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Civilian Radioactive Waste Management System
Management & Operating Contractor

Data Qualification Report for Thermodynamic Data File, Data0.ymp.R0 for Geochemical Code, EQ3/6

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RWB 10/10/00

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EXECUTIVE SUMMARY

The objective of this work is to evaluate the adequacy of chemical thermodynamic data provided by Lawrence Livermore National Laboratory (LLNL) as Data0.ymp.R0A in response to an input request submitted under AP-3.14Q. This request specified that chemical thermodynamic data available in the file, Data0.com.R2, be updated, improved, and augmented for use in geochemical modeling used in Process Model Reports (PMRs) for Engineered Barrier Systems, Waste Form, Waste Package, Unsaturated Zone, and Near Field Environment, as well as for Performance Assessment. The data are qualified in the temperature range 0° to 100° C. Several Data Tracking Numbers (DTNs) associated with Analysis/Model Reports (AMR) addressing various aspects of the post-closure chemical behavior of the waste package and the Engineered Barrier System that rely on EQ3/6 outputs to which these data are used as input, are Principal Factor affecting.

This qualification activity was accomplished in accordance with the AP-SIII.2Q using the Technical Assessment method. A development plan, TDP-EBS-MD-000044, was prepared in accordance with AP-2.13Q and approved by the Responsible Manager. In addition, a Process Control Evaluation was performed in accordance with AP-SV.1Q.

The qualification method, selected in accordance with AP-SIII.2Q, was Technical Assessment. The rationale for this approach is that the data in File Data0.com.R2 are considered Handbook data and therefore do not themselves require qualification. Only changes to Data0.com.R2 required qualification. A new file has been produced which contains the database Data0.ymp.R0, which is recommended for qualification as a result of this action. Data0.ymp.R0 will supersede Data0.com.R2 for all Yucca Mountain Project (YMP) activities.

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ACRONYMS AND ABBREVIATIONS

AMR	Analysis and Modeling Report
AT	Assessment Team
CD	Compact Disc
DTN	Data Tracking Number
EOS	Equation of State
LLNL	Lawrence Livermore National Laboratory
LANL	Los Alamos National Laboratory
NRC	U.S. Nuclear Regulatory Commission
PMR	Process Model Report
QARD	Quality Assurance Requirements and Description
ROM	Read Only Memory
YMP	Yucca Mountain Project

ACRONYMS AND ABBREVIATIONS (Continued)

Chemical

a	Parameter in Maier-Kelley expression (or other heat capacity equation)
a_1,a_2,a_3,a_4	Parameters in the HKF equation of state
b	Parameter in Maier-Kelley expression (or other heat capacity equation)
c	Parameter in Maier-Kelley expression (or other heat capacity equation)
c_1,c_2	Parameters in the HKF equation of state
Cp	Heat capacity at constant pressure
Δ	Finite difference (of a parameter)
d	Parameter in a heat capacity equation, or, mathematically, symbol for an infinitesimal
∂	Partial infinitesimal symbol
G	Gibbs free energy
H	Enthalpy
i	Designation for arbitrarily chosen species i
K	Equilibrium constant
ln	Natural logarithm (base e)
log	Common logarithm (base 10)
logK	Common logarithm of an equilibrium constant for a reaction.
P	Pressure
P_r	Reference pressure (1 bar)
S	Entropy
T	Absolute temperature (i.e., in Kelvin)
T_r	Reference temperature (298.15 K)
V	Molar volume (cc/mole)
ω	Parameter in the HKF equation of state
^{o}	Designation of standard state for a parameter, i.e. at 1 bar, when used as a superscript on a parameter

1. SCOPE

The EQ3/EQ6 codes solve chemical equilibrium problems using an approach based on the law of mass action (Wolery, 1992a; Daveler and Wolery, 1992; Wolery, 1992b; Wolery and Daveler, 1992). The data required by the codes consist of:

- Problem specific data,
- Temperature-dependent values for the logarithms of the equilibrium constants (logK(T)) of a number of reactions including those called for by the problem, and
- Data to support the algorithm chosen in the problem specification to calculate the activity coefficients, which describe the relationship between concentrations and thermodynamic activities.

The second and third types of data (above) are supplied to the EQ3/EQ6 programs through data files designated Data0.xxx, where xxx refers to a specific file. Several data files, including Data0.com.R2, are currently provided with the code, EQ3/6, CSCI/STN Number: LLNL:UCRL-MA-110662 (LSCR198)). Those data files contain all of the basic thermodynamic data needed to solve a broad range of problems. Special problems, such as those that involve prediction of the behavior of actinide species in high-level nuclear waste disposal require databases that are augmented by the inclusion of thermodynamic data describing those species and their chemical behavior. The result of the current effort will be to replace these existing files with the new qualified file, Data0.ymp.R0.

The activities described in this report were undertaken to qualify the data file Data0.ymp.R0 for the software code EQ3/6 V7.2b (Wolery 1992a describes version 7.2; subsequent revisions use the same references) previously qualified for Project work (CSCI/STN Numbers: LLNL: UCRL-MA-110662 (LSCR198), 10075-7.1bLV-00), and for other project activities requiring chemical thermodynamic data valid over the range of conditions for which Data0.ymp.R0 is qualified. Hereafter, this code package will be cited only as EQ3/6. The technical assessment procedure allows the Assessment Team (AT) only to review and either qualify or delete data, but not to select data.

This qualification of the Data0.ymp.R0 file covers its use on problems in which temperatures do not exceed 100°C and for which one of the conventional, extended forms of the Debye-Hückel algorithm for activity coefficients is appropriate. The activity coefficient algorithm is suitable only for dilute to moderately concentrated solutions. In the context of this qualification report, "dilute" refers to solutions with ionic strengths of less than about 1.0 molal. Another algorithm, the Pitzer equation, is also available within EQ3/6 for running problems that may include solutions of high ionic strength. However, the Data0.ymp.R0 data file does not include data supporting the Pitzer algorithm.

2. TEAM EXPERTISE

The Qualification Team consists of Dr. Paul L. Cloke, Dr. F. J. Pearson and Mr. Steve Frankiewicz.

Dr. Cloke is the Chairperson. Dr. Cloke has a PhD in Geological Sciences (minor in mathematics) from the Massachusetts Institute of Technology and an AB Degree in geology from Harvard College. He was a Postdoctoral Fellow at Harvard for two years following a few years in the mining industry. He has over 45 years experience in research and teaching, including 15 years in nuclear waste management at the Office of Nuclear Waste Isolation (the former Salt Repository Project) and the Yucca Mountain Project. He is Professor Emeritus of Geological Sciences at the University of Michigan and Adjunct Professor of Civil Engineering at the University of Nevada, Las Vegas.

Dr. Pearson is a Technical Representative and an expert in ground-water chemistry. He has PhD and MS Degrees in Geology (minor in chemistry) from the University of Texas at Austin and an AB Degree in geology from Harvard College. He has over 40 years experience in geochemistry, geology, and hydrogeology. He has worked on geochemical and geological projects throughout the United States, and in Switzerland, Germany, Great Britain, Canada, and Denmark. He has participated in numerous expert panels providing internal review and quality assurance of projects relating to the selection or remediation of chemical and radioactive waste sites. He has supported geochemistry in YMP Performance Assessment Operations for the past two years.

Mr. Stephen Frankiewicz is another Technical Representative. Mr. Frankiewicz has a Masters Degree in Nuclear Engineering and a Masters Degree in Physics from the Massachusetts Institute of Technology. He has over 30 years experience in technology management, including 6 years in nuclear waste management at the Waste Isolation Pilot Plant in New Mexico and the Yucca Mountain Project. He has spent the past two and a half years supporting Performance Assessment Operations in the areas of Quality Assurance and Total Systems Performance Assessment.

3. METHOD OF QUALIFICATION

This qualification activity has been accomplished in accordance with the AP-SIII.2Q using the Technical Assessment method. Following the evaluation and modifications, which were found necessary, the data file has been submitted to the Technical Data Management System (TDMS), and a new Data Tracking Number (DTN: MO0009THRMODYN.001) has been assigned. The data file considered for qualification is designated Data0.ymp.R0A (CRWMS M&O 2000a). Hereafter this file is referred to simply as Data0.ymp.R0A and in Appendix J and on the accompanying Compact Disc Read Only Memory (CD ROM) is designated data0A.ymp. The data file, modified as a result of this qualification process and qualified for YMP use, is designated Data0.ymp.R0 and in Appendix J and on the CD ROM as data0.ymp. The data file Data0.com.R2 is designated Data0.com on the CD ROM.

The steps taken by the data qualification team are described below.

The qualification team identified what changes have been made to the data in Data0.com.R2 to arrive at Data0.ymp.R0A.

The file (Data0.com.R2) has been widely distributed and used around the world and meets the essential criteria for a handbook (Mellington, 2000), which in this case can be used either manually or electronically. The changes made to create Data0.ymp.R0 are identified in Appendix A, which is also included on the CD ROM identified in Appendix J.

3.1 The team designated the data that are retained without change in Data0.ymp.R0 as accepted.

3.2 The team identified as accepted new data retrieved from internationally recognized handbooks and placed into Data0.ymp.R0A, either as replacements for older data or as augmentations.

3.3 New data developed under the auspices of the YMP Quality Assurance Requirements and Description (QARD) and placed into the Data0.ymp.R0 data set, either as replacements for older data or as augmentations, were identified as qualified.

3.4 The team performed a technical assessment on data obtained from other sources, for example from internationally recognized peer reviewed scientific and technical journals. Some of the journal articles recommended improvements to data already contained in Data0.com.R2. The AT recommends that these data be included in the qualified data set. Likewise, some new data, derived from controlled experiments and evaluated by the authors and technical reviewers for the journal in which published, in keeping with normal scientific practice, were recommended for inclusion in the qualified data file. The team found that most of the data in Data0.ymp.R0A from journals were revisions of the older data.

3.5 Some data were adjudged by the assessment team to be unreliable or from questionable sources. Those data were removed from the data set, Data0.ymp.R0A.

3.6 The assessment team corrected several typographical or editorial errors, such as incomplete citations for sources of the data.

3.7 The assessment team requested the qualified and controlled software code SUPCRT92 V1.0 (STN: 10058-1.0-00) from the Software Configuration Secretariat in accordance with AP-SI.1Q. Hereafter this code is referred to simply as SUPCRT92. Code documentation is contained in Johnson et al. (1992). The team ran the code on a random sample of different parts of the input data, including aqueous, solid, and gaseous chemical species. The output was compared to the corresponding data in Data0.ymp.R0A to evaluate whether the logK(T) data in Data0.ymp.R0A are correctly derived from the underlying handbook or qualified journal data. All of this output, as well as workbooks used in several cases to assist in the evaluations, is included in the CD ROM, identified in Appendix J that accompanies this report. All of these files are identified in Appendix J. Specific mention and discussion of these outputs are made in the Section 6 and in several of the other Appendices. The thermodynamic (input) data were subdivided in the file into several kinds, specifically, basis species, auxiliary basis species, aqueous species, solids, gases, and solid solutions. Respectively, there are 87 basis species (corresponding to 86 chemical elements plus water) (Aqueous species numbers 1 to 87 in AQ sheet of DATA0_ymp_sources.xls), 95 auxiliary basis species (Aqueous species numbers 88 to 182 in AQ sheet of DATA0_ymp_sources.xls), 995 additional aqueous species (Aqueous species numbers 183 to 1177 in AQ sheet of DATA0_ymp_sources.xls), 1037 solids (Solids numbers 1 to 1037 in MIN sheet of DATA0_ymp_sources.xls), 2 liquids (Liquids numbers 1 and 2 in GAS&LIQ sheet of DATA0_ymp_sources.xls), 95 gases (Gases numbers 1 to 95 in GAS&LIQ sheet of DATA0_ymp_sources.xls), and 10 solid solutions. From these, 14 auxiliary basis and other aqueous species, 11 solids, and 5 gases were randomly selected for detailed evaluation using SUPCRT92 or other suitable algorithm. Three of the randomly chosen cases used only a separate algorithm and did not involve the use of SUPCRT92. (In several cases the evaluation could be done either by using SUPCRT92 for some species and separate workbook calculations subsequently combined with the SUPCRT92 output, or directly by using available options within SUPCRT92.) The sampling also included some examples of each temperature extrapolation mode that SUPCRT92 may use. When species participating in the reactions of the randomly selected entities were included, check calculations embraced a total of 29 basis species (including O2(g) as a basis species), 20 auxiliary basis and other aqueous species, 14 solids, and 6 gases (including O2(g) as a gas species), as described in Appendix B. In some cases the data in Data0.ymp.R0 required conversion from joules to calories for use in SUPCRT92. These conversions are documented in file joules to calories.xls on the CD ROM included with this report. (See Appendix C).

Examination of the data provided in Data0.ymp.R0A revealed that one aqueous species, methane(aq), needed by Performance Assessment was inadvertently omitted in the update from Data0.com.R2. This update eliminated many organic species not required by the YMP and mistakenly deleted this species. Much of the organic data that was requested was updated by using a more recent data source (Shock 1995). The AT used this more recent data together with information from Data0.com.R2 for restoring methane (aq) to the file. Because methane referenced ethane, which in turn referenced acetic acid, the simplest procedure was to restore those species as well. This makes a total of 1180 aqueous species in Data0.ymp.R0.

