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MCRT User's Guide and Documentation

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GLOSSARY OF SYMBOLS

a_1, a_2, a_3, a_4 - equation of state coefficients for computing the standard state thermodynamic parameters for aqueous electrolytes at high temperatures and pressures; used in equations (35)-(39).

a,b,c,d - temperature/pressure-independent coefficients in heat capacity power functions [equations (2)-(3), (32)-(34)]; also used as constants in equations (17)-(18) and (20)-(23).

c_1, c_2 - heat capacity coefficients for computing extended term parameters for aqueous electrolytes; used in equations (35)-(37) and (39).

C_p° - standard heat capacity at constant pressure.

G° - standard molal Gibbs free energy.

K - equilibrium constant.

P - pressure (in bars).

P_r - reference pressure (1 bar).

R - gas constant (1.9872 cal mol^{-1} K^{-1}).

S_{abs}° - absolute entropy of an ion.

$S_{P,T}^\circ$ - standard molal entropy at subscripted pressure and temperature.

S_{std}° - standard conventional entropy of an ion.

S_e	-	internal electronic entropy.
T	-	temperature (in K).
T_r	-	reference temperature (298.15 K).
$Q_{P,T}, X_{P,T}, Y_{P,T}, Z_{P,T}$	-	Born functions at the subscripted pressure and temperature, defined by equations (40)-(43).
$\Delta C^{\circ}_{P,e}$	-	electrostatic contribution to the heat capacity change for a reaction.
$\Delta C^{\circ}_{P,n}$	-	nonelectrostatic contribution to heat capacity change for a reaction (DQUANT method).
$\Delta C^{\circ}_{P,r}$	-	standard heat capacity change for a reaction.
ΔG°_{f}	-	standard molal Gibbs free energy of formation of a given species from the elements.
$\Delta G^{\circ}_{P,T}$	-	apparent standard molal Gibbs free energy at subscripted pressure and temperature.
ΔG°_{r}	-	standard molal Gibbs free energy of reaction.
ΔH°_{f}	-	standard molal enthalpy of formation of a given species from the elements.
$\Delta H^{\circ}_{P,T}$	-	apparent standard molal enthalpy at subscripted pressure and temperature.
ΔH°_{r}	-	standard molal enthalpy of reaction.

ΔS_t° - standard molal entropy of transition.

ΔV_r° - standard molal volume of reaction.

ΔV_t° - standard molal volume of transition.

ε - dielectric constant of an electrolyte solution.

ε° - dielectric constant of water.

θ - structural parameter in equations (35)-(39).

ω_j - conventional Born coefficient of the subscripted aqueous species (or electrolyte) in equations (35)-(39).

ΔH_t° - standard molal enthalpy of transition.

ΔS_r° - standard entropy change for a reaction.

1. INTRODUCTION

MCRT is a FORTRAN computer program used to generate computer files containing thermodynamic data for chemical reactions involving solids, gases, and aqueous species. The MCRT code uses basic thermodynamic and reaction stoichiometry information stored in data and input files to produce an output file containing a grid describing the temperature dependence of equilibrium constants of mineral hydrolysis reactions and aqueous dissociation reactions. The reaction properties generated by MCRT comprise a critical portion of the thermodynamic data needed by the geochemical modeling codes in the EQ3/6 software package.* The set of files used to store the thermodynamic data for the aqueous, solid, and gaseous species and associated FORTRAN data base manipulation codes are also described in this user's manual. The data base structure and use of the data manipulation programs are described only in sufficient detail to illustrate their relationship to the MCRT code.

This user's guide is designed to acquaint a new user with the MCRT program and its associated data files, so as to facilitate the use of the code and its various options. The data base processing programs MDAP and DARP are briefly described, and several sample runs of the programs are included to illustrate the available options. In addition, the structure of the MCRT code, the coding conventions used throughout the EQ3/6 package, and the methods used in

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* The EQ3/6 software package is comprised of a family of computer codes and supporting data bases designed to calculate the equilibrium distribution of species in an aqueous solution and to model the interaction of this fluid with mineral phases, a gas phase, or another aqueous solution. Two computer programs, EQ3NR and EQ6, comprise the central elements of the package. EQ3NR performs aqueous speciation and solubility calculations (Wolery, 1979, 1983), and EQ6 models reaction paths between aqueous solutions and specified geochemical systems (Wolery, 1979). Other components of the EQ3/6 package include thermodynamic and activity coefficient data bases that support EQ3NR and EQ6 calculations, several codes and supporting data files for the construction and maintenance of the data files, and a library of FORTRAN subroutines that support the EQ3/6 codes (EQLIB).

MCRT to extrapolate thermodynamic data to elevated temperatures are described. Appendices 1-4 contain descriptions of the important variables defined in MCRT and a glossary of subroutines called by MCRT.

