01°C	25°C	60°C	100°C	150°C	200°C	250°C	300°C
H2O	-235515.2	-237181.4	-239777.8	-243083.7	-247664.6	-252690.6	-258112.4	-263889.6
O2(g)	5094.9	0.0	-7238.2	-15644.4	-26333.8	-37205.6	-48242.4	-59430.0
SiO2(aq)	-833534.0	-834875.4	-836421.3	-838273.2	-840960.2	-844076.0	-847492.6	-850867.4
SiO2(aq) [Fournier][a]	-831029.4	-833411.0	-835622.6	-837759.4	-840490.3	-843514.5	-846859.6	-850415.2
CO2(aq)	-383324.7	-385974.0	-390534.4	-396659.1	-405418.2	-415214.0	-425897.7	-437357.7
NH3(aq)	-24091.3	-26706.4	-30637.2	-35500.2	-42082.5	-49169.5	-56711.4	-64689.3
B(OH)3(aq)	-964947.1	-968763.4	-974283.7	-980836.7	-989362.9	-998246.3	-1007498.0	-1017234.2
H+	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Li+	-292380.9	-292599.7	-293112.8	-293956.0	-295312.0	-296897.2	-298576.7	-300157.6
Na+	-260453.0	-261880.7	-264011.4	-266667.3	-270285.9	-274164.3	-278198.4	-282228.1
K+	-279940.3	-282461.8	-286021.5	-290157.6	-295417.1	-300740.6	-306066.8	-311291.1
Cs+	-288301.1	-291666.6	-296286.9	-301563.1	-308201.8	-314889.3	-321589.5	-328231.6
Mg++	-457393.6	-453984.9	-449128.6	-443549.6	-436476.1	-429128.6	-421254.3	-412507.2
Ca++	-554160.3	-552790.1	-550758.3	-548307.3	-544995.7	-541280.7	-536953.6	-531681.0
Sr++	-564562.6	-563835.8	-562668.1	-561212.1	-559193.3	-556845.6	-553975.4	-550254.2
Ba++	-560475.3	-560781.5	-561028.4	-561118.8	-560930.5	-560321.3	-559121.7	-557026.0
Ra++	-560061.5	-561492.8	-563285.6	-565159.7	-567264.6	-569041.2	-570342.4	-570883.4
Ni++	-48757.1	-45605.6	-41016.9	-35615.7	-28593.2	-21131.9	-13005.8	-3888.7
Pb++	-23377.4	-23890.7	-24420.8	-24868.7	-25191.1	-25157.0	-24585.0	-23156.8
Al+++	-491668.5	-483708.1	-472099.1	-458325.8	-440299.1	-421159.3	-400564.5	-378103.9
Fe++	-94100.0	-91504.1	-87749.2	-83358.9	-77671.3	-71617.1	-64964.4	-57373.7
Fe+++	-24066.3	-17238.1	-7396.8	4142.0	19093.4	34868.4	51833.1	70451.5
Mn++	-232202.3	-230538.4	-228144.6	-225366.5	-221762.3	-217857.4	-213412.3	-208076.8
Mn+++	-92532.6	-84935.2	-73913.9	-60920.2	-44016.0	-26150.8	-6967.5	13968.2
MnO4--	-501783.8	-503753.6	-505533.9	-506564.4	-506422.2	-504443.1	-499925.2	-491118.8
Co++	-57166.2	-54392.0	-50388.9	-45715.0	-39670.3	-33251.8	-26224.2	-18249.2
Co+++	126390.5	133888.0	144756.1	157561.2	174212.8	191808.5	210706.9	231345.7

Table C-1. Gibbs Energy (Joule/mol) Grids for Aqueous Basis Species (Continued)