3.8 The data in Data0.ymp.R0 must be formatted in such a way as to be read by a data preprocessing code, EQPT, which is written in FORTRAN77 and is part of the previously qualified EQ3/6 code package. Because this format is specific to this version of the code, it differs from those found in the source documents. However, the same data, e.g., free energies of formation, equation of state (EOS) parameters, heat capacities, etc., in the source documents are readily found in the appropriate places in the data file. The assessment team needed only confirm that the same values appear in both places. All possible parameters are not listed for all species, partly because some are not known. Some may be derived from others; in such cases the algorithms used for extrapolation confirm the accuracy of the derivations. In other cases missing data mean either that a less accurate algorithm must be used for temperature extrapolations, or that temperature extrapolations cannot be done based on available information. In the last case the data file contains a logK only for 25° C. In every case the reference data used for other calculations are identified in the file, as is the extrapolation algorithm, if any, that was used. The data for reactions in Data0.ymp.R0 consist principally of the chemical composition of each species (aqueous, solid, or gas), the dissociation or dissolution reaction for the species, and a table of the logarithms of equilibrium constants for this reaction at several temperatures (logK(T)). Only the data for reactions are needed by EQ3/6. Calculations by which the logK(T) values are determined from the EOS parameters were made using the qualified code SUPCRT92. If additional supplemental calculations were required, they were made by hand (workbook) as described below and documented as part of this report.

4. EVALUATION CRITERIA

The evaluation criteria listed in Section 3, Data Qualification Criteria, of the Data Qualification Plan (CRWMS M&O, 2000b) were used to evaluate the differences, if any, between the electronic handbook file Data0.com.R2 (Mellington, 2000) and the Data0.ymp.R0A file being qualified. The data contained in Data0.ymp.R0A were evaluated to ascertain whether they met the following criteria.

- New or different data were obtained from internationally recognized handbooks (described in Section 3.2 above).
- New or different data were developed under the auspices of the QARD (qualified from origin) (described in Section 3.3 above).
- New or different data were obtained from internationally recognized peer reviewed scientific or technical journals (described in Section 3.4 above).
- In accordance with the Data Qualification Plan (CRWMS M&O, 2000b) differences of less than 5% were insignificant. As applied to the Log K values, this criterion applies throughout the temperature range 0° C to 100° C. Accordingly, deviations between data output of SUPCRT92 runs or between the two files (Data0.com.R2 and Data0.ymp.R0A) of less than 5% were qualified.

5. RECOMMENDATION CRITERIA

Data are included in the data file recommended for qualification, if they meet the following criteria:

- Data are included in internationally recognized handbooks (described in Section 3.3 above).
- Data were developed under the auspices of the QARD (qualified from origin) (described in Section 3.4 above).
- Data were determined to be from internationally recognized peer reviewed scientific or technical journals (described in Section 3.5 above).
- Data showed deviations between output of SUPCRT92 runs or between the two files (Data0.com.R2 and Data0.ymp.R0A) of less than 5%

6. EVALUATION RESULTS

6.1 DESCRIPTION OF THE DATA FILE AND COMPARISON OF DATA0.COM.R2 AND DATA0.YMP.R0A

The structure of the Data0.ymp.R0A data file is that required by the EQ3/EQ6 codes (Wolery, 1992a). Following a descriptive header text, the file begins with a data block containing values for miscellaneous parameters. These start with the temperature limits for the following data. Next is a listing of the temperatures for which reaction equilibrium constant (logK(T)) values will be provided in the data file, and pressures along the water vapor equilibrium curve at these temperatures. The temperatures specified and the corresponding pressures extend to 300°C, consistent with the general EQ3/EQ6 input format.

The next four groups of miscellaneous parameters list values for temperature-dependent coefficients of the activity coefficient algorithms used in EQ3/6. These values are equivalent to those in the Data0.com.R2 handbook (this file is provided with the code, EQ3/6; Mellington 2000).

The final group of miscellaneous parameters consists of data for converting values of O_2 partial pressures, in which oxidation-reduction conditions are expressed in the EQ3/6, to the Eh values commonly used in aqueous geochemistry. These values also equal those in the Data0.com.R2 handbook.

The next data block, "bdot" parameters (i.e., coefficients in the "salting out" term in the Hückel equation, one of the forms of the extended Debye-Hückel equation), contains values of species-specific parameters of the activity coefficient algorithm. Most of the species in Data0.ymp.R0A are the same as those in the Data0.com.R2 handbook. However, Data0.ymp.R0A includes some species that are not present in the Data0.com.R2 handbook, and it does not include some species that are in the Data0.com.R2 handbook. These differences are discussed in more detail in Section 6.2.1.3

The next data block, elements, contains the atomic weights of all elements in the database. The values in Data0.ymp.R0A are the same as those in the Data0.com.R2 handbook, or differ by less than 0.02 units. The differences in no case amount to more than the 5% tolerance deemed acceptable in the qualification plan. The atomic weights used in Data0.ymp.R0A are the same as those adopted for use in calculations by Waste Package Operations.

The following data block, basis species, lists the aqueous species (including H_2O and O_2) in terms of which all subsequent reactions in the database are ultimately written. The only information required by EQ3/6 from the entries in this block is the species identity, its charge, and the number and identity of the elements of which the species is composed. Both Data0.ymp.R0A and the Data0.com.R2 handbook include additional thermodynamic data for each species in the data block. This information has been used to derive the logK(T) values for each reaction given later in the databases, and is also useful as a source of thermodynamic values wherever such data are needed in the Yucca Mountain Project. This is discussed in more detail in Section 6.2.4.

The type of thermodynamic information included for each basis species is not the same in the Data0.ymp.R0A file and in the Data0.com.R2 handbook. Both contain values for the Gibbs energies of formation, delG0f, enthalpies of formation, delH0f, and entropies, S0PrTr, at the reference temperature and pressure. In addition, Data0.ymp.R0A includes values for the parameters of the equations of state (EOS) or other data that are used to extrapolate the properties of formation of the species to other temperatures and pressures.

Both the Data0.ymp.R0A file and the Data0.com.R2 handbook include sections for aqueous, solid, liquid, and gaseous species, as well as for solid solutions. The final section in both consists of a list of reference sources for the data. Each reference is preceded by an abbreviated notation consisting of the last two digits of the year of publication followed by the first three letters of the first author, followed in turn, if there are additional authors, by a virgule (/) and the first three letters of the second author. If there are two or more publications by the same first two authors in the same year, these are distinguished by adding a number at the end, e.g., 64cri/cob2. These shorthand notations are used throughout the preceding sections of the Data0.ymp.R0A file to document sources of the data.

6.2 QUALIFICATION PROCESS

During the qualification effort the AT examined and evaluated all sections of the data file, Data0.ymp.R0A, except for solid solutions. This section provides details of that evaluation.

Both liquids were included in Data0.com.R2 and remain unchanged in Data0.ymp.R0A. Thus, in accordance with the Data Qualification Plan they are qualified.

Solid solutions were excluded from review because they contain no additional thermodynamic data, and, thus, fall outside the scope of the Data Qualification Plan. The solid solutions block contains only specifications as to which solids in the preceding section for solids are included in individual solid solutions and designation of the type of solid solution and type of mixing site within the solid. (In September, 1992,the data files (through R16) included only one type, ideal, except for olivine, which is treated via a binary regular solution model (Wolery 1992b, p. 67). However, neither Data0.com.R2 nor Data0.ymp.R0A provide any specifications for this solid solution.)

The first effort produced a large workbook, Data_ymp_sources.xls, included on the CD ROM that accompanies this report that includes all species in Data0.ymp.R0A. This workbook documents the data sources for all data for these species in Data0.ymp.R0A and for data sources in Data0.com.R2, if the same species are also included there. Many new species have been added to Data0.ymp.R0A. This workbook documents whether the data in Data0.com.R2 file were changed, i.e. updated or replaced by newer data. Finally, at the end of the evaluation process, columns were added stating whether, and how, in accordance with this Qualification Plan, the data were qualified. This workbook, DATA0_ymp_sources.xls, is included in the CD ROM provided with this report. During the review the AT found that some of the references were incorrect and amended the citation in Data0.ymp.R0, if possible. These corrections were not incorporated into workbook, Data0_ymp_sources.xls.

The initial text section of Data0.ymp.R0A was changed to reflect the qualified status of Data0.ymp.R0. The text in Data0.ymp.R0A describes several acronyms for qualification status, such as A for "accepted" and Q for "qualified" in keeping with standard NRC and YMP usage.

The temperature limits in the miscellaneous parameters section have been respecified as 0° C to 100° C in Data0.ymp.R0 in keeping with the Qualification Plan. Nevertheless, the listing of temperatures for which logarithms of reaction equilibrium constants will appear in the data file was left unchanged. This is because not doing so may interfere with the operation of the codes, EQ3NR (Wolery 1992b) and EQ6 (Wolery and Daveler 1992), and because, in any case, the flag, "500.0000" has been entered in every species data block for temperatures above 100° C. This flag is interpreted by the codes to mean that data are not available for those temperatures. No changes are needed for pressures. Consistent with the limitations on the range of validity of the Data0.ymp.R0A data file, data for temperatures above 100 °C have not been examined as part of this qualification process.

In view of the temperature range considered it is worthwhile to point out that the pressure specified remains constant at 1.0132 bar. See the specifications for pressure under the miscellaneous parameters in Data0.ymp.R0.

The last two parts of the miscellaneous parameters section in Data0.ymp.R0A, activity coefficient algorithm parameters and O_2 partial pressure parameters, required no changes.

The values of the activity coefficient parameters for most of the species that are common to both databases are the same in Data0.ymp.R0A as in the Data0.com.R2 handbook. However, some of the Debye-Hückel a^0 (azer0) values differ between the two databases. These are shown in Table 6.2-1. For those species, the azer0 values in Data0.ymp.R0A correctly reflect those in Kielland (1937), a journal article accepted as the equivalent of a handbook source of these data.

Table 6.2-1. List of Aqueous Species Appearing Both in Data0.ymp.R0A and in the Data0.com.R2 Handbook but with Different Azer0 Values

Species	azer0 in Data0.ymp.R0A	Species	azer0 in Data0.ymp.R0A
MoO4--	4.5	Co++	6.0
CO3--	4.5	Cr++	6.0
S--	5.0	Hg++	5.0
S2O4--	5.0	Hg2++	4.0
SO3--	4.5	Ni++	6.0
Br-	3.0	Ra++	5.0
BrO3-	3.5	Co+++	9.0
CN-	3.0	Cr+++	9.0
ClO3-	3.5	Ga+++	9.0
F-	3.5	In+++	9.0
IO4-	3.5	Nd+++	9.0
MnO4-	3.5	Pr+++	9.0
NO2-	3.0	Sc+++	9.0
SCN-	3.5	Sm+++	9.0
Ag+	2.5	Tb+++	9.0
Cs+	2.5	Tl+++	9.0
Li+	6.0	U+++	9.0
NH4+	2.5	Y+++	9.0
Rb+	2.5	Sn++++	11.0
Tl+	2.5	Th++++	11.0
Cd++	5.0	Zr++++	11.0

NOTE: The azer0 values shown are those given in Data0.ymp.R0A, which correspond to those in Kielland (1937), a journal article accepted as the equivalent of a handbook source of azer0 data.

The AT noted that, whereas the azer0 parameters for Sn++++, Th++++, and Zr++++ were changed from 5.5 in Data0.com.R2 to 11in Data0.ymp.R0A, corresponding changes were not made for U++++, Np++++, Pu++++, and Am++++. The source of the azero data in Data0.com.R2 is not given, but is stated in Data0.ymp.R0A to be Kielland (1937). According to Johnson & Lundeen (1994 p.5), the activity coefficient expression used in EQ3/EQ6 is that described by Helgeson (1969). With respect to this equation, Helgeson (1969, p.774, footnote 7) states: "The values of azero were assigned on the basis of Kielland's (1937) azero values assuming equalities for similar complexes." Thus, it seems clear that the correct values for azero should equal or correspond to those given by Kielland (1937), and that where different values appear in Data0.com.R2 and/or) Data0.ymp.R0A, they must be considered typographical or oversight errors. Longstanding chemical principles dictate all chemical properties of closely related elements resemble each other very closely. Th, U, Np, Pu, and Am all belong to the actinide series of elements and have closer thermodynamic properties than most other groupings of elements within the periodic table of the elements. Therefore, in keeping with Kielland (1937) and the principles inherent in the arrangement of the elements in the periodic table the azer0 values for U++++, Pu++++, Np++++ and Am++++ were changed to 11.0 in

Data0.ymp.R0. This same logic applies only slightly less strongly to the similarity of properties between the actinide and lanthanide series of elements; accordingly, the azer0 value for Ce++++, which is not included in Data0.com.R2, was changed to 11.0 in Data0.ymp.R0. The AT concluded that these changes fall under the aegis of Section 2.h) of the Qualification Plan (CRWMS-M&O 2000b). This same principle applies equally well to comparisons between Zr and Hf. In fact it is very difficult to separate these two elements chemically. Accordingly, the azer0 for Hf++++, which is not included in Data0.com.R2, was entered as 11.0 in Data0.ymp.R0A. These changes do lead to substantial changes in activity coefficients at ionic strengths of 1.0 to less than 0.1. See workbook, change in gamma.xls, included on the CD ROM. Calculation of the first hydrolysis of Me++++ to MeOH+++, where Me stands for Ce, Hf, Np, Pu, or U, shows that these +4 ions are all hydrolyzed by 50% or more at pH less than 0.6 and more strongly as pH increases. Consequently, these ions have negligible effects on calculations relevant to the YMP. See workbook hydrolysis.xls included on the CD ROM. The situation for Am is more complex, but it is readily shown that the region on an Eh-pH diagram in which Am++++ would predominate lies entirely above the stability limits of water. See workbook hydrolysis.xls. The original discrepancies are attributed by the AT to oversight on the part of the compilers of the data file.