2. DATA BASE PREPROCESSORS

A convenient alternative to text editors is needed to manipulate the contents of the base level MDA and DATAO data bases, because their large sizes make them unwieldy to handle with most text editors. Two FORTRAN codes contained in the EQ3/6 package (MDAP and DARP) were designed to allow convenient and rapid access to the data.

Table 1 shows the content and purpose of the complete set of programs and data files in the data base preprocessing package along with a brief description of their content and purpose. Figure 1 illustrates the interrelationships of the data bases and the FORTRAN codes used to manipulate the data bases. The master data file (MDA) contains the thermodynamic properties of individual aqueous, solid, and gaseous species. A direct access version of MDA (MDAR) is created by the program MDAP to reduce the computer time needed to access data blocks. MDAP is used to search, add, and replace data blocks and reference information in the MDAR file. The program DARP, analogous to MDAP, is used to add, replace, and search the data in DATAO.

2.1 MDAP and Associated Files

MDAP is an interactive, menu-driven FORTRAN code that allows the user to search through the archival MDA data base. MDA (which is also accessed by MCRT) can be updated and individual data blocks can be retrieved using MDAP. Each of the more than 1400 species in MDA is represented by a block of 20-30 lines containing compositional and thermodynamic data. Sample aqueous species and solid phase data blocks listed in Figure 2 (a) and (b) illustrate the type of information in these data blocks. Each version of the MDA data base can appear in two different forms. The serial form of MDA is named MDAS, and

the corresponding direct-access file is named MDAR. The direct-access version is generated automatically by MDAP unless a current copy of MDAR exists in the default directory. MDAR can also be created with the serial to direct-access option in the UTILITIES menu (see Figure 3).

To begin a session using MDAP, the executable version of the code is initiated; the program responds with a few lines describing the recent modification history, the number of species in the data base, and a master menu. The user types a number corresponding to the menu selection desired. Figure 3 lists the contents of the help menu and details appropriate user responses for the options currently available in MDAP. The output files that can be generated by MDAP are listed in Table 1.

2.2 DARP and Associated Files

The DARP program operates in a manner similar to the one described above for MDAP, but DARP is structured to operate in conjunction with the DATAO data base instead of MDA. Like MDAP, the DARP code allows the user to search through a large data base (DATAO) and make additions or changes to selected data blocks. The options available for use with the DARP program are listed in Figure 4.

2.3 Data Conventions

There are a few conventions for writing chemical reactions and for general bookkeeping that must be followed when entering and retrieving data from the MDA and DATAO data bases. For each chemical element, an aqueous "basis species" must be designated. Minerals, gases, and other aqueous species are described in terms of reactions involving these basis species. The basis species are generally simple ions in geologically common oxidation states (Appendix 1 lists the current set of basis species). Basis species are also used in the input files to EQ3NR and EQ6 to describe solution compositions.

The choice of basis species is arbitrary when the data for a new component is entered into the data base. Thereafter the choice of basis species must be strictly maintained for internal bookkeeping consistency. Another group of aqueous species in the data base is designated "auxiliary basis" species. The auxiliary basis set represents aqueous species with different oxidation or protonation states than the basis species. (For example, Cu^{+} is a basis species and Cu^{++} is the corresponding auxiliary basis species. Similarly, HCO_3^- is a basis species and $CO_3^=$ is an auxiliary basis species.) One reason for maintaining both sets of strict and auxiliary basis species is that a pair of species, one from the basis set and the other from the auxiliary basis set, can be used to constrain the oxidation state of a solution in EQ3NR and EQ6. For example, Fe^{++} is the strict basis species for iron, and Fe^{+++} is an auxiliary basis species. The concentrations of these two species can be designated in conjunction with the appropriate setting of the UREDOX option to solve a model with EQ3NR where the Fe^{++}/Fe^{+++} concentration ratio is used to fix the oxidation state of the solution. The concentrations of both Fe^{++} and Fe^{+++} are given in the INPUT file, and UREDOX is specified to be Fe^{+++}. The oxygen fugacity is calculated by EQ3NR to be in equilibrium with the specified concentration ratio of Fe^{++} to Fe^{+++}.

The basis set of species also contains a few special species that are needed by EQ3NR and EQ6 but which do not fall into the categories described above. Examples of these species are liquid water and oxygen gas.