Species Name	0.01°C	25°C	60°C	100°C	150°C	200°C	250°C	300°C
Th++++	-715555.2	-705004.0	-690216.1	-673257.5	-651704.9	-629341.0	-605610.6	-579902.0
Sn++	-27818.6	-27488.9	-26797.2	-25806.5	-24277.0	-22335.3	-19800.2	-16352.7
Cr+++	-214196.2	-206271.2	-194830.6	-181396.1	-163981.8	-145639.7	-126003.5	-104639.6
CrO4--	-729590.4	-731363.2	-732922.6	-733756.0	-733429.7	-731322.6	-726720.6	-717866.0
U+++	-479717.8	-475093.2	-468077.9	-459518.3	-448026.1	-435503.4	-421651.4	-406012.0
U++++	-540310.5	-529903.6	-515323.6	-498609.4	-477372.6	-455336.8	-431948.2	-406589.0
UO2+	-961528.0	-961023.0	-959990.3	-958528.5	-956350.7	-953770.8	-950701.9	-946978.9
UO2++	-955112.2	-952613.1	-949240.8	-945502.0	-940848.1	-936013.1	-930720.3	-924587.0
F-	-281934.8	-281750.6	-281090.1	-279920.2	-277827.1	-274861.4	-270624.7	-264211.4
Cl-	-129722.2	-131289.7	-133051.6	-134583.0	-135778.3	-136040.9	-135016.1	-131830.1
I-	-49115.1	-51923.4	-55440.9	-58990.6	-62722.6	-65547.8	-67127.5	-66618.1
NO3-	-107140.4	-110905.2	-115939.7	-121493.9	-128133.3	-134303.5	-139676.6	-143464.7
NO2-	-29014.3	-32216.8	-36357.9	-40774.2	-45842.5	-50289.0	-53787.2	-55528.2
HCO3-	-584427.4	-586939.9	-590331.9	-594106.2	-598614.9	-602712.7	-606021.0	-607672.0
MoO4--	-837280.3	-838473.6	-839442.6	-839819.6	-839170.7	-836958.2	-832422.7	-823766.4
WO4--	-912953.0	-914204.0	-915297.7	-915862.1	-915496.9	-913613.2	-909440.1	-901170.0
HPO4--	-1096515.9	-1095986.2	-1094383.8	-1091655.8	-1086913.2	-1080381.6	-1071298.6	-1057863.7
HPO4-- [sprons98.dat][a]	-1089665.9	-1089137.0	-1087535.4	-1084808.7	-1080067.4	-1073537.4	-1064456.0	-1051022.9
H2P2O7--	-2022954.0	-2027118.7	-2033203.5	-2040394.1	-2049429.1	-2058041.8	-2065396.9	-2069692.2
HPO3--	-811063.0	-811696.0	-811987.2	-811693.9	-810329.9	-807513.3	-802468.6	-793390.6
H2PO2-	-509556.8	-512121.6	-515608.1	-519511.8	-524210.0	-528525.4	-532081.4	-534014.4
H2AsO3-	-584356.7	-587140.7	-590994.6	-595379.4	-600751.7	-605812.7	-610180.8	-612994.9
H2AsO4-	-750222.2	-753161.8	-757267.2	-761974.2	-767788.7	-773330.0	-778212.7	-781576.2
SO4--	-743646.2	-744459.1	-744654.5	-743944.5	-741724.0	-737749.2	-731282.9	-720538.4
SeO4--	-439769.4	-441412.0	-442891.9	-443736.2	-443540.8	-441669.7	-437389.9	-428928.2
VO2+	-587991.7	-587015.2	-585444.5	-583488.9	-580830.4	-577888.6	-574551.9	-570642.0
V++	-220744.5	-217568.0	-212955.9	-207539.1	-200508.0	-193045.5	-184921.3	-175808.6
VO++	-449931.0	-446432.8	-441989.8	-437384.1	-432089.2	-427028.7	-421877.7	-416243.4
V+++	-247952.6	-242253.6	-234143.5	-224737.9	-212647.7	-199933.1	-186216.5	-170997.4
ZrO++	-790493.6	-784918.4	-777107.3	-768184.9	-756906.9	-745272.9	-732984.5	-719709.9
Br-	-101828.2	-104056.0	-106728.1	-109306.0	-111833.6	-113465.4	-113854.3	-112137.1

Table C-1. Gibbs Energy (Joule/mol) Grids for Aqueous Basis Species (Continued)

Species Name	0.01°C	25°C	60°C	100°C	150°C	200°C	250°C	300°C
Bi+++	91029.4	95729.9	102306.6	109820.7	119371.5	129368.4	140198.1	152388.0
SbO2-	-346314.5	-344761.6	-341936.6	-338065.0	-332342.4	-325516.4	-317225.8	-306609.6
Ru++	147477.3	150205.6	154156.1	158780.9	164775.1	171150.1	178136.7	186071.1
Ru+++	166107.4	173384.9	183916.1	196306.2	212400.8	229400.2	247665.4	267643.0
RuO4--	-298629.0	-299574.4	-300187.4	-300147.9	-298969.3	-296331.5	-291886.3	-285379.8
Cu+	50951.9	49998.8	48464.9	46462.2	43657.2	40610.2	37438.2	34313.3
Cu++	63181.5	65584.2	68985.7	72872.0	77801.4	82975.5	88643.1	95152.3
Fr+	-291259.4	-294972.0	-300075.7	-305874.7	-313118.1	-320366.9	-327607.1	-334808.4
Tl+	-29216.6	-32384.1	-36758.0	-41754.1	-48024.3	-54316.8	-60596.5	-66796.5
Rb+	-280639.3	-283675.2	-287882.2	-292703.4	-298770.5	-304867.8	-310949.4	-316928.5
Cd++	-79447.5	-77655.1	-75090.3	-72130.3	-68328.9	-64275.4	-59747.9	-54401.9
Hg++	163772.3	164682.2	165927.3	167292.5	168988.8	170820.4	173007.9	175896.7
Hg2++	155175.5	153594.6	151180.8	148184.2	144199.4	140104.4	136118.3	132583.9
Pd++	174396.6	176564.8	179688.3	183328.4	188056.9	193148.3	198853.4	205513.8
Pt++	255311.6	257734.4	261234.0	265324.8	270644.1	276356.1	282711.2	290044.1
In+++	-104404.1	-97905.6	-88570.1	-77654.6	-63539.3	-48658.1	-32641.4	-15013.9
Rh+++	212127.9	219450.8	230154.9	242852.1	259458.9	277089.0	296085.4	316878.1
Sc+++	-592895.4	-586596.8	-577567.7	-567029.9	-553421.4	-539083.3	-523643.9	-506621.3
Hf++++	-566399.4	-554798.4	-538492.5	-519747.8	-495888.9	-471134.7	-444928.2	-416688.6
NbO3-	-949632.0	-950186.4	-950357.1	-949963.0	-948661.8	-946350.1	-942668.2	-936723.1
ReO4-	-689476.3	-694544.0	-701583.2	-709673.3	-719822.9	-729864.9	-739473.9	-747926.0
TcO4-	-627210.9	-632202.4	-639167.5	-647191.6	-657270.0	-667244.7	-676785.8	-685163.1
CN-	174833.1	172380.8	169208.6	165821.1	161956.3	158653.1	156272.3	155672.1
SCN-	96383.0	92717.5	87727.2	82137.5	75361.5	68975.3	63324.0	59211.4
HS-	13791.2	11966.3	9744.3	7547.1	5326.2	3843.5	3472.9	5104.4
SO3--	-486976.2	-486599.2	-485075.4	-482303.5	-477353.8	-470479.1	-460944.6	-446973.4
SeO3--	-369218.0	-369865.6	-369866.8	-368931.7	-366399.4	-362073.0	-355219.8	-344064.4
Acetic_acid(aq)	-392188.2	-396475.8	-403069.1	-411398.0	-422879.4	-435436.0	-448975.8	-463495.6
La+++	-691413.5	-686176.0	-678291.3	-668729.1	-655986.3	-642228.5	-627170.3	-610351.0
La++	-324953.1	-325096.8	-325119.7	-324999.2	-324627.3	-323918.3	-322693.5	-320637.2
Ce+++	-681004.6	-676134.4	-668610.3	-659301.7	-646674.9	-632829.2	-617488.1	-600217.4