Similar changes have been made to assure consistency among the azer0 values for trivalent actinide and lanthanide cations, as well as for Bi+++, Mn+++, and Ru+++. These have been changed as needed to equal 9.0, the value given by Kielland (1937) for Al+++, Fe+++, and other similar ions included in Kielland (1937). The calculations shown in workbook, change in gamma.xls, show that the maximum effect of the change in azero at ionic strength 1, the maximum to which the data are being qualified, results in a change in the activity coefficient by a factor of about 3, which is less than an order of magnitude. Neither Bi nor Ru is considered important for applications needed by the YMP, and Mn is of only minor importance. The AT believes that this higher value of the activity coefficient more nearly represents the correct relationship.

The database includes several complex aqueous ions that have charges of +4 (++++) or higher. The azer0 values for these species are specified as 6.0 in both Data0.com.R2 and Data0.ymp.R0A. These are lower values than assigned to other +4 ions such as Th++++, as discussed in the previous paragraphs. No such complex ions appear in Kielland (1937), but the AT concludes that the lower azer0 value assigned to them in both databases is correct because their ion size is so much larger than the simple ions for which a higher azer0 value is appropriate.

The data block for atomic weights, which was changed slightly between Data0.com.R2 and Data0.ymp.R0A to achieve greater consistency with the standard adopted by Waste Package Operations, required no changes.

Most effort focused on the data blocks for individual chemical species, as detailed in the following subsections.

6.2.1 Evaluation of Data in Chemical Species Blocks

The first two lines in blocks for aqueous species provide the name and species type. These data are read by EQ3/6. In the case of named solids, e.g., minerals, the latter part of the first line also includes the conventional chemical formula, which is not read by the codes. The third line states which EQ3/EQ6 data files include the species block. The files are designated ymp, com, ree, pit, alt, and sup for Data0.ymp, Data0.com, etc., followed by a period and a revision number. The .ymp, .com, and .pit files are discussed in Section 1.0, above. Of the others, .ree includes a rare earth element set, .alt a composite data base that resembles .com, but in addition includes a substantial amount of unqualified data for actinides and organics, and .sup only data supplied with the SUPCRT92 computer program.

The next line states the qualification status at the time that Data0.ymp.R0A was compiled. It reflects the perspective at that time that this data file would be subjected to the data qualification process under the Data Acceptance Panel. Subsequently, it was recognized that it would be more suitable to qualify the data under a data qualification plan. Virtually all entries for these lines required changing from the previous designation to Q.

The next two lines, not read by EQ3/6, provide the molecular weight and the azer0 (for ions); the azer0s are read instead from the block of data near the top of the file. Values are provided here only for the convenience of users who wish to review the data.

The next several lines provide specifications for ionic charge, the chemical composition, and the dissociation reaction. These data are processed by the code, EQPT, which is part of the EQ3/6 code package, to produce the binary Data1 file, the file actually read by EQ3NR and EQ6. EQPT checks the data for consistency, and, if errors are found, will not create the corresponding Data1 file. Potential errors include an unbalanced dissociation reaction, a composition of the species in the reaction that does not correspond to the specified composition, and data (notably numbers and names of species) that appear in the wrong columns. The next few lines of data report the values for the logarithm of the equilibrium constant for the dissociation reaction for the temperature grid. The final several lines, all unread by EQ3/6, provide details of the data, as noted above in Section 6.1, and the data sources. Entries for basis species include the same information, except do not include reactions. Basis species data are used together with the corresponding data for individual species entered later in the file to calculate equilibrium constants for species which undergo dissociation (aqueous species) or dissolution (solid and gaseous species). These calculations are the ones described in this report and are made external to the EQ3/EQ6 package of codes.

Data blocks for solid, liquid, and gaseous species closely resemble those for aqueous species. Differences arise because these species aren't charged (ionic); because entries are made for molar volumes and heat capacities, when available; and because, in general, the equations of state (EOS), are not the same for aqueous species as for solids, liquids, and gases. The equations of state are the algorithms used to extrapolate reference state thermodynamic data to other temperatures and pressures. Different sets of parameters are required by the different types of species. In particular, the variations of thermodynamic properties of aqueous species with temperature are calculated using the modified Helgeson/Kirkham/Flowers (HKF) equation of state (Helgeson et al. 1982, Tanger and Helgeson 1988). The Maier-Kelley expression (Maier and Kelley 1932, Helgeson et al 1978) for Cp(T) is used for most solids, liquids and gases. Other expressions for Cp(T), such as those adopted for certain species in Robie et al., (1979), are used for certain species in Data0.ymp.R0. These are described in Appendix E. For solids, liquids and gases the portion of the data block designated for aqueous species as EOS parameters contains heat capacity data, but no longer specifically labels the data as EOS parameters, a more inclusive term.

Qualification of data included in the solid solution blocks lies outside the scope of the qualification effort. However, for completeness, some comments are included, even though the various entries have not been studied thoroughly by the AT and do not appear to be fully described in the user's manuals. (Some of the remarks here are derived from examination of the source code for EQ3NR) The first line in the solid solution block contains the name of the solid solution and its chemical formula. This includes data on what elements in the solid may vary. For example, for orthopyroxene, (Fe,Mg)SiO3, the formula indicates that the ratio of Fe to Mg may vary. The next line specifies the species type, ss for solid solution; the type of solid solution, e.g., ideal; and the word "active". This appears to be the default value, which EQ3/6 may change, if it is found that a particular solid solution is not actually to be included in the calculations. The section on components specifies which solids previously included earlier in the file are to be included in the solid solution. The number preceding each solid appears to be the limit of the range of composition for the corresponding solid. For example, a specification of 0.1 for smithsonite (ZnCO3) in the "carbonate-calcite" solid solution would apparently mean that ZnCO3 could not constitute more than 10% of the total composition (on a mole fraction basis) of the solid solution. No example of actual use of this option is known to the AT. The type designation, next in the file, evidently refers to the type of model, e.g., ideal, regular, etc. Finally, the site parameter section refers to the number of crystallographic sites that may have variable composition. For all the solid solutions in Data0.com.R2 or Data0.ymp.R0A this is one. The first value in the last line of the block refers to the number of atoms (in the formula) that may occupy this site, i.e. 1 for the two examples cited so far, but 5 for "chlorite-ss", (Fe,Mg)5Al2Si3O10(OH)8. Presumably a biotite model that permitted some substitution of Rb for K, (K,Rb)(Fe,Mg)2AlSi3)10(OH)2, would have 2 site parameters with values 1 (for K and Rb) and 2 (for Fe and Mg), respectively. This option has been used for modeling of some zeolites and clays (Wolery 1992b, p. 67). Details of use of such an option are given by Viani and Bruton (1992) and appear to require a different version of EQ3/6 than the one qualified for YMP use.

The volume data for solids are needed for applications by Waste Package Operations in conjunction with determining the volumes of corrosion and degradation products of waste packages. Unfortunately, many of the data required, although readily available, were not entered. The AT has added some of these data, as detailed in Appendix D and documented in Data0.ymp.R0. Others will be needed, but cannot be added by the AT without violating the restriction that members of the AT may not select data, only review and either qualify or delete them. The added volume data were not selected by any member of the AT.

The charge and elemental composition data given for each basis species were qualified by inspection. The values of the properties of formation at the reference temperature and pressure were qualified by comparison with values in the Data0.com.R2 handbook or by comparing them with the handbook or other qualified literature values cited as their source in Data0.ymp.R0A. The values of the EOS parameters, which do not appear explicitly in the Data0.com.R2 handbook were qualified by comparing them to the literature cited in the Data0.com.R2 handbook as their source or by comparing them with the handbook or other qualified literature values cited as their source in Data0.ymp.R0A. The Data Qualification Plan specifies that data will be checked and qualified only in the range 0° C to 100° C. This reflects uncertainties in the determination of the experimental data as well as possible differences in choices made by experimentalists in computing equilibrium constants, or other thermodynamic data, from the measurements. For example, one investigation may use a slightly different value for the second dissociation constant of some acid than does another. Possibly neither one used data that are now generally accepted as standard, such as those in the CODATA file (Cox et al. 1989). These kinds of differences do not lead to discrepancies of significance for the intended applications for the YMP, so long as data are not extrapolated too far from the conditions under which they were obtained, typically at or near 25° C. Limiting the extrapolations to 100° C provides a range of data suitable for virtually all YMP needs with reasonable assurance that the extrapolations do not lead to any significant discrepancies.

6.2.2 Comprehensive Listing of Species, Sources, Extrapolation Algorithms, and Qualification Results

The file data0_ymp_sources.xls lists (included in the CD ROM identified in Appendix J) list all the species, except solid solution species, included in Data0.ymp.R0A in accordance with Section 2.a) of the Data Qualification Plan (CRWMS-M&O 2000b). It indicates whether they also appear in the Data0.com.R2 handbook, and refers to the sources of data for the values of reference state properties and for the extrapolation algorithm for both data files. There are 2,311 species in the Data0.ymp.R0A data file: 87 basis species, 95 auxiliary basis species, 995 additional aqueous species, 1,037 solids, 2 liquids, 95 gases, and 10 solid solutions. (As noted in Section 3.7, the restoration of one species, methane(aq) and two associated species, that were inadvertently deleted, brings the subtotal of additional aqueous species from 995 to 998, and the grand total to 2314. Subsequent examination of the older data revealed that the retained organic species had been updated. This virtually dictates that the restored data should be similarly updated. The AT did this using the same reference as chosen for the retained organic species. The review, however, did not qualify all of these data and several were deleted. See Section 6.2.6.) The listing also includes notations as to whether any type of data included in Data0.ymp.R0A differs from corresponding values in Data0.com.R2. The process of constructing this workbook also served to check whether all references cited were in the reference list. Identification of these changes is required by the specifications in the Qualification Plan.

The data available for the standard reference conditions, 25° C and 1 bar, were extrapolated to other temperatures using a variety of algorithms, depending upon what data were available for this purpose. In many instances no extrapolations were possible, owing to a lack of data.

In view of the large number of species the AT decided to evaluate extrapolations for arbitrarily selected species. See Sections 6.2.3 and 6.2.4. The selection consisted of examining the column toward the right side of the worksheet listing of species that indicated whether any change was made. This column was far enough to the right that the name of the species could not be seen on the computer screen. For each type of extrapolation algorithm, which was entered into a nearby column, scrolling down the worksheet was performed in arbitrary intervals, e.g., near the first quarter, near the middle, etc. The intent was to select a line that showed both a change and a specific type of algorithm. The species was then identified by scrolling to the first columns in the worksheet. In some cases the final selection did not include a change (probably because when the selection was made a change had erroneously been indicated). The main concern, however, was to check several species for each extrapolation method. Table 6.2-2 shows the algorithms and the species selected for evaluation, 30 in all.

Table 6.2-2. Species Arbitrarily Selected for Detailed Comparison

Extrapolation Method/Abbreviation in workbook DATA0_ymp-sources.xls	**Species Selected**	**Species Type**
Cp(T), V(P) integration/Ct,Vp	UO2+, Pm++, Cr+++	Aqueous auxiliary species
Cp(T), V(P) integration/Ct,Vp	BaCl+, HSO4-, RuO+,RhO+, ZnCl2(aq)	Aqueous species
const-Cp(T) integration/Cc	Am++	Aqueous auxiliary species
const-Cp(T) integration/Cc	Cd(NH3)4++, USCN+++	Aqueous species
[Cp_rxn](T) integration/Cr	RuO4(aq)	Auxiliary aqueous species
[Cp_rxn](T) integration/Cr	H2CrO4(aq), CdSO4(aq)	Aqueous species
const-Cp(T) integration/CCp	CaHfO3, Tc2O7	Solid
const-Cp(T) integration/CCp	TcO(g)	Gas
const-Cp(T), const-V(P) int./Ccp,Vc	Morenosite, Ba2Si3O8	Solid
Cp(T) integration/Ct	UO2F2, Hydrophilite	Solid
Cp(T) integration/Ct	NO2(g)	Gas
Cp(T), const-V(P) integration/Cr,Vc	Hydromagnesite, Monticellite,	Solid
Cp(T), const-V(P) integration/Ct,Vc	N2(g), CO2(g)	Gas
const-H(T) integration/Hc	Pb2SiO4, ThS	Solid
const-H(T) integration/Hc	RuCl3(g)	Gas
const-H(T), const-V(P) int/Hc,Vc.	Okenite	Solid

The reactions by which these arbitrarily selected species plus supplementary added minerals dissociated or dissolved included a number of basis species and additional auxiliary basis species and gases, the data for which were also evaluated. These additional 35 species, all aqueous or gaseous, are: Al+++, Am+++, Ba++, Ca++, Cd++, Cl-, CrO4--, F-, H+, H2O, HCO3-, Hf++++, HS-, Mg++, Mn++ , MnO4--, Na+, NH3(aq), Ni++, NO3-, O2(g) [as a basis species], O2(g) [as a gas species], Pb++, Pm+++, Rh+++, Ru+++, RuO4--, SCN-, SiO2(aq), SO4--, TcO4-, Th++++, U++++, UO2++, and Zn++. The complete list of arbitrarily selected and additional species checked, together with descriptions of their extrapolation algorithm and the sources of reference state and extrapolation data, is given in Appendix B (file Ch_Calc_Sum.xls).