2.4 Aqueous Species Data Blocks

The MDA master data file contains species data blocks, each having approximately 20-30 lines of thermodynamic data and documentation on the sources of data. Much of the data block is comprised of information with self-explanatory labels such as "ENTERED BY:", "DATE:", and "CHEMICAL COMPOSITION". However, several data in these blocks are less self-explanatory and are described as follows:

"ION TYPE" is a flag used in MCRT to determine the appropriate method for extrapolation of thermodynamic data for aqueous species and reactions to elevated temperatures (Section 4.4.1). A value for this flag is assigned to each aqueous species based on the charge type and the chemical characteristics of the species. Values that can be assigned to ION TYPE and the designations associated with these values are:

ION TYPE Value	Designation
0	neutral complex
1	cation
2	simple anion
3	oxyanion
4	acid oxyanion

This method of grouping aqueous species was used by Criss and Cobble (1964a, 1964b) to delineate the empirical relationships between absolute ion entropies at 25°C and entropies at higher temperatures for different types of ions. The category designated as cations includes most positively charged species (such as Na^+ and UO_2^{++}); the simple anion group includes such ions as OH^-, Cl^-, and Br^-; and oxyanions include SO_4^{2-}, SeO_4^{2-}, NO_3^-, etc. Acid-oxyanions are oxyanions with an attached hydrogen ion (i.e., protonated oxyanions) such as HPO_4^- and HSO_4^-. For a species of uncertain type, refer to Criss and Cobble (1964a, 1964b) to identify the best choice for the ION TYPE setting. The ION TYPE parameter is used only to extrapolate thermodynamic data to higher temperatures for those species that have no high-temperature data in the MDA species block. The ION TYPE value chosen does not affect calculations at 25°C. If a grid of high-temperature data appears in the MDA data block, values are not extrapolated using the Criss-Cobble method, and the ION TYPE setting is not used. The Criss-Cobble method is never used for ION TYPE = 0 species (i.e., neutral aqueous species and complexes). The DQUANT method (Section 4.3.4) is used for neutral species.

The Debye-Hückel "ION SIZE" parameter is used by EQ3NR and EQ6 for activity coefficient calculations that use the B-dot method (Helgeson, 1967, 1969). The values assigned to the individual ION SIZE parameters are chosen to best reproduce experimentally determined mean molal properties (e.g., osmotic coefficients and mean molal activity coefficients), and their values depend on such things as the activity coefficient model chosen and ion-splitting conventions used. Kielland (1937) is the source for almost all of the ion sizes currently specified in the MDA data file. For many ions, the value of the ION SIZE parameter which would result in the best fit of the activity/composition behavior of an aqueous species is not known, and a value of "0.0" is entered for ION SIZE. A value of "0.0" for ION SIZE causes MCRT to resort to choosing a default value based on the charge of the species being considered. Default values that are chosen by MCRT, based on ion charge, are summarized as follows:

Charge Type	ION SIZE (in Å)
+1 or -1	4
+2 or -2	5
+3 or -3	8
>+3 or <-3	11

The thermodynamic properties contained in the species blocks include values inserted in fields labeled DELGO, DELHO, SO, SE, CP, and VO, which are defined as follows:

DELGO -- ΔG_f°, the apparent standard partial molal Gibb's free energy of formation from the elements at the reference temperature (T_r) and pressure (P_r).

DELHO -- ΔH_f°, the apparent standard partial molal enthalpy of formation from the elements at T_r and P_r.

SO -- S°, the conventional entropy at T_r and P_r.

SE -- S_e, the internal electronic entropy at T_r and P_r.

VO -- V°, the standard partial molal volume at T_r and P_r.

CP -- C_p°, the standard partial molal heat capacity at T_r and P_r.

It is critical that a value of "500.0" be entered for all of the variables for which no data are available because this value is a flag that MCRT interprets as "no data are available." If a variable field is left blank or if a zero is entered, MCRT will cause a value of zero to be used for that parameter in any subsequent thermodynamic calculations, which might yield erroneous results. The internal electronic entropy (S_e) is used in the Criss-Cobble temperature extrapolations for the thermodynamic properties of some lanthanide and rare earth species. Except for these rare earth and lanthanide species, S_e is zero.

The apparent molal properties discussed above are consistent with the standard state used by Helgeson et al. (1981), where the free energy of formation of a compound or aqueous species is defined by the equation

$$\Delta G_f^\circ = G^\circ(T, 1 \text{ bar}) - G^\circ(\text{elements}, T_r, P_r) \quad . \qquad (1)$$

This convention should not be confused with another commonly used standard state that references the thermodynamic properties to the properties of the elements at the temperature of interest (T) and 1 bar (e.g., Robie et al., 1978). All high-temperature thermodynamic data calculated assuming the latter standard state must be converted to the 25°C, 1 bar state before being entered into the EQ3/6 data base. Because differences resulting from choosing one or the other standard state cancel when considering a balanced chemical reaction, reaction properties are not affected by the choice of standard states.

The partial molal volume (V°) for aqueous species at T_r and P_r is not used currently by MCRT, but pressure corrections to the thermodynamic data base utilizing V° data are planned. The partial molal heat capacity values for aqueous species are not currently used. Both the partial molal volume and heat capacity data fields (labeled VO and CP, respectively) may be left blank.

Thermodynamic data for some species are available at temperatures above 25°C and can be entered in a temperature grid that has fields for temperature, pressure, $\Delta G^\circ_{f,T,P}$, $\Delta H^\circ_{f,T,P}$, $S^\circ_{T,P}$ and $V^\circ_{T,P}$. MCRT will use these data rather than extrapolated properties to calculate high-temperature reaction properties. An option is available in the MCRT input file to overwrite these high-temperature grids.