Table C-1. Gibbs Energy (Joule/mol) Grids for Aqueous Basis Species (Continued)

Species Name	0.01°C	25°C	60°C	100°C	150°C	200°C	250°C	300°C
Ce++	-313163.7	-313381.6	-313505.5	-313497.8	-313264.2	-312692.0	-311603.7	-309684.7
Ce++++	-517977.5	-507519.2	-492865.2	-476064.7	-454716.3	-432564.5	-409054.2	-383570.7
Pr+++	-685330.0	-680318.4	-672701.4	-663391.6	-650884.8	-637268.0	-622245.7	-605370.8
Pr++	-387713.1	-387856.8	-387879.7	-387759.2	-387387.3	-386678.3	-385453.5	-383397.2
Pr++++	-314470.6	-304176.9	-289760.9	-273240.6	-252254.3	-230478.6	-207359.2	-182276.0
Nd+++	-676895.9	-671950.4	-664386.6	-655101.0	-642588.8	-628944.3	-613886.9	-596970.2
Nd++	-419219.6	-419236.8	-419085.3	-418768.2	-418150.8	-417194.5	-415717.2	-413400.3
Nd++++	-206962.1	-196648.1	-182202.1	-165645.9	-144613.3	-122789.5	-99620.7	-74486.8
Pm+++	-666062.3	-661072.0	-653424.5	-644019.7	-631324.6	-617455.5	-602127.4	-584901.0
Pm++	-387987.5	-387856.8	-387502.6	-386957.2	-386057.4	-384818.1	-383054.0	-380443.7
Pm++++	-153510.0	-143092.9	-128498.2	-111767.3	-90509.4	-68452.8	-45043.1	-19663.1
Sm+++	-670744.6	-665674.4	-657934.0	-648443.9	-635669.3	-621751.2	-606405.5	-589188.8
Sm++	-515216.5	-514632.0	-513653.8	-512405.3	-510631.7	-508515.0	-505859.4	-502336.9
Sm++++	-177503.1	-166941.7	-152138.9	-135163.6	-113590.0	-91205.1	-67454.2	-41724.6
Eu+++	-579808.3	-574463.2	-566436.2	-556715.5	-543764.4	-529771.0	-514434.5	-497300.6
Eu++	-540756.5	-540572.8	-540146.0	-539518.9	-538518.0	-537177.5	-535310.6	-532595.2
Eu++++	10132.1	20919.9	36050.1	53410.7	75481.3	98380.1	122662.3	148934.7
Gd+++	-668533.7	-663582.4	-656116.9	-647048.1	-634922.0	-621761.6	-607262.8	-590969.9
Gd++	-295774.1	-295390.4	-294687.7	-293748.6	-292359.1	-290627.5	-288362.8	-285239.6
Gd++++	41488.0	52718.3	68488.8	86603.7	109649.5	133561.1	158894.1	186241.5
Tb+++	-672801.0	-667348.0	-659178.7	-649301.6	-636153.8	-621952.0	-606384.6	-589001.3
Tb++	-332445.9	-332209.6	-331710.4	-331001.7	-329899.6	-328457.6	-326488.0	-323668.0
Tb++++	-379909.3	-369028.9	-353764.6	-336246.0	-313971.1	-290860.1	-266357.9	-239860.4
Dy+++	-669601.1	-664000.8	-655688.0	-645710.4	-632513.7	-618336.6	-602861.7	-585629.9
Dy++	-430425.2	-430115.2	-429514.4	-428690.1	-427443.7	-425855.5	-423735.0	-420758.5
Dy++++	-243908.9	-233048.9	-217814.6	-200331.8	-178103.4	-155040.4	-130587.7	-104140.7
Ho+++	-680795.8	-675297.6	-667104.5	-657240.3	-644156.5	-630065.2	-614651.8	-597461.0
Ho++	-405813.3	-405429.6	-404726.9	-403787.8	-402398.3	-400666.7	-398402.0	-395278.8
Ho++++	-138492.5	-127612.1	-112347.8	-94829.2	-72554.3	-49443.3	-24941.1	1556.5
Er+++	-674932.8	-669021.6	-660235.2	-649677.7	-635707.8	-620710.6	-604371.7	-586241.2
Er++	-383764.6	-383254.4	-382377.3	-381241.3	-379606.2	-377626.6	-375108.3	-371723.3