Some additional tests were performed to evaluate the "const-H" and Criss-Cobble extrapolations. These involved the minerals albite and calcite and the aqueous species CaHCO3+ and CrCl2+. Two species needed for these additional tests, Al+++ and Na+, are included in the list above. Temperature extrapolations for albite and calcite, using the Const-H(T) integration method, discussed below in Section 6.2.3 and found by the AT to be unacceptable, were compared with the results in Data0.ymp.R0A calculated in accordance with the standard Const-Cp(T) integration technique to illustrate the disagreement. The temperature extrapolations for CaHCO3+ and CrCl2+, using the Const-Cp(T), or Criss-Cobble, integration, also discussed below in Section 6.2.3, were similarly compared to the Data0.ymp.R0A results that used the Const-Cp(T) integration. This comparison showed the inapplicability, at present, of the Criss-Cobble method to complex cationic species. The method may succeed, if and when appropriate fitting parameters for this type of ion are developed.

Examination of the documentation of the parameters used for heat capacity extrapolations showed that in some cases the equations used differ from the standard Maier-Kelley equation (Maier and Kelley 1932). One of these variants was already included among the solids arbitrarily selected. To check another the mineral, pyrolusite, was added; this required the inclusion of the aqueous species, Mn+2 and MnO4--, in the evaluation.

6.2.3 Description of Comparisons for the Various Extrapolation Methods

Descriptions of all the extrapolation algorithms are provided in Johnson and Lundeen (1994), to which the reader is referred for further details. The discussion below follows the sequence in Table 6.2-2, which lists the species evaluated. A few additional species are noted in the second paragraph below that table. Results of all these evaluations may be found in the files included on the CD ROM. Names of these files are intended to guide the reader to the type of species, or to specific species.

Cp(T), V(P) integration:

This was the simplest to evaluate inasmuch as, with few exceptions, it corresponds exactly to the results of SUPCRT92 output (Johnson, et al. 1992). The comparisons are described Appendix B and full details, including the output files (which automatically include all necessary data from the input files), are provided in the CD ROM identified in Appendix J in files ending with the extension ".out".

As described in the code documentation (Johnson et al. 1992), SUPCRT92 calculates the variation of thermodynamic properties with temperature using the modified Helgeson/Kirkham/Flowers (HKF) equation of state (Helgeson et al. 1982, Tanger and Helgeson 1988) for aqueous species and the Maier-Kelley expression (Maier and Kelley 1932; Helgeson et al. 1978) for solids, liquids, and gases. In some instances terms in addition to, or instead of, those included in the Maier-Kelley equation were used. Because SUPCRT92 cannot handle these variants, the AT performed separate evaluations using SUPCRT92 for that part of the dissolution reaction to which it could be applied and a separate workbook, file Cp_extrapolation.xls included in the CD ROM, for extrapolation of data for solids and for combining the two parts of the calculations. These extrapolation algorithms are designated "Cp(T), V(P) integration" and "Cp(T) integration", respectively, in the sixth column of file Ch_Calc_Sum.xls included in the CD ROM included with this report and in Data0.ymp.R0A. These designations are abbreviated to "Ct,Vp" and "Ct", respectively, in file DATA0_ymp_sources.xls included in the CD ROM accompanying this report.

For aqueous species, all logK(T) values calculated with SUPCRT92 agree with those in Data0.ymp.R0A at 25° C. Also, results for those species for which data for temperature extrapolation by Cp(T) integration are available agree with the Data0.ymp.R0A values at temperatures away from the reference temperature. For species for which temperature corrections are made using other algorithms however, SUPCRT92 results do not agree with those in Data0.ymp.R0A (see file Ch_Calc_sum.xls and Table 6.2-2). When SUPCRT92 results do not support the Data0.ymp.R0A values, the Data0.ymp.R0A values have been checked using hand (workbook) calculations as described in the remainder of Section 6.2.3.

For solids and gases, the SUPCRT92 logK(T) values agree with the Data0.ymp.R0 values for all cases, including those for which this code may not correctly be applied, except for the minerals hydrophilite and pyrolusite. Note, however, that to achieve such agreement for the solid Tc_2O_7 and the gas TcO, it was necessary to correct an apparently incorrect reference to the data for the aqueous species TcO_4^- in the Data0.ymp.R0A file (see file Ch_Calc_sum.xls, footnote 2). This reference was corrected in Data0.ymp.R0.

The extrapolations for hydrophilite and pyrolusite used extrapolation equations not incorporated into SUPCRT92 as noted, in principle, above. The results of combined SUPCRT92 and workbook extrapolations are shown in Appendix E. For both minerals agreement within the 5% specification is obtained over the temperature range, 0° C to 100° C, if the data in Data0.ymp.R0A are used. However, a small copying error was discovered between the source document (Shock, et al. 1997a) and Data0.ymp.R0A for the entropy of MnO_4^{--}. This ion appears in the dissolution reaction used for pyrolusite. This small error has very little impact on the calculated equilibrium constants, as shown by the comparison in file Cp_integration.xls between the original and corrected values. The ion in question, MnO4--, is designated as an auxiliary basis species, which means that it may be incorporated into other reactions in the data file, as was done for pyrolusite. This was done in only two other cases, $BaMnO_4$ and MnO_2(gamma). In both of these instances equilibrium constants were calculated only at 25° C directly from free energy data. This means that this error was not propagated to other locations within the data file. To avoid any possible propagation in applications yet to be performed by the YMP the AT has changed the data in Data0.ymp.R0 to agree with the corrected equilibrium constants shown in file Cp_integration.xls for both pyrolusite and MnO4--.

The other exceptional cases arise when no heat capacity data are available for the species whose dissociation or dissolution constant is being extrapolated to other temperatures. Often, however, such data do exist for other species in the dissociation or dissolution reaction. Use of heat capacity data for some, but not all, species in a reaction is inconsistent with conventional thermodynamic practice. When full sets of thermodynamic data for reactants and products are not available, it is not uncommon to assume that the heat capacity of a reaction is constant or even equal to zero. As illustrated in many thermodynamics textbooks, when these assumptions are used to calculate Gibbs energies of reaction and logK(T) values at temperatures away from the reference temperature, the results differ from values calculated using correct expressions for the temperature variation of reaction, by amounts that increase with the temperature difference. The constant Cp approximation is useful over a wider temperature range than the Cp = 0 (delta H constant) approximation.

The const-H(T) integration scheme in SUPCRT is inconsistent with conventional thermodynamic practice because it maintains constant only the enthalpy of the dissolving or dissociating species while allowing the enthalpy of some or all of the product species to vary with temperature. Thus, it calculates with delta H values for the reaction that vary with temperature instead of the constant values the convention requires. The effects of this inconsistency on Gibbs energies of reaction and logK(T) values have not been evaluated. Absent such an evaluation as an indication of the errors introduced by the approximation, the AT has selected only 25C values for all species evaluated by the const-H(T) algorithm.

Const-Cp(T) integration:

This was the most complex algorithm to evaluate. It applies only to aqueous reactions involving only ions. The description in Johnson and Lundeen (1994) does not suffice to enable the reader to perform the extrapolation. Moreover, the literature articles (Criss and Cobble, 1964 a and b) are very difficult to decipher. Essentially, Criss and Cobble (1964a) showed that, by suitable choices of the entropy of the hydrogen ion, thereafter called the absolute entropy in their papers, but hereafter called CC-entropy in this report, it is possible to obtain linear relationships for the entropies of other aqueous ions. In the second paper (Criss and Cobble, 1964b) they derived average values for heat capacities of these ions over the temperature intervals that they chose, specifically 25° C to 60° C, 25° C to 100° C, 25° C to 150° C, 25° C to 200° C. In fact this was the reason that the logK(T) grid in the several versions of Data0 files uses 60° C, 100° C, and 150° C (Johnson and Lundeen, 1994) was chosen. To use this technique, it is necessary to convert entropies, as conventionally reported at 25° C, to CC-entropies (Step 1). The second step makes the temperature extrapolation in accordance with the algorithm in Criss and Cobble (1964a) to one of the higher temperatures. The third step converts back to conventional entropies at elevated temperature. The next step determines the average heat capacity for the ion over the relevant temperature using the algorithm in Criss and Cobble (1964b). This must be done for all species in the reaction. Finally, that result is used to estimate the free energy of the reaction at the elevated temperature from that at 25° C. The equation for that last calculation is rather standard, but for convenience for the reader is rederived in Appendix F. This last step involves knowledge of the free energies of formation of all the other species in the reaction. The heat capacity of the reaction is calculated from the values for each individual species in the reaction. It is a simple matter to calculate the equilibrium constant from the derived free energy of reaction. Full details of this procedure and the equations used are provided in the workbook in Appendix F, which is also included in the CD ROM identified in Appendix J.

Comparisons for the arbitrarily selected species, shown in file Criss_Cobble_checks.xls, of the output with the data reported in Data0.ymp.R0A all agree within the specified 5% at temperatures at or below 100° C, except for Cd(NH3)4++ at 100° C and for the added comparison case, CaHCO3+. (The AT did not investigate the reason for the out of bounds discrepancy for Cd(NH3)4++ because, for reasons discussed in Section 6.2.5, extrapolated data for this species were not qualified.) These comparisons are discussed in some detail below in Section 6.2.5. No check was made for 25° C, because this involves no extrapolation, and no data are available in the source documents, Criss and Cobble (1964a and b) for 0° C. Ordinarily, one would expect, as in the instances in which SUPCRT92 may appropriately be used for comparisons, that results of the present evaluation should agree exactly with those reported in Data0.ymp.R0A, because the same equations are used. However, in the case of those done by the Criss-Cobble method one can infer some reasonable explanations. In the tables provided in Criss and Cobble (1964a and b) the fitting parameters for the entropy correlations and for the heat capacity calculations are rounded to two significant figures. The latter can be derived from the former, and if this is done, considerable differences appear. For example, for the average heat capacity for H+ between 25° C and 60° C, Table II of Criss and Cobble (1964b) shows 23, whereas calculation from the entropy values in Table III in Criss and Cobble (1964a) yields 22.52. Moreover, it is possible that the fits for the entropy correlations were recalculated in conjunction with producing Data0 files and additional digits retained. These differences are sufficient to explain the lack of exact matching. In principle, of course, if the same equations are used with the same data, the answers should agree within the precision of the different computational platforms.

This extrapolation algorithm is designated "Const-Cp(T) integration" in the sixth column of file Ch_Calc-Sum.xls included in the CD ROM included with this report and in Data0.ymp.R0A. This designation is abbreviated to "Cc" in file DATA0_ymp_sources.xls included in the CD ROM included with this report.

[Cp_rxn](T) integration:

This algorithm uses equation (23) in Johnson and Lundeen (1994) (See Appendix G). This equation is identical to the well-known and long established van't Hoff equation, described in all textbooks on physical chemistry, except for the coefficient for the entropy term. This has been adjusted to provide a better match to the thermal properties of uncharged aqueous species. As utilized in producing Data0 files, this equation is applied to uncharged aqueous species to obtain a free energy for that species at elevated temperature. The free energies of all other species in the reaction must be obtained by running SUPCRT92 (Johnson, et al. 1992). File Helgeson.xls shows the results for the three species selected in Table 6.2-2, as well as the comparison against Data0.ymp.R0A values. For RuO4(aq) and CdSO4(aq) the comparisons lie within 5% at temperatures at or below 100° C, but differ substantially for H2CrO4(aq). A more detailed examination of the data, however, provided an explanation for this discrepancy. The direct application of equation (23) in the file Helgeson.xls calculated the enthalpy and entropy of reaction from data reported for these parameters in Data0.ymp.R0A. These data yield a free energy of reaction at 25° C (from use of the equation, $\Delta G^{o}_{r} = \Delta H^{o}_{r} - T\Delta S^{o}_{r}$, where ΔG^{o}_{r} is the free energy of reaction, ΔH^{o}_{r} is the enthalpy of reaction, and ΔS^{o}_{r} is the entropy of reaction, all under "standard" conditions) in considerable disagreement with the value calculated directly from the reported free energies of the species in the reaction. This discrepancy is calculated in file Helgeson.xls. This type of disagreement is quite common and provides an indication of the uncertainty of the data. File Helgeson.xls also shows that the values for logK(T) in Data0.ymp.R0A was obtained from the direct calculation of ΔG^{o}_{r}. To obtain comparable numbers for logK(T) at other temperatures, it is necessary to start from the same logK at 25° C. This is accomplished by adjusting the value of ΔH^{o}_{r} at 25° C to produce, from use of the equation above, the same value of ΔG^{o}_{r} as results from the direct calculation, and using that value of ΔH^{o}_{r} consistently at all other temperatures as required by equation (23). This results in matches within the 5% criterion in the temperature range, 0° C to 100° C. Back calculation of both ΔH^{o}_{r} and ΔS^{o}_{r} from logK(T) values in Data0.ymp.R0A at 25° C and 100° C resulted in matches that differ only slightly from those shown in file Helgeson.xls. Whereas less uncertainty would be desirable, H2CrO4(aq) is of very minor importance to YMP; it would constitute a major portion of dissolved chromium only at pH below 2, which is beyond the range of interest. In other words the AT concluded that the data are adequate for the intended purpose.