2.5 Solid and Gaseous Species Data Blocks

The data block format used for solid and gaseous species is slightly different from the one used for aqueous species. These differences are illustrated in a sample data block for hematite shown in Figure 2(b). Two names can be entered as labels in every data block. A mineral or gas name usually occupies one of the fields, and the corresponding chemical formula is in the other. If no mineral name exists for a solid, the chemical formula can be entered in the first field and the second field can be left blank. The solids and gases can be indexed and retrieved using either label. Currently, mineral and gas names and chemical formulae are restricted to fields less than or equal to 24 characters.

The thermodynamic properties for the solid and gas species blocks are entered in fields that are labeled DELGO, DELHO, SO, SE, and VO. These labels correspond to the definitions given in Section 2.4 on aqueous species and to a choice of standard states equivalent to those used by Helgeson et al. (1978, 1981) for solids and gases. The standard state used for solids calls for unit activity of the pure solid at any temperature and pressure, but the standard state for gases is one of unit fugacity of the hypothetical perfect gas at 1 bar and any specified temperature.

The data blocks for solids and gases can also contain heat capacity data used to determine high-temperature thermodynamic properties (Sections 4.1-4.4). The heat capacity data can be entered in the form of polynomial coefficients that correspond to one of the two optional polynomials shown in equations (2) and (3). An appropriate value for the "NCODE" variable must be supplied in the data block because it designates which heat capacity polynomial is to be used with the given coefficients. NCODE is denoted by a field labeled "EQUATION =" in the data block. The two possible settings for NCODE and their corresponding heat capacity polynomials are:

NCODE	Heat Capacity Polynomial	
0	$C_p^\circ = a + (b\times10^{-3})T + (c\times10^{5})\ T^{-2} + (d\times10^{-6})\ T^{2}$,	(2)
1	$C_p^\circ = a + (b\times10^{-3})T + (c\times10^{5})\ T^{-2} + (d\times10^{8})\ T^{-3}$,	(3)

The parameters a, b, c, and d in equations (2) and (3) are temperature- and pressure-independent coefficients for the heat capacity polynomials, and T is temperature (in K). For many cases one or more of the fit parameters (a, b, c, and d) in equation (2) or (3) are set equal to zero. If no data are available other than the heat capacity at the reference conditions, either form of the equation can be used with "a" equal to the heat capacity at the reference temperature and all the other coefficients equal to zero. If no data are available, each of the coefficients should be equal to zero.

For solids that undergo one or more phase transitions in the 0-300°C temperature range, two or more heat capacity functions can be defined. This is done by setting a variable in the data block equal to the number of phase transitions that occur and supplying the additional heat capacity polynomial coefficients. Currently, no more than four heat capacity ranges can be considered by the code for a given solid. The variable which is used to specify the number of heat capacity power functions to be evaluated is labeled

by the string "X HEAT CAPACITY RANGES", where X stands for the number of sets of polynomial coefficients entered in the data block. If X is greater than one, values for the enthalpy and entropy of each phase transition must be entered. The use of the enthalpy and entropy of transition data are discussed more fully in Section 3.

3. MCRT

The FORTRAN program MCRT (for Mineral and Compound Reaction Thermodynamics) is used to calculate thermodynamic properties of reactions involving species in the MDA data file and to extrapolate equilibrium constants for various reactions to elevated temperatures. Resulting values are placed into a master data file for reaction thermodynamics called DATAO. The derivative data file (DATA1) is obtained by processing DATAO through the EQPT code (this code was formerly named EQTL) described by Wolery (1983). DATA1 is read by EQ3NR and EQ6 as an input file and provides these codes with requisite thermodynamic and activity coefficient data. A generalized flow chart for the MCRT code is depicted in Figure 5.

The three major functions performed by the MCRT program are summarized as follows:

(1) MCRT calculates thermodynamic properties of reactions at 25°C from the species data in the MDA data base and the associated reaction in the MDA data block.

(2) High temperature (up to 300°C) thermodynamic data for reactions or for individual aqueous species, gases, and solids are calculated using one of several methods specified by the user.

(3) MCRT searches for mass and charge balance inconsistencies in reaction stoichiometries that have been specified on input files and checks for thermodynamic consistency among some of the information in the MDA data base blocks. If MCRT detects an error in these parameters, an error message is printed.

When MCRT is run to create new data for a DATAO data file (e.g., the sample MCRT input files shown in Figure 6 as examples 2 and 3), a balanced chemical reaction is read from the MDA data file for each species to be processed by MCRT. The first reactant listed in the reaction must be the name of the species for which a data block is being created. All other species in the reaction must belong to the set of basis or auxiliary basis species in the MDA data base. (See Section 2.4 for information on the basis species set. Species names that comprise the basis and auxiliary basis is given in Appendix 1.) Each species in the reaction is preceded by its stoichiometric coefficient. Negative coefficients represent reactants, and positive coefficients designate reaction products. Redox reactions are balanced using $O_2(g)$.