Table C-1. Gibbs Energy (Joule/mol) Grids for Aqueous Basis Species (Continued)

Species Name	**0.01°C**	**25°C**	**60°C**	**100°C**	**150°C**	**200°C**	**250°C**	**300°C**
Er++++	-128502.2	-117570.5	-102231.4	-84624.1	-62233.2	-39000.0	-14369.2	12261.0
Tm+++	-674911.8	-669021.6	-660264.5	-649739.6	-635807.8	-620843.3	-604530.3	-586419.4
Tm++	-450835.6	-450198.4	-449147.8	-447817.3	-445942.4	-443724.5	-440966.0	-437338.0
Tm++++	-136963.2	-125938.5	-110466.1	-92703.1	-70112.5	-46673.4	-21830.0	5016.5
Yb+++	-645905.8	-640152.0	-631554.7	-621181.7	-607403.0	-592556.5	-576330.9	-558283.3
Yb++	-538755.7	-537644.0	-535940.3	-533873.0	-531081.8	-527942.6	-524248.9	-519664.1
Yb++++	4771.3	15899.1	31520.2	49458.0	72273.9	95946.1	121030.6	148123.2
Lu+++	-673350.4	-666929.6	-657451.6	-646123.8	-631212.0	-615287.7	-598030.8	-578994.1
Lu++++	101696.3	112967.9	128797.8	146982.4	170118.8	194125.7	219559.4	247010.3
Section B. The following Gibbs energy grids were computed using the isocoulombic/isoelectric method.								
Species Name	**0.01°C**	**25°C**	**60°C**	**100°C**	**150°C**	**200°C**	**250°C**	**300°C**
Am+++	-603601.4	-598698.0	-591510.4	-582964.5	-571700.5	-559550.7	-546146.8	-531053.9
Am++	-376839.8	-376780.0	-376794.7	-376862.8	-376854.2	-376520.5	-375587.5	-373682.6
Am++++	-356498.8	-346358.0	-332160.1	-315902.1	-295279.2	-273912.5	-251261.4	-226724.4
AmO2+	-740200.4	-739796.0	-738913.6	-737643.1	-735748.1	-733506.3	-730843.6	-727611.8
AmO2++	-588044.1	-585801.0	-582796.6	-579498.0	-575437.9	-571251.9	-566676.4	-561345.2
Np+++	-517589.6	-512866.0	-505946.7	-497723.7	-486877.9	-475153.8	-462178.2	-447512.3
Np++++	-502425.0	-491774.0	-476861.1	-459777.7	-438103.6	-415661.3	-391910.3	-366251.4
NpO2+	-908792.5	-907765.0	-906009.7	-903733.2	-900561.2	-897018.1	-893029.9	-888450.5
NpO2++	-798292.4	-795939.0	-792779.8	-789295.9	-784984.6	-780523.2	-775648.1	-769995.0
Pu+++	-583480.2	-578984.0	-572383.7	-564533.3	-554172.5	-542957.2	-530513.8	-516401.8
Pu++++	-488342.2	-477988.0	-463491.4	-446891.9	-425841.8	-404047.3	-380967.7	-356001.6
PuO2+	-852488.7	-852646.0	-852550.5	-852179.1	-851407.6	-850288.8	-848748.4	-846638.2
PuO2++	-764177.5	-762353.0	-759935.1	-757306.5	-754083.6	-750734.3	-746994.8	-742498.9
Ti(OH)4(aq)	-1321681.7	-1322665.2	-1324272.3	-1326913.6	-1331535.5	-1337521.2	-1344633.7	-1352444.8
Sn++++	-397.4	2510.4	6625.4	11419.4	17798.3	25011.5	33604.2	44188.9

Source: Output DTN: SN0702T0502404.015, folder: *\Library Workbooks*, workbook: *BasisSpeciesLib_j_TJW_2p0.xls*.

[a] These are deprecated data that may be required to convert data for other species to achieve consistency with the recommended data for these species.