This extrapolation algorithm is designated "[Cp_rxn](T) integration" in the sixth column of file Ch_Calc-Sum.xls included in the CD ROM included with this report and in Data0.ymp.R0A.

This designation is abbreviated to "Cr" in file DATA0_ymp_sources.xls included in the CD ROM included with this report.

Const-Cp(T) integration; const-Cp(T), const-V(P) int.; Cp(T) integration; and Cp(T), const-V(P) integration:

These four algorithms, "const-Cp(T) integration", "const.Cp(T), const-V(P)", "Cp(T) integration", and "Cp(T), constV(P) integration", all use the Maier-Kelley equation, $Cp = a + bT + c/T^2$, where a, b, and c are the Maier-Kelley coefficients and T is the absolute temperature (Maier and Kelley, 1932). (As used in Johnson and Lundeen (1994), the sign of c has been reversed.) All four are used only for non-aqueous species.

For "const-Cp(T) integration" and "const.Cp(T), const-V(P)" only the value of a is known. These two algorithms differ only in that the aqueous partial molal volumes are known for the latter, but not the former. At temperatures from 0° C to 100° C the impact of taking pressure effects on logK(T) into account, by use of these volume data, is negligible. In the last two algorithms, "Cp(T) integration", and "Cp(T), constV(P) integration", values of b and possibly c are also known. Otherwise, they are the same as the first two.

For aqueous species extrapolated by one of these algorithms, all logK(T) values calculated with SUPCRT92 agree with those in Data0.ymp.R0A at 25 degrees C as reported in Appendix B and full details, including the output files (which automatically include all necessary data from the input files), are provided in the CD ROM identified in Appendix J in files ending in the extension ".out". Also, results for those species for which data for temperature extrapolation by Cp(T) integration are available agree with the Data0.ymp.R0A values at temperatures away from the reference temperature. (For species for which temperature corrections are made using other algorithms, however, SUPCRT92 results do not agree with those in Data0.ymp.R0A (see file Ch_Calc_Sum.xls, Table 6.2-2, and other subsections in Section 6.2.3).

These extrapolation algorithms are designated "const-Cp(T) integration", "const.Cp(T), const-V(P)", "Cp(T) integration", and "Cp(T), constV(P) integration" in the sixth column of file Ch_Calc-Sum.xls included in the CD ROM included with this report and in Data0.ymp.R0A. These designations are abbreviated to "CCp", "Ccp,Vc", "Ct" and "Ct,Vc" in file DATA0_ymp_sources.xls included in the CD ROM included with this report.

Const-H(T) integration/Hc and const-H(T), const-V(P) int/Hc,Vc:

These algorithms may be considered together, as they differ only in respect to the absence or availability of partial molal volume data. In the temperature range from 0° C to 100° C this difference has negligible impact. For these algorithms equation (16) in Johnson and Lundeen (1994) (see file ConstantHcheck.xls for the equation) was used for the species in question, together with data from SUPCRT92 (Johnson, et al. 1992) for other species in the reaction. The comparisons were in all cases satisfactory, as documented in file ConstantHcheck.xls and the CD ROM identified in Appendix J. They also agree with results from SUPCRT92, even though that code should not be used for these cases. The AT noted that the sentence in Johnson *and Lundeen* (1994) in which equation (16) appears includes the assumption that $(\partial H/\partial T)_P = 0$, in other words that $Cp = 0$ for the species in question. Effectively, in the integration of the well known thermodynamic relationship, $\Delta G_P = -\int S\,dT$, this means that S is assumed constant to give the value of the integral as $-S\Delta T$, as shown in the first term on the right in equation (16). (In these relations, G stands for Gibbs free energy, H for enthalpy, and S for entropy.) In contrast, the assumption of $Cp = 0$ is not made for other species, i.e. from SUPCRT92, in the reaction. As discussed above, this is inconsistent with conventional thermodynamic practice.

6.2.4 Qualification of Thermodynamic Data Included in Data0.ymp.R0A, but not in Data0.com.R2

This Section deals with the qualification of basic data, specifically for free energies, enthalpies, entropies, EOS parameters, and heat capacities, at 25° C, i.e. at the reference temperature and pressure. If these data are qualified, and a suitable extrapolation algorithm is used, the data at other temperatures will be qualified.

Initiation of the updates from Data0.com.R2 to Data0.ymp.R0A began during mid to late 1999. At a workshop held in Las Vegas on October 14, 1999, basic concepts of what is needed by the YMP and what constituted acceptable publicly available data sources came under detailed discussion, species by species. Decisions made at that time included the need to decrease the quantity of some categories of data in the file (owing to practical computing time considerations). In addition the need was identified to find suitable replacements for data retrieved from internal laboratory memoranda and personal computations, or from sources not generally accepted by the scientific and technical community. Substantial data needs were identified for elements not included in Data0.com.R2. As a consequence, many changes were made in Data0.com.R2 in response to an AP-3.14Q (Input Tracking No. WP-LLN-99336.R; see CRWMS M&O 2000a) data request. This included deletion of most of the data for organic species because, for most purposes, such data are not required for YMP applications. A large amount of data was incorporated from a Swedish review of lanthanide data (Spahiu and Bruno 1995).

The general thrust of the revisions leading to Data0.ymp.R0A was to provide a data file that included the required data, did not include burdensome quantities of unneeded data, but equally importantly provided data that could be adequately supported by defensible experimental studies.

The rationale for qualification of these basic data follows that specified in the Data Qualification Plan (CRWMS-M&O 2000b). Specifically, if there is no change in the basic 25° C data from Data0.com.R2 to Data0.ymp.R0A, the AT qualified the data, as indicated in file Data0_ymp_sources.xls and CD ROM identified in Appendix J in accordance with Section 2.b) of the Data Qualification Plan. The next to last column in the worksheet shows the qualification method used. Similarly, the AT qualified data taken from handbooks in accordance with Section 2.c) of the Data Qualification Plan; most of these handbooks postdate the creation of Data0.com.R2 and thereby represent updates. Data for only one species, Np2O5, were developed under the auspices of the QARD (Kaszuba and Runde 1999). These were qualified in accordance with in accordance with Section 2.d) of the Data Qualification Plan.

Many of the data have been taken from literature data, mostly published since the creation of Data0.com.R2. For the most part these actually represent updates by the same group, albeit sometimes with different scientists, which developed the original data in Data0.com.R2.

Specifically, these publications are Shock, et al. (1997a), Shock, et al. (1997b), Sassani and Shock (1998), Shock (1995), Sverjensky, et al. (1997), Shock and Koretsky (1995, and McCollom and Shock (1997). These articles are used as input to, or actually report results of parameter fittings to the modified Helgeson/Kirkham/Flowers (HKF) equation of state (Helgeson et al. 1982, Tanger and Helgeson 1988), and are suitable for input to SUPCRT92. The data from these papers are notable for having been derived from an extensive experimental data base over a wide range of temperatures. In many instances even though the reference for the data for individual species has changed, the actual data have not, as stated in the relevant papers. The EOS parameters derived from these investigations for aqueous species include a term, ω, that corresponds to a Born parameter for the species, two c parameters fitted to heat capacity data and utilizing the Born parameter, and four a parameters fitted to pressure (i.e. volume measurements) that utilize both ω and the c parameters. These parameters are reported in the data blocks in Data0.ymp.R0A. Thus, as a bare minimum there must be 7 data points; in point of fact there must be many more to obtain suitable fits. Moreover, the data, to be acceptable, must be smooth functions of pressure and temperature, except at phase transition points. Thus, it is clear that the data provided by these papers rest on a large high quality base of experimental data. For these reasons those data are qualified in accordance with Section 2.e) of the Data Qualification Plan (CRWMS M&O 2000b).

Among aqueous species this left only five references that needed examination, Vasil'ev, et al. (1974), Stipp, et al. (1993), Millero, et al. (1995), Satoh and Choppin (1992), and Zachara, et al. (1989). The AT concluded that the data taken from these references are satisfactory for use by the YMP.

For solid species fewer revisions of the type discussed were needed. Mostly new data were added from handbooks and fewer revisions of the type discussed above were needed. The situation for references resembles that for aqueous species. Journal articles from the same group as noted above or from scientists at LLNL or LANL are Viani and Bruton (1992), Chen, et al. (1999), Kaszuba and Runde (1999), Sassani and Shock (1998), and McCollom and Shock (1997). Other journal articles accepted by the AT are Stipp, et al. (1993), Bowers and Helgeson (1983), Baglan, et al. (1994), Östhols, et al. (1994), and Efimov, et al. (1989). The AT concluded that the data taken from these references are satisfactory for use by the YMP. The amount of data available for temperature extrapolations varies a great deal. For many solids heat capacity data exist over a wide temperature range. Thus, as for many aqueous species, a very large experimental data collection supports the algorithm for extrapolation that used Cp as a function of temperature.

These considerations resulted in qualification of most of the 25° C reference data. Exceptions are noted the file, Sp Check List.xls, on the CD ROM included with this report.

6.2.5 Qualification of Extrapolation Algorithms

Essentially, five different algorithms were used to produce the equilibrium constant grids in Data0,ymp.R0A:

- SUPCRT92 (Johnson et al. 1992; STN: 10058-1.0-00) calculates the variation of thermodynamic properties with temperature using the modified Helgeson/Kirkham/

Flowers (HKF) equation of state (Helgeson et al. 1982, Tanger and Helgeson 1988) for aqueous species and the Maier-Kelley expression (Maier and Kelley 1932; Helgeson et al, 1978) for solids and gases. These extrapolation algorithms are designated "Cp(T), V(P) integration" and "Cp(T) integration".

- The Criss-Cobble technique (Criss and Cobble 1964a and b) combined with the SUPCRT92 algorithms. This extrapolation algorithm is designated "Const-Cp(T) integration".

- The constant heat capacity of reaction extrapolation (Helgeson 1969). This extrapolation algorithm is designated "[Cp_rxn](T) integration".

- Constant, but non-zero heat capacity or heat capacity as a function of temperature, combined with SUPCRT 92 algorithms (equations 11 and 13 of Johnson and Lundeen, 1994). These extrapolation algorithms are designated "const-Cp(T) integration", "const.Cp(T), const-V(P)", "Cp(T) integration", and "Cp(T), constV(P) integration".

- The constant enthalpy (heat capacity equals zero) extrapolation (equation 16 of Johnson and Lundeen 1994) combined with SUPCRT92 algorithms. As noted in Section 4.2.3, this combination with SUPCRT92 is inconsistent with conventional thermodynamic practice. These extrapolation algorithms are designated "Const-H(T) integration" and "const-H(T), const-V(P) int".

SUPCRT92 (Johnson et al. 1992) is a widely used and accepted computer program qualified and under configuration management for the YMP (STN: 10058-1.0-00). Therefore, the first extrapolation method and the data produced thereby are qualified.

The second method is more problematic. The AT believes the method is qualified provided that it is applied to cases for which it has been shown to produce results in accordance with experiments. This has been done, evidently, only for rather limited data sets. In any event, if more extensive support exists, it has not been cited among the references supplied with Data0.ymp.R0A. Criss and Cobble (1964a and b) have demonstrated its usefulness and reasonable accuracy in reproducing experimental data for only four classes of ions: simple cations, simple anions and OH-, oxyanions, and acid oxyanions. Consequently, the AT has restricted the qualification of data in Data0.ymp.R0A at temperatures other than 25° C to these classes of ions. This excludes most of the data extrapolated by this technique. It does appear to the AT, however, that data exist to support the method for additional classes of data. For example, data very similar to those used by Criss and Cobble (1964a and b) are presented in Shock et al. (1997a) for a large number of hydroxide complexes. At present the known documentation to support wide use of this method has not been provided. Supplemental tests were run for types of ion not included within any of these types, namely, for CrCl2+ and CaHCO3+ for comparison against the more reliable HKF equations of state (Helgeson, et al. 1982) used by SUPCRT92. Data0.ymp.R0A includes data for these complexes as extrapolated by integrated heat capacity plus SUPCRT92 technique. Results are provided in file Criss_Cobble_checks.xls. The agreement for CaHCO3+ lies well outside the 5% criterion set in the Data Qualification Plan (CRWMS-M&O 2000b), indicating that the Criss-Cobble technique is not always reliable when applied to species types other than those investigated by Criss and

Cobble (1964a and b). Worksheet CcChanges in workbook DATA0_ymp_sources.xls (see Appendix I) lists the species affected File DATA0_sources_ymp.xls included on the CD ROM.