Each species encountered in a given reaction is located, and the corresponding data read from the data file. The reaction is checked to make sure that there is no mass or charge imbalance, and that the ION TYPE parameter has a reasonable value (Section 2.5). The thermodynamic data in the data block are then checked for internal consistency among the Gibbs free energy, enthalpy and entropy values [That is, does the relationship $\Delta G_f^\circ = \Delta H_f^\circ - T(S^\circ - S^\circ_{elements})$ hold for these values?]. The Gibbs free energy value is used if it is present; otherwise, a value of ΔG_f° is calculated from the entropy and enthalpy values. If values for ΔG_f°, ΔH_f°, and S° are present, the reported and calculated values of ΔG_f° are compared. If the value of ΔG_f° computed from ΔH_f° and S° differs from the value entered for ΔG_f° by more than 150 calories, an error message is printed to the OUTPUT file.

MCRT can alternatively be run using an input file that is written in terms of any of the species in MDA. This option is used to compare reaction data computed by MCRT using the MDA data base with data from other sources. For example, if experimentally determined values for the equilibrium constant for the reaction

$$2NpO_2(s) + 4H^+ + O_2(g) = 2NpO_2^{++} + 2H_2O \qquad (4)$$

were available, one could write an input file in terms of reaction (4). MCRT

could be used to compute values of the equilibrium constant to compare with the experimental values. The data block generated by MCRT for equation (4) cannot, however, be placed in DATAO because NpO_2^{++} is not a basis species.

An input file is used to define the MCRT task and to stipulate options to be used in the MCRT calculations. The options that can be set in the MCRT input file are listed in Table 2. These options are used to tell MCRT how to extrapolate reference temperature (25°C) data to higher temperatures, what to print, and what the maximum temperature is for the thermodynamic parameter extrapolations.

Different settings for the IOPT1 option switch allow the user to process the entire MDA data base (IOPT1=1) or a selected set of species corresponding to a particular SUBSET or KEY (IOPT1=0). Individual species can also be run. Examples of input files invoking these options are given in Figure 6, examples 1, 2, and 3.

Several options are available in MCRT for extrapolating reference temperature thermodynamic data for aqueous species to higher temperatures. These options are selected by setting the IOPT2 switch. Using the method specified by the IOPT2 switch, MCRT fits polynomials to the temperature, pressure, and Criss-Cobble ion parameter grids. The code then reads the first reaction from MDA and begins processing the data. The default setting for the IOPT2 switch (IOPT2=0) causes the following calculations to be performed:

(1) The Criss-Cobble method (Section 4.4.1) is used to extrapolate the thermodynamic properties of ions for those charged species for which entropy data have been entered into the data file or for which the entropy can be calculated from Gibbs free energy and enthalpy data. This extrapolation is carried out to 300°C.

(2) For charged species with no entropy data given or calculated, the reference condition log K value is assumed constant from 0-100°C. The species will not be used by EQ3/6 above 100°C.

(3) For uncharged aqueous species, the temperature grid values are calculated by assuming constant enthalpy of reaction. The extrapolated values are entered to 300°C. (This data is not actually used because it will later be overwritten by the results of the DQUANT method described in Section 4.3.4.)

Other methods are less commonly used to extrapolate the temperature dependence of the thermodynamic functions of aqueous species. These options are invoked by setting IOPT2 equal to any of the other available values.

MCRT calculates the thermodynamic properties of liquid water, $O_2(g)$, and many simple ionic species using the algorithms and data base of the SUPCRT program described by Helgeson and Kirkham (1976) and Helgeson et al. (1978, 1981). A modified version of SUPCRT has been incorporated into MCRT to perform these calculations. (See subroutine SUBCRT in Appendix 3.) Values generated using the Helgeson and Kirkham (1976) and Helgeson et al. (1978, 1981) equations of state are used by default; the user must specifically ask for the SUPCRT to be overwritten by setting IOPT2 equal to -2, 1, 2, or 3.

The IOPT3 switch specifies which method will be used to compute the thermodynamic properties of solids and gases. The default setting for IOPT3 (IOPT3=0) causes the following calculations to be performed:

(1) If a heat capacity or heat capacity polynomial is present in the data block, it will be used to calculate the high-temperature values using the appropriate heat capacity polynomial [i.e., equations (2) or (3) will be used].

(2) If no heat capacity polynomial parameters are present, the thermodynamic properties are calculated assuming a constant enthalpy of reaction.