APPENDIX D

LIMITS OF TEMPERATURE EXTRAPOLATION IN THE ABSENCE OF HEAT CAPACITY DATA

INTENTIONALLY LEFT BLANK

A problem frequently encountered in dealing with calculating thermodynamic data for higher temperatures is the lack of heat capacity data. Methods exist for estimating heat capacity coefficients of solids in the absence of experimental data (see Section 6.1.4). For aqueous species, the effect of heat capacities can be well approximated by using the isocoulombic/isoelectric method (see Section 6.1.3). Thus, there is usually no good reason to calculate temperature corrections for thermodynamic data by ignoring heat capacities. However, it does occur. Then to what temperatures can data be extrapolated in the absence of such data? Section 6.1.1 reviews the calculation of the apparent Gibbs energy of formation as a function of temperature. The so-called *retrieval* equation (Equation 6-3) for the apparent standard partial molar Gibbs energy of a chemical species as a function of temperature T and pressure P is in Helgeson et al. (1978 [DIRS 101596], p. 28):

$$\Delta G^{o(app)}_{f,\,T,\,P} = \Delta G^{o}_{f,\,T_r,\,P_r} - S^{o}_{T_r,\,P_r}(T - T_r) + \int_{T_r}^{T} C^{o}_{P_r}\,dT - T\int_{T_r}^{T} C^{o}_{P_r}\,d\ln T + \int_{P_r}^{P} V^{o}_{T}\,dP \quad \text{(Eq. D-1)}$$

where T_r is the reference temperature of 298.15 K (25°C), P_r is the reference pressure of 1 bar, $\Delta G^{o}_{f,\,T_r,\,P_r}$ is the actual standard partial molar Gibbs energy of formation from the elements at the reference temperature and pressure, $S^{o}_{T_r,\,P_r}$ is the corresponding standard molar entropy, $C^{o}_{P_r}$ is the standard partial molar heat capacity at the reference pressure, and V^{o}_{T} is the corresponding standard partial molar volume at absolute temperature *T*. For the present analysis, the pressure correction term containing V^{o}_{T} will be ignored. This condition is satisfied if $P = P_r$, if *P* is sufficiently close to P_r, or if V^{o}_{T} is sufficiently small.

The pressure representation on the EQ3/6 temperature of 0-25-60-100-150-200-250-300°C is fixed at 1.013 bar (very close to the reference pressure of 1 bar) up to 100°C, and at the steam/liquid saturation pressure for pure water at higher temperature. By limiting the maximum temperature under consideration to 100°C, it can be assumed that *P* is sufficiently close to P_r to ignore the pressure correction term. Equation D-1 then reduces to:

$$\Delta G^{o(app)}_{f,\,T,\,P} = \Delta G^{o}_{f,\,T_r,\,P_r} - S^{o}_{T_r,\,P_r}(T - T_r) + \int_{T_r}^{T} C^{o}_{P_r}\,dT - T\int_{T_r}^{T} C^{o}_{P_r}\,d\ln T \qquad \text{(Eq. D-2)}$$

The question then is, how sensitive is the result to the terms containing the heat capacity? What is the error if the heat capacity is ignored and one uses:

$$\Delta G^{o(app)}_{f,\,T,\,P} = \Delta G^{o}_{f,\,T_r,\,P_r} - S^{o}_{T_r,\,P_r}(T - T_r) \qquad \text{(Eq. D-3)}$$

This could be termed the *constant entropy approximation*, as assuming the heat capacity is zero implies that $S^{o}_{T,\,P_r} = S^{o}_{T_r,\,P_r}$ (cf. Helgeson et al. 1978 [DIRS 101596], p. 29). This is equivalent to the better known *constant enthalpy approximation*, as assuming that heat capacity is zero also implies that $\Delta H^{o}_{T,\,P_r} = \Delta H^{o}_{T_r,\,P_r}$, where $\Delta H^{o}_{T,\,P_r}$ is the enthalpy of formation at temperature *T* (cf. Helgeson et al. 1978 [DIRS 101596], p. 28).

The isocoulombic/isoelectric method of temperature extrapolation (see Section 6.1.3) uses the reaction equivalent of Equation D-3:

$$\Delta G^o_{r,T,P} = \Delta G^o_{r,T_r,P_r} - \Delta S^o_{r,T_r,P_r}(T - T_r) \tag{Eq. D-4}$$

where $\Delta G^o_{r,T,P}$ is the Gibbs energy of reaction and $\Delta S^o_{r,T_r,P_r}$ is the entropy of reaction at the reference temperature and pressure. The key assumption of the isocoulombic/isoelectric method is that the heat capacity of reaction ($\Delta C^o_{P,r,T_r,P_r}$) is zero (or can otherwise be ignored).

For simplicity, we will assume that $C^o_{P_r} = a$, where a is a constant. Then it may be obtained that:

$$\int_{T_r}^{T} C^o_{P_r} dT - T\int_{T_r}^{T} C^o_{P_r} d\ln T = a(T - T_r) - Ta\ln(T/T_r) \tag{Eq. D-5}$$

Hence for a chemical species, one has that:

$$Error(\Delta G^{o(app)}_{f,T,P}) = a[(T - T_r) - T\ln(T/T_r)] \tag{Eq. D-6}$$

For a reaction, taking that $\Delta C^o_{P,r,T_r,P_r} = a$ (changing the meaning of a), one similarly obtains that:

$$Error(\Delta G^o_{r,T,P}) = a[(T - T_r) - T\ln(T/T_r)] \tag{Eq. D-7}$$

The Gibbs energy of reaction is related to the log K by:

$$\Delta G^o_r = -\ln(10)RT\log K \tag{Eq. D-8}$$

where R is the gas constant (8.31441 J/mol-K, Weast and Astle 1981 [DIRS 100833], p. F-203).

$$Error(\log K) = -a[(T - T_r) - T\ln(T/T_r)]/\ln(10)RT \tag{Eq. D-9}$$

Equation D-9 can be interpreted in two equivalent ways. First, a can represent the heat capacity of reaction and the calculated error is the error in ignoring it. Second, a can represent some contribution to the heat capacity of reaction (such as the heat capacity of a mineral in a dissolution reaction), and the calculated error is the error in failing to account for that.