The constant heat capacity of reaction extrapolation (Helgeson 1969) comes from an extensive theoretical development for aqueous thermodynamics and is adjudged by the AT to be soundly based, in spite of the somewhat greater deviation from the exact match to be expected by the tests performed. Consequently, extrapolations by this technique are qualified.

Extrapolations by integrating the heat capacity have been extensively used and accepted by chemists for many years. Accordingly, extrapolations made in this way and combined with SUPCRT92 results are qualified.

In the case of the last, constant enthalpy, technique, no documentation is known to the AT that would demonstrate agreement with experimental data at elevated temperatures. To test the technique two special cases were run, for albite and for calcite, which were extrapolated using the heat capacity as a function of temperature plus SUPCRT92 method. Results are recorded in file ConstantHcheck.xls. The agreement was unsatisfactory for both albite and calcite. In accordance with these considerations no data obtained by this extrapolation method were qualified. Worksheet HcChanges in workbook DATA0_ymp_sources.xls (see Appendix I) lists the species affected File DATA0_sources_ymp.xls included on the CD ROM. The reader should not interpret this difficulty as indicating that there is any software defect in SUPCRT92. Rather, it has been applied to a case for which it is not suitable.

The constant enthalpy technique superficially resembles the van't Hoff approach. The latter approach is a generally accepted method for extrapolating logK values or Gibbs energies of reactions from 25° C to other temperatures. Examples of this method are included in workbook, ConstantHcheck.xls, on the CD ROM included in this report and discussed above and in Appendix H. The constant enthalpy calculations described by Johnson and Lundeen (1994), and embodied in SUPCRT92 do not correctly represent the van't Hoff approach. They extrapolate Gibbs energies of formation of reacting species by whatever algorithm the available data permit, including heat capacities for all species in the reaction to the extent that they exist in the data file. Finally, they calculate the reaction logK(T) values from these extrapolated Gibbs energies of formation. This does not correspond to the van't Hoff approach in which all heat capacities are taken to be zero.

Sufficient data are available within the Data0.ymp.R0 file to make van't Hoff constant enthalpy extrapolations correctly. This could be done by calculating the Gibbs energies and enthalpies of reaction at 25° C, and using these properties of reaction to find logK(T) values at other temperatures. Worksheet van't Hoff of workbook ConstantHcheck.xls gives examples of such calculations. The logK values in the Data0 file are in close agreement with the calculated values at 25° C, but at other temperatures, differences between the Data0 values and the correctly calculated values in the worksheet are too large to be acceptable. The AT does not view its charge as extending to the recalculation of values incorrectly generated for inclusion in Data0.ymp.R0. Thus, values based on the constant enthalpy extrapolation method have not been accepted, and new values calculated correctly to replace them have not been generated. The data for temperatures other than 25° C have been deleted from Data0.ymp.R0.

The AT views these limitations on qualification of extrapolated data to be in keeping with the spirit and intent established at the October workshop. Namely, the intent was to upgrade the data file to the point wherein all the data can be shown to be adequate for the intended purpose. The AT did not, however, evaluate whether all thermodynamic data that may be needed are included. The AT, also, did not flag data in Data0.ymp.R0 that appear not to be needed for YMP applications, such as for the alkali and alkaline earth metals (i.e. in metallic form), nor data for species that would be important only outside the limitations specified by the Qualification Plan (CRWMS M&O 2000b), such as salts readily soluble in water.

The user is cautioned to check on the temperature limitations for individual species. If a temperature other than 25 C is used for calculations and if equilibrium constants exist only for 25 C for a species involved in the calculation, EQ3/6 will use the 25 C data. This can result in errors. Users are advised to examine outputs carefully to determine whether such species have had a significant effect on the output.

6.2.6 Check of Data in DATA0.com.R0 against Source Documents

In view of the percentage of errors identified during the review described in preceding Sections and the additional discovery of a major error for H2O2(aq), the AT proceeded to compare the data entered for all changed or newly added species thought to be significant to YMP applications. Significance was taken to mean that an element contained in the species (aqueous, solid, or gaseous) would be needed by Waste Package Operations or Performance Assessment. Of the 86 elements included in Data0.ymp.R0, the following 46 were adjudged to be significant: Ag, Al, Am, B, Ba, C, Ca, Cd, Cl, Cr, Cs, Cu, F, Fe, Gd, H, Hf, I, In, K, Li, Mg, Mn, Mo, N, Na, Nb, Ni, Nd, Np, O, P, Pb, Pu, Ra, Rn, S, Si, Sm, Sn, Sr, Tc, Th, Ti, U, and Zr. Species that contain one of these elements and some other not in this list were not checked.

All 185 basis and auxiliary basis species were checked, regardless of which elements were included. In addition 370 other aqueous species, 273 solids, and 13 gases were checked. Of these the species in need of sufficient correction to warrant making additional runs with SUPCRT92 included only 13 aqueous, 2 solid, and no gaseous entities. In addition several minor, i.e. less than about 0.1%, discrepancies were corrected. The list of species checked together with comments is included as file Sp Check List.xls in the CD ROM accompanying the report. SUPCRT92 was run to correct the data for H2O2, formic acid, acetic acid, ethane, methane, formaldehyde, BO2-, La++, NaHSiO3(aq), CrOH++, FeO(aq), KAl(SO4)2, HfBr4, and mordenite-dehy. (The output for H2CrO4 in corr1.out should be ignored because SUPCRT92 does not incorporate the extrapolation algorithm needed. See below for correction at 25° C.)The data file for this run is schkfil5.dat, and converted into dchkfi5l.dat in the usual way. The input files are corr1.rxn and KAl(SO4)2.rxn and the output files are corr1.out and KAl(SO4)2.out. These files are included on the CD ROM provided with this report.

During this checking process a discrepancy was discovered between data for several solids that contain Ca and the reference cited. The data in Data0.ymp,R0 agree with updated values available from a widely available source of thermodynamic data for SUPCRT92, SLOP98.dat, a copy of which is included on the CD ROM included with this report. The update is explained in text at top of this file, under references 18 and 19. In order to avoid reverting to older less accurate data the AT recommends retaining the data as entered for these Ca solids and has added an explanatory note within Data0.ymp.R0 for each species involved. The references involved are Shock and Helgeson (1998) and Plummer and Busenberg (1982).

In addition to the checking discussed above data for numerous other species, especially solids were checked, even though there was no change from Data0.com.R2. As a consequence of these data checks the following species were deleted from the Data0.ymp.R0A: CaH2PO4+, Cu(NO2)2(aq), CuHPO4(aq), CuNO2+, FeHPO4(aq), FeHPO4+, HCl(aq), KHPO4-, MgH2PO4+, Zr3(OH)4(8+), Zr4(OH)8(8+), PbH2PO4+, SrH2PO4+, NaHPO4-, H2SiO4--, H4(H2SiO4)4----, H6(H2SiO4)4(--), hydrocerussite, KMgCl3, Pb(SCN)2, and zirconolite. Corrections or updates (to achieve consistency with reference sources for other species – these were not new selections by the AT) were made, by way of SUPCRT92 runs for formic acid, acetic acid, ethane, methane, formaldehyde, La++, NaHSiO3, H2O2, BO2-, CrOH++, FeO(aq), H2CrO4(aq), HfO++, and mordenite-dehy. Corrections for H2CrO4(aq), TcCO3(OH)3-, and ZrF4(g) were made for 25° C directly in workbook Sp Check List.xls, on the CD Rom included with this report. As a consequence of these changes, Data0.ymp.R0 contains data for 1160 aqueous species (including the basis and auxiliary species), 1033 solids, 95 gases, and 10 solid solutions.

6.2.7 Corrections to References and Data

In addition to the apparently erroneous reference for TcO4-, noted above in Section, The AT noted that the reference given for Ti(OH)4 needed correction. The actual authors of the article are Vasil'ev, Vorob'ev, and Khodakovskii, not Khodakovskii alone (Vasil'ev et al. 1992). This was corrected in Data0.ymp.R0. The team, also, noted that the references for heat capacity data for the gases CO2, H2, H2S, NH3, S2, and SO2 are not in the reference cited, but instead may be found in Kelley (1960). The references have been amended. The AT also noted that numerous references to molar volume data for solids and gases were to SUPCRT92 (Johnson et al. 1992); this article is primarily a description of the code and directly contains little data. The reference was changed to Helgeson et al. 1978, which is the actual source for the data. The copying error for the entropy of the aqueous ion, MnO4--, was corrected from 14.4 cal/mol/K to 15.5 cal/mol/K, as were the derived equilibrium constants for this ion and for pyrolusite (see file ManganOK.out in the CD ROM). Another copying error, for NO2(g), from the c parameter in the Maier-Kelley equation, was corrected from –0.167E+01 to –1.67E+05, and the corresponding equilibrium constants changed correspondingly (see file Gases2.out in the CD ROM; this discovery resulted in creating data files schkfil4.dat and dchkfil4.dat in the same manner as described above). The value for H2CrO4(aq) in the reference cited is given as $-181._8$ kcal/mol, and was changed to correspond in Data0.ymp.R0. The subscripting means that the "8" lies beyond the precision or accuracy of the measurement, but is included to indicate the value calculated before rounding. Other corrections are detailed in the file, Sp Check List.xls, included on the CD ROM included with this report.

7. RECOMMENDATION

Based on the Technical Assessment reported here, the qualification team recommends that the following DTN be qualified for inclusion in technical products in support of the Site Recommendation for all geochemical modeling applications on the YMP. This DTN consists of the data file Data0.ymp.R0, which has been modified from the unqualified Data0.ymp.R0A, as described in this Data Qualification Report.

This Technical Assessment resulted in the creation of DTN MO0009THRMODYN.001. This DTN is made up of the data file Data0.ymp.R0 and supporting information is qualified as a source of thermodynamic chemical data for use in geochemical and chemical calculations on the YMP. The data file is formatted for use with the qualified EQ3/6 package of codes, although the information therein is valid for use in any application where thermodynamic data related to chemical species and reactions among them are required. The data file is valid for use for chemical calculations at temperatures up to 100^0 C: extrapolations beyond that temperature may be made for specific applications at the user's discretion and with appropriate justifying documentation on a case-by-case basis. The data file is also valid only for solutions sufficiently dilute for one of the conventional, extended forms of the Debye-Hückel algorithm for activity coefficients to be applicable. In the context of this qualification report, "dilute" refers to solutions with ionic strengths of less than about 1.0 molar.

Calculations using Data0.ymp.R0A will need to be revisited to determine the impact of the changes made during the qualification process as reflected in the qualified data file Data0.ymp.R0 (DTN: MO0009THRMODYN.001). Specifically, this applies at least to geochemical modeling used in PMRs for Engineered Barrier Systems, Waste Form, Waste Package, Unsaturated Zone, and Near Field Environment, as well as for Performance Assessment.

A new file has been produced which contains the database Data0.ymp.R0, which is considered qualified pending AMOPE concurrence, as a result of this action. Data0.ymp.R0 will supersede Data0.com.R2 for all Yucca Mountain Project activities.

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APPENDIX A

DATA SOURCES, DATA MODIFIED, AND DATA ADDED DURING QUALIFICATION

APPENDIX A–DATA SOURCES, DATA MODIFIED, AND DATA ADDED DURING QUALIFICATION

Worksheets, AQ for aqueous species, MIN for solids, and GAS&LIQ, for gases and liquids in file DATA0_ymp_sources.xls, contained on the CD ROM and included as part of this report, document the sources of the data in Data0.ymp.R0A, and the corresponding sources, if any, in Data0.com.R0. These tables also document whether there was any change between Data0.com.R2 and Data0.ymp.R0A and the method by which the data were qualified.

The logK(T) data for temperatures above 100° C have all been removed from the Data0.ymp.R0A file in preparing the Data0.ymp.R0 file. In addition, all data above and below 25^{0} C have been removed for all cases where the extrapolation technique is considered to be insufficiently documented. These species are listed in worksheets labeled CcChanges and HcChanges in the file DATA0_ymp_sources.xls, contained on the CD ROM included as part of this report. See Appendix I.

A limited number of molar volumes, previously selected by persons other than those on the AT, were added to Data0.ymp.R0. These are documented in Appendix D.

APPENDIX B

DESCRIPTION AND RESULTS OF CHECK CALCULATIONS MADE USING THE QUALIFIED AND CONTROLLED SOFTWARE CODE SUPCRT92 V1.0
(STN: 10058-1.0-00)

APPENDIX B–DESCRIPTION AND RESULTS OF CHECK CALCULATIONS MADE USING THE QUALIFIED AND CONTROLLED SOFTWARE CODE SUPCRT92 V1.0 (STN: 10058-1.0-00)

The files referred to in this Appendix may be found on the CD ROM included with this report. Appendix J has a listing of all files on the CD-ROM.