(3) For solids that undergo phase transitions, calculations 1 and 2 are performed, but the following additional protocols are used to determine the enthalpy and entropy of phase transitions:

a. Establish the entropy of transition (ΔS_t°) by
   1. Using the input file value for ΔS_t° (a value of "500." is interpreted as meaning that no data are known for ΔS_t°, whereas 0. is interpreted as a legal value for ΔS_t°).
   2. Calculating ΔS_t° from the enthalpy of transition (ΔH_t°), if one exists (500. = no value, 0. = legal value).
   3. Estimating ΔS_t° from the Clapeyron slope and volume of transition (ΔV_t°) (zero is used as the default value for each variable).
   4. Setting ΔS_t° to zero (results from step #3 if either the Clapyron slope or ΔV_t° is zero).

b. Get a value for the enthalpy of transition (ΔH_t°) by computing ΔH_t° from ΔS_t°. An error message is written and the input value is ignored if the computed and input values differ.

c. Get a value for the volume of transition (ΔV_t°) by
   1. Using the input value, if a nonzero value is entered.
   2. Calculating ΔV_t° from the Clapeyron slope and ΔS_t°.
   3. Setting $\Delta V_t^\circ = 0$.

d. Set a value for the Clapeyron slope by
   1. Using the input value if both ΔS_t° and ΔV_t° are zero.
   2. Calculating a value from the volume and entropy data. An error message is written and the input value is ignored if the computed and input values differ.

IOPT3 can also be assigned values of 2 or 3 by the user. These option settings apply to the extrapolation of log K values for reactions involving minerals, but the equilibrium constants are extrapolated using the following

assumptions about the behavior of reaction properties as a function of temperature: if IOPT3 = 2, the equilibrium constant is computed according to a constant enthalpy of reaction approximation; if IOPT3 = 3, the equilibrium constant is calculated using an assumed linear dependence on temperature (i.e., $\partial \log K/\partial T$ = constant).

If a mineral species in a given reaction was involved in a previous reaction, the high-temperature data grid already exists and the processing determined by the IOPT3 setting is skipped.

The thermodynamic data for the individual species are summed according to the reaction stoichiometry and used to calculate the log K values for every reaction at each temperature. The log K grids are printed on the OUTPUT file, and the DATAO blocks are written to the DFILE file. Examples of OUTPUT and DFILE resulting from the use of the input file in example 3 of Figure 6 are given in Figures 7(a) and (b).

MCRT checks the upper temperature limit for each species involved in the reaction and limits the calculation of log K for that reaction to the lowest temperature limit found. The limit will be 100°C for reactions that involve species for which no entropy data are given or calculated, 200°C for reactions extrapolated using the DQUANT method, and 300°C for reactions that involve species for which thermodynamic data was input or has been calculated up to the maximum of 300°C. Note, however, that any data block for which log K values are tabulated at temperatures above 100°C will have those data fit to a polynomial that is used to extrapolate the log K values to 300°C. The user might want to check the log K values used at temperatures above 200°C by selecting the appropriate print options in EQ3NR or EQ6.

4. METHODS OF EXTRAPOLATION OF THERMODYNAMIC DATA TO ELEVATED TEMPERATURES

4.1 Introduction

High-temperature thermodynamic data for aqueous and solid species important in geochemical calculations commonly are not available. Several methods have been developed, however, that can be used to extrapolate 25°C data to temperatures up to 300°C. Some of these methods have been incorporated into the MCRT program to allow calculation of thermodynamic properties of aqueous and solid species at elevated temperatures if such data are not available from experimental determinations. Some of these techniques (e.g., the method of Criss and Cobble, heat capacity integration, and the SUPCRT algorithm) extrapolate the properties of individual species. Others (DQUANT and constant enthalpy of reaction) are used to extrapolate overall reaction properties. The thermodynamic basis for extrapolating data to high temperatures is presented in Section 4.2, followed by a brief discussion of the methods used in the MCRT program (Section 4.3).

4.2 Thermodynamic Framework

The change in the Gibbs free energy of a reaction as a function of temperature (at constant pressure) is given by

$$\left(\frac{\partial \Delta G_r^\circ}{\partial T}\right)_P = -\Delta S_r^\circ \quad . \tag{5}$$

By combining equation (5) with the relationships

$$\Delta G_r^\circ = \Delta H_r^\circ - T\Delta S_r^\circ \tag{6}$$

and

$$\Delta G_r^\circ = -RT \ln K \quad , \tag{7}$$

the van't Hoff expression for the change in the equilibrium constant as a function of temperature can be derived:

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta H_r^\circ}{RT^2} \tag{8}$$

If it is assumed that ΔH_r° does not vary with temperature, equation (8) can be rewritten as

$$\int_{T_r}^{T} d \ln K = \frac{\Delta H_r^\circ}{R} \int_{T_r}^{T} \frac{1}{T^2}\, dT \tag{9}$$

and integrated to give

$$\ln \frac{K_T}{K_{T_r}} = -\frac{\Delta H_r^\circ}{R}\left(\frac{1}{T} - \frac{1}{T_r}\right) \tag{10}$$

where K_T and K_{T_r} are the equilibrium constants at the temperature of interest and the reference temperature, respectively.