Table D-1 shows *Error*(log K) as a function of *a*, for *a* ranging from 0 to 1000 J/mol-K. It is not necessary to consider negative values of *a*, as we are interested in the magnitude of the error, and this is independent of the sign of *a*. In Section 7 of this report, it is noted that the uncertainty in log K values is often about 0.1 unit. Taking this as an approximate acceptable error (not quibbling over the difference between say 0.1 and 0.12), the data in Table D-1 suggest that extrapolation down to 0°C is reasonable for *a* up to 500 J/mol-K, that extrapolation up to 60°C is reasonable for *a* up to 400 J/mol-K, and that extrapolation up to 100°C is reasonable for *a* less than 100 J/mol-K.

Table D-1. Error in log K due to neglecting $C_p = a$

***a* J/mol-K**	**0°C**	**25°C**	**60°C**	**100°C**
0	0.0000	0.0000	0.0000	0.0000
50	0.0103	0.0000	0.0155	0.0611
100	0.0206	0.0000	0.0310	0.1222
150	0.0309	0.0000	0.0465	0.1833
200	0.0413	0.0000	0.0620	0.2444
250	0.0516	0.0000	0.0775	0.3055
300	0.0619	0.0000	0.0931	0.3666
400	0.0825	0.0000	0.1241	0.4887
500	0.1031	0.0000	0.1551	0.6109
750	0.1547	0.0000	0.2326	0.9164
1000	0.2063	0.0000	0.3102	1.2219

Source: Output DTN: SN0702T0502404.015, folder: *\Miscellaneous*, spreadsheet: *Cp_effect_vs_T.xls*, worksheet: "Analysis."

The heat capacity for any species or reaction is not necessarily constant, but *a* as used above can be treated as a characteristic or bounding value. The heat capacity of a solid, pure liquid, or gas typically does not vary much over small ranges of temperature, say a few tens of degrees Celsius. Table D-2 illustrates this by presenting heat capacities for eight simple oxide minerals in the temperature range of interest. Many other examples (including gas and pure liquid species) can be found in the volumes by Barin and Platzki (1995 [DIRS 157865]) and Chase (1998 [DIRS 157874]). For species of comparable complexity, the heat capacity in the temperature range of interest in most cases does not exceed 100 J/mol-K, and values generally are bounded by 200 J/mol-K. Therefore, if the heat capacity of one such species is the only missing part of the heat capacity of reaction, then extrapolations to down to 0°C and up to 60°C are not likely to be at all problematic. In fact, a fairly good argument could be made that extrapolation to 100°C could be justified in many instances.

Solids often show greater compositional complexity. More complex solids have greater heat capacities. This can be simply illustrated by noting that by doubling the formula of Calcite [from $CaCO_3$ to $Ca_2(CO_3)_2$], one then doubles the molar heat capacity. Also, it is known (see Section 6.1.4.1) that the heat capacities of complex oxides can be approximated by summing the heat capacities of the pure component simple oxides. Hence, for more complex minerals, the heat capacities are greater than those illustrated in Table D-2. Nevertheless, approximation to 60°C would in most instances still be justified.

Table D-2. Heat Capacities (Cp, Joule/mol-K) for Some Simple Oxide Minerals

Temp °C	Lime CaO	Calcite $CaCO_3$	Anhydrite $CaSO_4$	Brucite $Mg(OH)_2$	Corundum Al_2O_3	Hematite Fe_2O_3	Uraninite UO_2	Quartz SiO_2
0.01	41.4	75.7	97.1	71.5	71.1	99.6	61.1	41.0
25	42.7	82.0	99.6	77.4	79.1	104.6	63.6	44.4
60	44.4	88.3	102.9	83.7	87.4	110.9	66.5	48.1
100	46.0	94.1	107.1	89.1	94.1	116.7	69.0	51.5
Average	43.6	85.0	101.7	80.4	82.9	107.9	65.1	46.2

Source: Output DTN: SN0702T0502404.015, folder: *\Miscellaneous*, spreadsheet: *Cp_effect_vs_T.xls*. These data were extracted from DTN: MO0302SPATHDYN.001 [DIRS 161886], folder: *\CD\SUPCRT_runs_TJW\SUPCRT_reference_species*, file: *bitsso1.out* and converted from cal/mol-K to Joule/mol-K using the conversion factor 4.184 Joule/cal (Weast and Astle 1981 [DIRS 100833], p. F-304).