INTRODUCTION

Sample check calculations were made for the species listed in file Ch_Calc_Sum.xls, contained on the CD ROM and included as part of this report. These included 6 gases (the 5 arbitrarily selected gases described in Section 6.2.2 and listed in Table 6.2-2, above, and O2(g) which is considered a basis species), 14 minerals (arbitrarily selected as described in Section 6.2.2 and listed in Table 6.2-2, above, plus albite, calcite, and pyrolusite which were added for special checks identified during the review for reasons described in the main text), 20 aqueous and auxiliary basis species (the 14 arbitrarily selected aqueous and auxiliary basis species described in Section 6.2.2 and listed in Table 6.2-2, above plus 6 additional auxiliary basis species required for the dissociation or dissolution reactions of the arbitrarily selected aqueous, auxiliary basis, mineral and gas species) and 29 basis species, including those needed for dissociation of auxiliary species. This list includes H2O and O2(g) as a gas in addition to O2(g) as a basis species.

The first column of file Ch_Calc_Sum.xls gives the name and (or) chemical formula of each species. The dissociation or dissolution reaction for each species, for basis species, is given in column 2, and in column 3 an indication is given of whether the data for the species in Data0.ymp.R0A match those in Data0.com.R0. Columns 4 - 8 have two lines for most species. One refers to the .ymp and the other to the .com data files. Column 4 designates the data file to which the following three columns refer. Column 5 gives the source of the thermodynamic data at the reference temperature and pressure. Column 6 names the algorithm used to extrapolate these data to higher or lower temperatures and pressures (see Sections 6.2.1.2 and 6.3.1.4). Column 7 gives a reference to a description of the algorithm and Column 8 provides the source of the extrapolation algorithm parameter values. Note that the forms of the references are those used in the Data0.com.R0 and Data0.ymp.R0A files themselves. These data files contain the full citations.

To construct file Ch_Calc_Sum.xls, the data blocks for each species were located in both the Data0.com.R0 and Data0.ymp.R0A files. The reactions, algorithm identities, and data sources cited, were copied from these files into file Ch_Calc_Sum.xls.

SUPCRT92 CALCULATIONS

The SUPCRT92 code and its use are described in detail by Johnson et al, 1992, and in documentation supplied with the YMP version of this code (STN: 10058-1.0-00). The calculations made here to check Data0.ymp.R0A required the following steps:

First, a text file corresponding to the SPRONSxx.dat file described in the SUPCRT92 documentation was developed. It contains thermodynamic properties of formation at reference temperatures and pressures and values for the coefficients of the algorithms used to extrapolate these properties to different temperatures and pressures for aqueous species, solids and gases listed in file Ch_Calc_Sum.xls. This file is designated schkfil1.dat. Subsequently, to complete the evaluations of selections made and to make calculations that used SUPCRT92 together with another algorithm, as described in other Appendices, additional data were added in the same manner. That subsequent file is schkfil2.dat. Both files were used in order to obviate the necessity of rerunning the original set of inputs with the later file and both may be found on the CD ROM included with this report. A third data file, schkfil3.dat, was created to make a single SUPCRT92 run for the evaluation of the impact of the erroneous entry for entropy for the species, MnO4 - -, and a fourth data file, schkfil4.dat, was similarly created for evaluating the impact of an erroneous entry for NO2(g). During the comprehensive review described in Section 6.2.6 an additional data file, schkfil5.dat was created in order to correct or check on equilibrium constants generated by use of data that were not copied correctly into Data0.ymp.R0A.

The data in schkfil1.dat, schkfil2.dat, schkfil3.dat, and schkfil4.dat were taken from the corresponding data for each species in Data0.ymp.R0A, except for the entropy for MnO4--, which was taken directly from Shock, et al. (1997a), and the third heat capacity parameter for NO2(g), which was taken directly from Kelley (1960). Correct data for entry into schfil5.dat were taken directly from the references cited in Data0.ymp.R0A. SUPCRT92 input data must be in calories. Thus, it was necessary to convert Data0.ymp.R0A data that were given in joules or kilojoules before entering it into the schkfil files. The conversion factor used was 4.184 j/cal (Lide and Frederikse 1997). The conversions of the data are documented in Appendix C.

The data in schkfil1.dat and schkfil2.dat were also checked against the original references. The ninth column of file Ch_Calc_Sum.xls gives the results of this comparison. In some cases, data were not checked against the original sources cited but against an updated publication for the same data. In particular, many of the data in Shock et al. (1997a) are identical with data previously reported (see Shock et al. (1997a), Table 1). For these, the data in schkfil1.dat and Data0.ymp.R0 were checked against Shock et al. (1997a) rather than against the original. This procedure is noted in Column 9.

After the text files schkfil1.dat,schkfil2.dat, schkfil3.dat, schkfil4.dat, and schkfil5.dat were complete, they were converted to their direct access equivalents, dchkfil1.dat, dchkfil2.dat, dchkfil3.dat, dchkfil4.dat, and dchkfil5.dat, using the CPRONS92 program included in the SUPCRT92 package (STN: 10058-1.0-00). SUPCRT92 requires the direct access file as input.

Second, a set of files (`*.rxn`) was developed that describe the reactions by which each species being checked dissociates or dissolves. The reaction files are developed within and saved from SUPCRT92 itself. To assure that the logK(T) results calculated by SUPCRT92 would be directly comparable with values in Data0.ymp.R0, the reactions entered in SUPCRT92 were those given in the second column of file Ch_Calc_Sum.xls, except for runs corr1.rxn and KAl(SO4)2.rxn. The reactions for these runs, as well as for all others, are specified in the corresponding output files.

Eleven files containing groups of reactions were developed and are included in the CD ROM identified in Appendix J (Files AQ_SP.rxn, AUX_BAS.rxn, AUX_BAS1.rxn, GASES.rxn, MINERALS.rxn, SOLID.rxn, Mangan.rxn, CRICOB.rxn, RuCl3gas.rxn, corr1.rxn, and KAl(SO4)2.rxn). SUPCRT92 was run using these files and dchkfil1.dat, dchkfil2.dat, dchkfil3.dat, dchkfil4.dat or dchkfil5.dat as input, and the results were saved as corresponding *.out files. The file, Mangan.rxn was run with both dchkfil2.dat and dchkfil3.dat, producing ManganOK.out and ManganNG.out, respectively, to check on the impact of the erroneous entry for MnO4--. Similarly, GASES.rxn was run with dchkfil1.dat and dchkfil4.dat to produce GASES.out and Gases2.out, respectively. Corr1.rxn and KAl(SO4)2.rxn were run using dchkfil5.dat.

The final step was to compare the logK(T) values from the `*.out` files with the values for corresponding reactions and temperatures in Data0.ymp.R0A. The results of this comparison are given in Column 10 of file Ch_Calc_Sum.xls, or in other Appendices, and are discussed in Section 6.2.3 of the report.

References are given in the main body of the text.

APPENDIX C

CONVERSIONS FROM JOULES TO CALORIES

APPENDIX C–CONVERSIONS FROM JOULES TO CALORIES

This file shows the calculations needed to convert data in Data0.ymp.R0A from joules or kilojoules to calories, when needed, for entry into calculations performed by SUPCRT 92. This is the same as file "joules to calories.xls" in the CD ROM included in this report. The conversion factor used was 4.184 j/cal (Lide and Frederikse 1997). Table C-1 (worksheet Aqueous) is for aqueous species and Table C-2 (worksheet Solids & Gases) for solids and gases.

Table C-1 Conversion of Joules to Calorie

Conversion file, joules to calories

Conversion factor, joules to calories: 0.23901 Reference: Lide and Frederikse 1997, p. 1-25

(all entries are per mole of species; entropies are per mole per degree K)

Species	Units	ΔG	ΔH	S	a1	a2	a3	a4	c1	c2	ω
Am+++	joules	-598698	-616700	-201	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	calories	-143092	-147395	-48.0402	N/A	N/A	N/A	N/A	N/A	N/A	N/A
TcO4-	joules	-637408	-729400	199.6	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	calories	-152344	-174331	47.70554	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Am++	joules	-376780	-354633	-1	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	calories	-90052.6	-84759.3	-0.23901	N/A	N/A	N/A	N/A	N/A	N/A	N/A
RuO4(aq)	joules	-154000	-238100	156.7	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	calories	-36806.9	-56907.3	37.4522	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Cd(NH3)4++	joules	-226100	-450200	336.4	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	calories	-54039.2	-107600	80.40153	N/A	N/A	N/A	N/A	N/A	N/A	N/A
CdSO4(aq)	joules	-822130	-985160	-53.1	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	calories	-822130	-822130	-822130	N/A	N/A	N/A	N/A	N/A	N/A	N/A
USCN+++	joules	-454113	-541800	-306.326	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	calories	-822130	-822130	-822130	N/A	N/A	N/A	N/A	N/A	N/A	N/A

Table C-2 Conversion of Joules to Calorie

Conversion file, joules to calories

Conversion factor, joules to calories | 0.23901Reference: Lide and Frederikse 1997, p. 1-25

(all entries are per mole of species; entropies are per mole per degree K)

Species	Units	DG	DH	S	a	b	c	d	Equation
Ba2Si3O8	joules	-3963000.000	-4184800.000	258.200	224.60000				$C^o_{Pr,i} = a_i + b_iT + c_iT^{-2}$
	calories	-947179.732	-1000191.205	61.711	53.681	0.000	0.000	0.000	
CaHfO3	joules	-1728424.000	-1811701.000	113.386					$C^o_{Pr,i} = a_i + b_iT + c_iT^{-2}$
	calories	-413103.250	-433006.931	27.100	0.000	0.000	0.000	0.000	
Hydrophilite	joules	-748063.000	-795800.000	104.600	76.84600	6.64900E-06	-1.28470E+08		$C^o_{Pr,i} = a_i + b_iT^2 + c_iT^{-3}$
	calories	-178791.348	-190200.765	25.000	18.367	1.58915E-06	-3.07051E+07	0.000	
Kal(SO4)2	joules	-2239790.000	-2479150.000	204.600	237.00000	7.82840E-02	-5.98840E+06		$C^o_{Pr,i} = a_i + b_iT + c_iT^{-2}$
	calories	-535322.658	-592531.071	48.901	56.644	1.87103E-02	-1.43126E+06	0.000	
Mordenite-dehy	joules	-5319200.000	-5672300.000	299.100	305.95000	3.04470E-01	-7.70457E+06	-1.60833E-04	$C^o_{Pr,i} = a_i + b_iT + c_iT^{-2} + d_iT^2$
	calories	-1271319.312	-1355712.237	71.487	73.124	7.27701E-02	-1841435.229	-3.84400E-05	
Morenosite	joules	-2461830.000	-2976330.000	378.940	364.59000				$C^o_{Pr,i} = a_i + b_iT + c_iT^{-2}$
	calories	-588391.491	-711359.943	90.569	87.139	0.000	0.000	0.000	
Pb2SiO4	joules	-1252600.000	-1363100.000	186.600					$C^o_{Pr,i} = a_i + b_iT + c_iT^{-2}$
	calories	-299378.585	-325788.719	44.598	0.000	0.000	0.000	0.000	
Pyrolusite	joules	-465138	-520030.000	53.050	57.66500	1.33830E-02	2.66880E+02	-.20526E+07	$C^o_{Pr,i} = a_i + b_iT + c_iT^{-0.5} + d_iT^{-2}$
	calories	-111170.650	-124290.153	12.679	13.782	3.19861E-03	6.37859E+01	-4.90583E+05	
Tc2O7	joules	-950284.000	-1126500.000	192.000	160.40000				$C^o_{Pr,i} = a_i + b_iT + c_iT^{-2}$
	calories	-227123.327	-269239.962	45.889	38.337	0.000	0.000	0.000	
ThS	joules	-390800.000	-395400.000	69.790					$C^o_{Pr,i} = a_i + b_iT + c_iT^{-2}$
	calories	-93403.442	-94502.868	16.680	0.000	0.000	0.000	0.000	
UO2F2	joules	-1557321.000	-1653500.000	135.560	77.28650	8.69782E-02			$C^o_{Pr,i} = a_i + b_iT + c_iT^{-2}$
	calories	-372208.652	-395195.985	32.400	18.472	0.021	0.000	0.000	

Conversion file, joules to calories

Conversion factor, joules to calories 0.23901Reference: Lide and Frederikse 1997, p. 1-25

(all entries are per mole of species; entropies are per mole per degree K)

Species	Units	DG	DH	S	a	b	c	d	Equation
NO2(g)	joules	86550.000	-1653500.000	210.761	7.03000	9.20000E-01	-1.40000E-01		$C^{o}_{Pr,i} = a_i + b_iT + c_iT^{-2}$
	calories	20685.946	-395195.985	50.373	1.680	0.220	-0.033	0.000	
RuCl3(g)	joules	16700.000	16900.000	363.700					$C^{o}_{Pr,i} = a_i + b_iT + c_iT^{-2}$
	calories	3991.396	4039.197	86.926	0.000	0.000	0.000	0.000	
TcO(g)	joules	357492.000	390000.000	244.109	31.25600				$C^{o}_{Pr,i} = a_i + b_iT + c_iT^{-2}$
	calories	85442.639	93212.237	58.343	7.470	0.000	0.000	0.000	

APPENDIX D

MOLAR VOLUME ADDED BY THE AT TO DATA0.YMP.R0

APPENDIX D–MOLAR VOLUME ADDED BY THE AT TO DATA0.YMP.R0

This Appendix includes needed molar volume data previously selected by members of Waste Package Operations, but not placed into Data0.ymp.0A. The data are as follows:

Molar volume data previously used within Waste Package Operations, but not included in Data0.ymp.R0A

Mineral	Formula	Density[1]	Molecular Weight[2]	Molar Volume, cm^3/mol
Baddeleyite	$ZrO2$	5.739	123.223	21.471
Pyrolusite	$MnO2$	5.06	86.937	17.181
Trevorite	$NiFe2O4$	5.165	234.382	45.379
Zircon	$ZrSiO4$	4.65	183.307	39.421

[1] Roberts, et al. (1974), g/cm^3

[2] Data0.ymp.R0, g/mol

APPENDIX E

EXTRAPOLATIONS WITH HEAT CAPACITY ALGORITHMS USING A COMBINATION OF SUPCRT92 AND WORKBOOK INTEGRATIONS

APPENDIX E–EXTRAPOLATIONS WITH HEAT CAPACITY ALGORITHMS USING A COMBINATION OF SUPCRT92 AND WORKBOOK INTEGRATIONS

The AT noted that, whereas in most instances the integration of heat capacity was performed for production of Data0.ymp.R0A using the standard Maier-Kelley equation, this was not always the case. In the standard case, $Cp = a + bT - c/T^2$ (as noted above in the main text, the sign of c was reversed in Data0.ymp.R0A). However, in some instances a different fit to the experimental data was used, as reported by Robie, et al (1979). For example, for hydrophilite, the equation, $Cp = a + bT^2 + c/T^3$, was used, and for pyrolusite, $Cp = a + bT + c/T^{1/2} + d/T^2$. These formulas are correctly reported in Data0.ymp.R0A. File Cp_integration.xls, contained on the CD ROM and included as part of this report, shows results of evaluating the extrapolations for these two minerals and for CaHfO3 and morenosite.