A more rigorous set of equations for calculating high temperature reaction properties data does not assume a constant value of ΔH_r° and can be obtained by expressing the enthalpy and entropy of reaction in terms of the temperature dependance of the heat capacity change for the reaction where

$$\Delta H_{r,T}^\circ = \Delta H_{r,T_r}^\circ + \int_{T_r}^{T} \Delta C_{p,r}\, dT \tag{11}$$

and

$$\Delta S^{\circ}_{r,T} = \Delta S^{\circ}_{r,T_r} + \int_{T_r}^{T} \Delta C_{p,r}\, d \ln T \quad . \tag{12}$$

By substituting equations (11) and (12) into equation (7), the following relationship is obtained for calculating the equilibrium constant at elevated temperature:

$$\ln K_T = \ln K_{T_r} - \frac{\Delta H^{\circ}_{r,T_r}}{R}\left(\frac{1}{T} - \frac{1}{T_r}\right) - \frac{1}{RT}\int_{T_r}^{T} \Delta C_{p,r}\, dT + \frac{1}{R}\int_{T_r}^{T} \Delta C_{p,r}\, d \ln T \quad , \tag{13}$$

where $\ln K_{T_r}$ is the log of the equilibrium constant for the reaction at the reference conditions, $\Delta H^{\circ}_{r,T_r}$ is the standard enthalpy of the reaction at 25°C, and $\Delta C_{p,r}$ is the heat capacity change for the reaction that is a function of temperature. Equation (13) is a rigorous expression for the value of the equilibrium constant for a reaction at elevated temperatures as a function of K_{T_r}, $\Delta H^{\circ}_{T_r}$, and the heat capacity change for the reaction as a function of temperature.

4.3 Methods Used for Temperature Extrapolation of Reaction Properties

In many cases the heat capacity change for a reaction is not known as a function of temperature, and approximations are generally used to estimate the values of the integrals of the last two terms in equation (13). These are described in the following sections in increasing order of complexity as the constant enthalpy, constant slope, constant heat capacity, and the DQUANT methods.

4.3.1 Constant Enthalpy

The heat capacity change for a reaction is assumed to be zero in the constant enthalpy method; therefore, the last two terms of equation (13) disappear. This is equivalent to saying that ΔH_r° does not vary as a function of temperature. The truncated form of equation (13), which results from setting the last two terms equal to zero, is identical to the van't Hoff equation [i.e., equation (10)]. The equilibrium constant for a reaction at elevated temperature is calculated by evaluating the first two terms on the right side of equation (13). This method is commonly used to extrapolate 25°C data up to about 80°C but is seldom accurate much above that temperature (Krauskopf, 1967).

4.3.2 Constant Slope

As with the constant enthalpy method, the heat capacity change for a reaction is assumed to be zero, so the last two terms of equation (13) drop out. It is further assumed that the right side of equation (8) remains constant (at the 25°C value) as a function of temperature. This assumption requires that the change of log K as a function of temperature be approximately linear and that the linear slope of the temperature dependence is given by the term $\Delta H^\circ_{r,T_r}/RT_r^2$. Thus the logarithm of the equilibrium constant at T is given by

$$\ln K_T = \ln K_{T_r} + \frac{\Delta H^\circ_{r,T_r}}{RT_r^2}(T - T_r) \quad . \tag{14}$$

The constant slope method can also be used to interpolate a value of log K between log K values known at two different temperatures. As with the constant enthalpy method, the constant slope method should be used only if requisite information is unavailable for the more accurate methods described in Sections 4.3.3 and 4.3.4.

4.3.3 Constant Heat Capacity

In many cases, the temperature dependence of the heat capacities of aqueous species is not known. The absence of heat capacity data for these aqueous species makes exact evaluation of high-temperature reaction properties (i.e., log K_T) for reactions involving these species impossible. As a first approximation, however, it can be assumed that $\Delta C^{\circ}_{p,r}$ is independent of temperature, and the 25°C value for $\Delta C^{\circ}_{p,r}$ can be used to calculate higher temperature equilibrium constant values. This contention is supported by recent work which has shown that the constant heat capacity assumption is valid for some types of reactions and can be used to accurately extrapolate log K values to temperatures as high as 300-350°C (Murray and Cobble, 1981; Jackson and Helgeson, 1985). Murray and co-workers found that, for hydrolysis reactions written with an identical number of like charges on each side of the reaction, a constant enthalpy of reaction was observed for several reactions for which high temperature thermodynamic data were available. For example, the reaction

$$H_2S + OH^- = HS^- + H_2O \qquad (15)$$

has identical like charges on each side. Within experimental error, agreement was obtained by using a constant 25°C value for $\Delta C^{\circ}_{p,r}$ for reaction (15) and calculating log K values for the reaction up to 300°C using equation (13). Only at the highest experimental value (276°C) was there a significant difference between experimental and predicted values. If, on the other hand, the reaction is written as

$$H_2S = H^+ + HS^- \quad , \qquad (16)$$

the temperature dependence of the equilibrium constant is much more complex, and log K_T for reaction (16) cannot be predicted accurately using a constant $\Delta C^{\circ}_{p,r}$ method. [Note that reaction (16) does <u>not</u> have the same number of like charges on each side of the reaction.] Hydrolysis reactions in the data base are being rewritten where possible to take advantage of the

principle of balance of identical like charge so that the constant heat capacity method can be used to more accurately perform the temperature extrapolations.