The situation may be different for missing heat of reaction data when the reaction involves the consumption or formation of aqueous ions. Table D-3 presents data for the aqueous dissolution reactions for some common minerals (the actual reactions are those used in the EQ3/6 data files in the data0.ymp.R* series). The data here vary much more extremely, and achieve much greater magnitude, especially at the low temperature end around and below 25°C. These data suggest that routine extrapolation up to 60°C may be commonly justified, though it may be necessary to accept a somewhat higher error (say $\Delta\log K = 0.2$). More problematic is that these data suggest that extrapolation down to 0°C may also require accepting a higher error.

Table D-3. Heat Capacities of Reaction ($\Delta C_{p,\,r}$, Joule/mol-K) for Some Common Minerals

Temp °C	Albite $NaAlSi_3O_8$	Calcite $CaCO_3$	Cristobalite SiO_2	Halite NaCl	K-Feldspar $KAlSi_3O_8$	Muscovite $KAl_3Si_3O_{10}(OH)_2$	Pyrite FeS_2
0.01	-1469.4	-239.3	-439.3	-246.9	-1451.8	-1759.4	-660.2
25	-424.7	-147.7	-138.1	-135.1	-434.3	-526.8	-400.8
60	-58.2	-136.8	-25.1	-106.7	-85.4	-137.2	-340.6
100	26.4	-165.3	12.1	-117.6	-10.9	-112.1	-376.1
Average	-481.5	-172.3	-147.6	-151.6	-495.6	-633.9	-444.4

Source: Output DTN: SN0702T0502404.015, folder: *\Miscellaneous*, spreadsheet: *Cp_effect_vs_T.xls*. These data were extracted from DTN: MO0302SPATHDYN.001 [DIRS 161886], folder: *\CD\SUPCRT_runs_TJW\SUPCRT_Mins,* files: *supmins1.out, supmins2.out,* and *supmins3.out* and converted from cal/mol-K to Joule/mol-K using the conversion factor 4.184 Joule/cal (Weast and Astle 1981 [DIRS 100833], p. F-304).

The behavior of the heat capacities illustrated in Table D-3 is driven by the behavior of the heat capacities of the aqueous ions involved in the corresponding reactions. The heat capacities of aqueous ions show a more extreme behavior (cf. Helgeson et al. 1981 [DIRS 106024], p. 1424; Nordstrom and Munoz 1994 [DIRS 168480], p. 217-220). Excluding the data for 0.01°C, the data for Cristobalite do not seem so extreme. That is because the reaction is Cristobalite = $SiO_2(aq)$, which involves no ions. Nevertheless, the behavior is more extreme below 25°C than at higher temperature.

Table D-4 shows some heat capacities of reaction for the dissolution of some common gas species. The behavior is not quite as extreme as for the minerals listed in Table D-3. The reactions for H2 ($H_2(g) = H_2(aq)$), He ($He(g) = He(aq)$), Rn ($Rn(g) = Rn(aq)$), and Xe ($Xe(g) =$

Xe(aq)) involve no ions. But the data in this table also support the notion that extrapolation down to 0°C and up to 60°C is generally justifiable in the absence of heat capacity of reaction data.

Table D-4. Heat Capacities of Reaction ($\Delta C_{p,\,r}$, Joule/mol-K) for Some Common Gas Species

Temp °C	**CO_2**	**H_2**	**H_2S**	**He**	**Rn**	**SO_2**	**Xe**
0.01	-208.8	33.1	-208.8	190.8	494.1	-624.3	373.2
25	-147.3	31.8	-128.0	135.1	326.4	-395.8	250.2
60	-135.6	31.8	-109.2	115.1	262.8	-334.3	203.8
100	-148.1	31.8	-119.7	110.0	241.0	-350.2	188.7
Average	-159.9	32.1	-141.4	137.8	331.1	-426.1	254.0

Source: Output DTN: SN0702T0502404.015, folder: *\Miscellaneous*, spreadsheet: *Cp_effect_vs_T.xls*. These data were extracted from DTN: MO0302SPATHDYN.001 [DIRS 161886], folder: *\CD\SUPCRT_runs_TJW\SUPCRT_Mins,* file: *supmins4.out* and converted from cal/mol-K to Joule/mol-K using the conversion factor 4.184 Joule/cal (Weast and Astle 1981 [DIRS 100833], p. F-304).

Table D-5 presents some heat capacities of reaction for the dissociation of some aqueous complexes. These data are similar to the data shown for solids in Table D-3 and support similar conclusions.

Table D-5. Heat Capacities of Reaction ($\Delta C_{p,\,r}$, Joule/mol-K) for Some Aqueous Complexes

Temp °C	**$AlCH_3COO^{2+}$**	**$Al(CH_3COO)_2^{+}$**	**$Al(CH_3COO)_3(aq)$**	**$NaSO_4^{-}$**	**$MgSO_4(aq)$**
0.01	-520.9	-1012.5	-1453.1	-418.0	-414.2
25	-262.8	-497.9	-698.3	-206.3	-197.1
60	-166.5	-304.6	-421.3	-141.4	-150.6
100	-136.8	-243.5	-343.1	-143.5	-189.5
Average	-133.1	-233.5	-346.0	-194.6	-312.1

Source: Output DTN: SN0702T0502404.015, folder: *\Miscellaneous*, spreadsheet: *Cp_effect_vs_T.xls*. These data were extracted from DTN: MO0302SPATHDYN.001 [DIRS 161886], folder: *\CD\SUPCRT_runs_TJW\ SUPCRT_Mins,* files: *supaqs1.out* and *supaqs2.out* and converted from cal/mol-K to Joule/mol-K using the conversion factor 4.184 Joule/cal (Weast and Astle 1981 [DIRS 100833], p. F-304).