The agreement for hydrophilite between the results in the workbook, Cp_integration.xls, with data in Data0.ymp.R0A is excellent, but the direct SUPCRT92 results for hydrophilite are completely unacceptable, except at 25° C, where no extrapolations are done. For pyrolusite the agreement between the direct SUPCRT92 calculation with the Data0.ymp.R0A values lie within the specified 5%, but the workbook calculations are notably better, except at 200° C. The substantial deviation at 200° C is probably attributable to pressure effects that were not taken into account in the evaluations in this report. These results confirm that SUPCRT92, at least in its unmodified qualified form, was not always used for temperature extrapolations. (The results in the workbook, for CaHfO3 and morenosite simply show the good agreement between the dual approach, SUPCRT92 for aqueous species plus a separate Maier-Kelley integration for solids, and the straight SUPCRT92 calculation.)

A small copying error was discovered between the source document (Shock, et al. 1997a) and Data0.ymp.R0A for the entropy of MnO_4^{--}. This ion appears in the dissolution reaction used for pyrolusite. This small error has very little impact on the calculated equilibrium constants, as shown by the comparison in file Cp_integration.xls between the original and corrected values. The ion in question, MnO4--, is designated as an auxiliary basis species, which means that it may be incorporated into other reactions in the data file, as was done for pyrolusite. This was done in only two other cases, $BaMnO_4$ and MnO_2(gamma). In both of these instances equilibrium constants were calculated only at 25° C directly from free energy data. This means that this error was not propagated to other locations within the data file. To avoid any possible propagation in applications yet to be performed by the YMP the AT has changed the data in Data0.ymp.R0 to agree with the corrected equilibrium constants shown file Cp_integration.xls for both pyrolusite and MnO4--.

APPENDIX F

TEMPERATURE EXTRAPOLATIONS USING THE CRISS-COBBLE METHOD

APPENDIX F–TEMPERATURE EXTRAPOLATIONS USING THE CRISS-COBBLE METHOD

This method is described in two papers by Criss and Cobble (1964a and b). To use this technique, it is necessary to convert entropies, as conventionally reported at 25° C, to CC-entropies (Step 1). The second step makes the temperature extrapolation in accordance with the algorithm in Criss and Cobble (1964a) to one of the higher temperatures. No data are provided for extrapolating to lower temperatures. The third step converts back to conventional entropies at elevated temperature. The next step determines the average heat capacity for the ion over the relevant temperature using the algorithm in Criss and Cobble (1964b). This must be done for all species in the reaction. Finally, that result is used to estimate the free energy of the species that requires this extrapolation technique for the higher temperature. The equation for this last calculation is rather standard, but for convenience for the reader is rederived in the workbook. The algebraic sum of the other species in the reaction at the specified temperature was determined by SUPCRT92 and combined with that for the species extrapolated by the Criss-Cobble technique to obtain the free energy of reaction. The equilibrium constant was calculated from that result. The heat capacity of the reaction is calculated from the values for each individual species in the reaction. It is a simple matter to calculate the equilibrium constant from the derived free energy of reaction. The results of the SUPCRT92 calculations are reported in the file, CRICOB.out, which is included in the CD ROM together with the workbook that shows the remainder of the calculations, Criss_Cobble_checks.xls.

The AT qualified the results for those ion types examined by Criss and Cobble (1964a and b), but not for more complex types, as described in Section 6.2.3 and 6.2.5.

APPENDIX G

TEMPERATURE EXTRAPOLATIONS FOR UNCHARGED AQEUOUS SPECIES

APPENDIX G–TEMPERATURE EXTRAPOLATIONS FOR UNCHARGED AQEUOUS SPECIES

This technique utilizes equation (23) of Johnson and Lundeen (1994). This equation is reproduced in workbook Helgeson.xls, included in the CD ROM. All results matched satisfactorily with those reported in Data0.ymp.R0A.

APPENDIX H

TEMPERATURE EXTRAPOLATION USING THE CONST-H(T) INTEGRATION METHOD OF JOHNSON AND LUNDEEN (1994)

APPENDIX H–TEMPERATURE EXTRAPOLATION USING THE CONST-H(T) INTEGRATION METHOD OF JOHNSON AND LUNDEEN (L994)

These extrapolations used equation (16) of Johnson and Lundeen (1994), but did not apply it to all species in the reaction. In the view of the AT this constitutes an unacceptable error. This Appendix includes the evaluations performed and provides some evidence that, whereas in some cases the match is within the specified tolerance of 5%, in other cases it is far from satisfactory. SUPCRT92 output files used in this evaluation are MINERALS.out, SOLIDS.out, and RuCl3gas.out. These and the workbook that combines some of these results with workbook calculations, file ConstantHcheck.xls, are included on the CD ROM. Worksheet Const-H shows extrapolations according to equation (16), and worksheet van't Hoff provides a comparison between the van't Hoff extrapolation method and the corresponding values in Data0.ymp.R0A.

The accompanying workbook, rows 31 through 36 in worksheet "Const-H" (the first section in which calculations of thermodynamic properties are calculated) gives the results of applying equation (16) to individual species (all solids, except for RuCl3(g)) to obtain the free energy of the solid (or gas) at an elevated temperature. (Rows 29 and 30 show the column headings for this subsection. The pressure-volume term is ignored because of the low pressures up to 100° C.) The next section, rows 38 through 45, reports the results of SUPCRT92 calculations for the algebraic sum of free energies for all other species in the reactions, labeled as "Quasi-reactions". These two results are combined in the final section, in rows 50, 53, 56, 59, 62, and 65 to obtain the free energies of reaction, from which the logarithms of equilibrium constants are calculated. These are given in columns H through K in the same rows just above the corresponding values reported in Data0.ymp.R0A. The good agreement between these numbers for Pb2SiO4, Okenite, and RuCl3(g) shows that this is in fact the way in which the results were calculated. Unhappily, this procedure utilizes the heat capacities of all species in the reaction, except for those two solids and the one gas; such a procedure is incompatible with conventional thermodynamic practice. Albite and calcite were included because the extrapolations for these minerals were done in SUPCRT92 using the Maier-Kelley equation, which does utilize the heat capacity of the solid and is, therefore, in keeping with conventional thermodynamic practice, but can be done also using equation (16). This was performed for comparison purposes only. For albite the agreement is especially poor, and is also outside the specified limit of 5% for calcite, thus documenting the unreliability of this "const-H(T) integration" technique.

APPENDIX I

EXTRAPOLATED DATA DELETED FROM DATA0.YMP.ROA

APPENDIX I–EXTRAPOLATED DATA DELETED FROM DATA0.YMP.ROA

This Appendix provides or refers to files for the species for which data were deleted from or corrected in Data0.ymp.R0A. Worksheet CcChanges in file DATA0_ymp_sources.xls shows the species that were extrapolated using the Criss-Cobble technique that were restricted to the data at 25 C, and Worksheet HcChanges in file DATA0_ymp_sources.xls shows the corresponding set for the "const-H(T) integration" method. The file is included on the CD ROM that accompanies this report. Worksheet SP Check List.xls provides details for deletions for other reasons and for corrections.

APPENDIX J

LIST OF FILES ON THE CD ROM

APPENDIX J–LIST OF FILES ON THE CD ROM

```
AQ_SP    out        35,717  06-05-00  3:27p AQ_SP.out
AQ_SP    rxn         3,401  06-05-00  3:17p AQ_SP.rxn
AUX_BAS  out        44,231  06-05-00  2:55p AUX_BAS.out
AUX_BAS  rxn         4,464  06-05-00  2:54p AUX_BAS.rxn
AUX_BAS1 out         5,560  06-05-00  6:18p AUX_BAS1.out
AUX_BAS1 rxn           993  06-05-00  6:18p AUX_BAS1.rxn
CHANGE~1 XLS        15,872  09-11-00  1:14p Change in gamma.xls
CH_CAL~1 XLS        75,776  08-09-00 10:53a Ch_Calc_Sum.xls
CONSTA~1 XLS        34,304  09-11-00  1:39p ConstantHcheck.xls
corr1    out        59,064  09-06-00  2:36p corr1.out
corr1    rxn         3,383  09-06-00  2:34p corr1.rxn
CP_INT~1 XLS        37,888  08-17-00  5:59p Cp_integration.xls
CRICOB   out        19,059  07-10-00  4:22p CRICOB.out
CRICOB   rxn         1,801  07-10-00  4:22p CRICOB.rxn
CRISS_~1 XLS        65,536  08-17-00  6:35p Criss_Cobble_checks.xls
DATA0    COM     2,167,750  08-18-95  8:48p DATA0.COM
data0    ymp     2,649,470  09-11-00  5:23p data0.ymp
data0A   ymp     2,704,726  03-24-00  7:34p data0A.ymp
DATA0_~1 XLS       619,008  07-17-00  2:07p DATA0_ymp_sources.xls
dchkfil1 dat        32,040  06-06-00  3:25p dchkfil1.dat
dchkfil2 dat        35,910  07-11-00 11:06a dchkfil2.dat
dchkfil3 dat        35,910  07-10-00 11:27a dchkfil3.dat
dchkfil4 dat        32,040  07-13-00 11:17a dchkfil4.dat
dchkfil5 dat        43,920  09-08-00  2:19p dchkfil5.dat
files                    0  09-12-00 11:05a files
GASES    out        23,835  06-06-00  3:33p GASES.out
GASES    rxn         2,461  06-05-00  5:59p GASES.rxn
Gases2   out        23,824  07-13-00 11:19a Gases2.out
Helgeson xls        23,040  09-06-00  4:24p Helgeson.xls
HYDROL~1 XLS        23,552  08-19-00  5:45p Hydrolysis.xls
JOULES~1 XLS        25,088  09-12-00 10:04a Joules_to_calories.xls
KAL(SO~1 OUT         5,458  09-08-00  2:21p KAl(SO4)2.out
KAL(SO~1 RXN           927  09-08-00  2:16p KAl(SO4)2.rxn
Mangan   rxn         1,698  07-10-00 11:35a Mangan.rxn
ManganNG out        16,757  07-10-00 11:36a ManganNG.out
ManganOK out        16,757  07-10-00 11:35a ManganOK.out
MINERALS out        50,813  06-06-00  3:26p MINERALS.out
MINERALS rxn         4,765  06-05-00  4:31p MINERALS.rxn
RuCl3gas out         4,205  07-11-00  2:55p RuCl3gas.out
RuCl3gas rxn           795  06-01-00  5:09p RuCl3gas.rxn
schkfil1 dat        33,661  06-06-00  3:24p schkfil1.dat
schkfil2 dat        39,612  07-11-00 11:05a schkfil2.dat
schkfil3 dat        39,317  08-10-00  2:12p schkfil3.dat
schkfil4 dat        33,660  08-10-00  2:13p schkfil4.dat
schkfil5 dat        44,101  09-08-00  2:10p schkfil5.dat
slop98   dat       444,646  04-04-00  6:25p slop98.dat
SOLID    out        61,640  07-17-00  4:16p SOLID.out
Solid    rxn         5,109  07-17-00  4:14p Solid.rxn
SPCHEC~1 XLS        91,648  09-11-00  4:25p Sp Check List.xls
Volumes  xls        13,824  08-09-00 11:15a Volumes.xls
        50 file(s)      9,759,016 bytes
```