In summary, one may conclude that in the absence of heat capacity data for a single mineral, pure liquid, or gas in a dissolution reaction for that species, extrapolation of 25°C data down to 0°C and up to 60°C is generally well justified for an uncertainty of $\Delta\log K = 0.1$. In the absence of total heat capacity of reaction data, the same extrapolation is generally also justified, if one is willing to accept a higher uncertainty ($\Delta\log K = 0.2$).

INTENTIONALLY LEFT BLANK

APPENDIX E

QUALIFICATIONS OF THE DATA QUALIFICATION TEAM FOR QUALIFYING DATA0.YMP.R2

INTENTIONALLY LEFT BLANK

The following information is reproduced from *Technical Work Plan for: Near-Field Environment and Transport In-Drift Geochemistry Analyses* (BSC 2004 [DIRS 172402], Appendix A):

Chairperson

Carlos F. Jove Colon (SNL) obtained his B.Sc. (1990) degree with honors in Geology from the University of Puerto Rico (Mayagüez campus), M.S. (1993) in Geology (petro-tectonic relations between discontinuous strike-slip faults), and Ph.D. (1997) in Geological and Environmental Sciences from Stanford University (experimental studies on reactive-transport in porous media and kinetics of mineral phase transformations). His current research interests in geochemistry include: 1) thermodynamic and structural properties of synthesized zeolitic material observed in high level waste solutions, 2) theoretical modeling of equilibria between aqueous solutions and minerals encompassing multi-phase multi-component systems, 3) characterization of natural attenuation of contaminated plumes with radionuclides (U, Cs, and Sr) found at various natural and engineered sites, 4) phase chemistry and metal uptake capacity of contaminant getters in sludges analogous to those found in decommissioned high level waste storage tanks, 5) reactive transport in porous media and its effect on rock hydraulic properties, such as permeability and porosity, and 6) characterization of radionuclide sinks in soil through the use of novel analytical techniques. He has been involved in the retrieval and analysis of thermodynamic data to study chemical reactions applied to systems of geochemical interests. In the course of many years he has been using geochemical codes such as EQ3/6 to perform solution-mineral-equilibria calculations and reaction path modeling. Recently, he has been involved in a concerted effort to expand the Pitzer thermodynamic database to model concentrated electrolytes at high temperatures. He is a member of the American Geophysical Union.

Technical Representatives

Dr. Charles R. Bryan has a B.A. in Geology (1981), and an M.S. (1988) and Ph.D. (1995) in Geology with emphasis on geochemistry and igneous petrology. Dr. Bryan has thirteen years of experience in the development of caution/anion getters and experimental studies of metal sorption onto iron oxides, layered double hydroxide materials, and mesoporous materials. Dr. Bryan has been employed as a geochemist at Sandia National Laboratories for eight years, and has worked on environmental site assessment and remediation projects in support of a number of DOE sites, including the Hanford Nuclear Reservation, and the Fernald, Ohio facility. In addition, he has worked on a variety of projects for the Waste Isolation Pilot Plant, including (1) designing and populating a geochemistry/materials characterization laboratory in Carlsbad, NM, (2) research to evaluate cement/brine interactions, and brine and waste interactions with magnesium oxide (the engineered barrier at the Waste Isolation Pilot Plant), (3) modeling and experimental investigations in actinide transport to determine matrix diffusion parameters for a multirate transport model, and (4) the development of the disturbed rock zone, the zone of deformation in the salt host rock surrounding the repository. Dr. Bryan currently provides scientific support for the Engineered Barrier Systems and Waste Package Criticality Departments of the Yucca Mountain Program as co-author/checker/reviewer of several project documents.

Dr. Russell Jarek has a B.S. in Chemistry/Chemical Physics (1991) and a Ph.D. in Chemistry (1998) from the University of California, Santa Barbara, primarily in physical chemistry involving ion-molecule reactions and kinetics. Thesis work focused on mass spectral examination of gas phase ion-molecule reactions of organic as well as clustering energetics and kinetics of inorganic compounds. Ab-initio theoretical calculations of structure and energy, and RRKM transition-state kinetics supported these works. Postdoctoral work at Sandia National Laboratories included study of chlorosilane reactivity as applied to the semiconductor industry and laser ablation study of various zeolitic materials in attempt to determine chemical catalytic unit. For the past two years, Dr. Jarek has been a member of the Yucca Mountain Project as a Senior Member of the Technical Staff in support of chemistry and geochemistry for Engineered Barrier Systems, Waste Package Criticality, and Licensing Departments of the Yucca Mountain Program. During that time he has qualified and utilized the computer code EQ3/6 for evaporation and deliquescence calculations; worked on creation and qualification of Pitzer thermodynamic databases; developed the GetEQData software; and has been co-author/checker/reviewer on several project documents including the Physical and Chemical Environments model report, TBD05, and SAR chapter 2.3.5.