4.3.4 DQUANT

The DQUANT method for predicting high-temperature thermodynamic properties of reactions was proposed by Helgeson (1967, 1969) and originated with a computer program of the same name written by Helgeson and co-workers. The entropy of reaction is separated into two parts, a nonelectrostatic part and an electrostatic part. A general form of the Born-Bjerrum equation is used to evaluate the electrostatic contribution to the free energy of a dissociation reaction. This relationship can be written as (Helgeson, 1967)

$$\Delta G^{\circ}_{r,T} = \hat{a} + \frac{\hat{b}}{\varepsilon^{\circ}} \quad , \tag{17}$$

where ε° is the dielectric constant of pure water at the temperature of interest, $\hat{b}$ is the slope parameter, and $\hat{a}$ is the integration constant for $-\int \Delta S^{\circ}_{e,T} dT$. At any temperature, the electrostatic contribution to the entropy of a reaction can be expressed as a function of the electrostatic contribution to the entropy of reaction at 25°C and the dielectric constant of water. The value of the electrostatic contribution to the total entropy of reaction at 25°C must be determined by curve fitting.

The nonelectrostatic contribution to the entropy of reaction takes into account the covalency of the interaction of the molecules and therefore is more difficult to predict theoretically. The DQUANT method uses a polynomial of the form

$$\Delta C_{p,r} = a + bT + cT^2 \tag{18}$$

to fit the heat capacity data over the temperature range of interest, if such

data are available. The polynomial fit constants (a,b, and c) in equation (18) are temperature- and pressure-independent constants characteristic of a given reaction. The nonelectrostatic contribution to the entropy can then be expressed as a function of the nonelectrostatic contribution at 25°C and the parameters a, b, and c. The terms for the electrostatic and nonelectrostatic contributions are then summed and used to derive an expression for the log K at a given temperature (equation (18) in Helgeson, 1967). Helgeson's (1967) equation for log K is a function only of the reaction properties at 25°C (enthalpy and entropy) and the three fit parameters. In practice, high-temperature equilibrium constants for aqueous reactions are not usually known accurately enough to use more than two of the three fit parameters in equation (18), so c is commonly set equal to zero.

If no high-temperature data are available for an aqueous reaction, the reaction properties can be predicted assuming b and c in equation (18) are approximately equal to zero, which is equivalent to assuming that the nonelectrostatic contribution to the entropy is independent of temperature. The temperature effect on the electrostatic contribution, however, is still considered. Because reactions in aqueous solution at high temperatures are strongly dominated by the electrostatic term (Cobble et al., 1981), this assumption commonly provides a reasonably good approximation to the temperature dependence of equilibrium constants. This method is equivalent to assuming that the total heat capacity of reaction is proportional to the electrostatic heat capacity of reaction or that

$$\frac{\Delta C^{\circ}_{p,r}}{\Delta C^{\circ}_{p,e}} = n \quad , \tag{19}$$

where n is a constant, $\Delta C^{\circ}_{p,r}$ is the total heat capacity change for the reaction, and $\Delta C^{\circ}_{p,e}$ is the electrostatic contribution to the total heat capacity change for the reaction. This method is better than assuming constant heat capacity for a reaction because the temperature dependence of the electrostatic contribution to the heat capacity term is included in the calculation.

The resulting equation used to make the DQUANT extrapolation (Helgeson, 1967) is

$$\ln K_T = \frac{\Delta S^{\circ}_{r,T_r}}{RT}\left[T_r - \frac{\theta}{\omega}\left(1 - e^{\{e^{(\hat{b} + \hat{a}T)} - c + (T - T_r)/\theta\}}\right)\right] - \frac{\Delta H^{\circ}_{r,T_r}}{RT} \quad (20)$$

where $\hat{a}$ and $\hat{b}$ are from equation (17), θ is a fixed constant (219.0) determined from an expression for the dielectric constant of pure water as a function of temperature, $\Delta S^{\circ}_{r,T_r}$ is the entropy change of the reaction at 25°C, $\Delta H^{\circ}_{r,T_r}$ is the enthalpy change of the reaction at 25°C, and ω and c are constants (Helgeson, 1967, 1969) given by

$$\omega = 1 + ac\theta = 1.00322 \quad (21)$$

and

$$c = e^{(\hat{b} + \hat{a}T_r)} = 7.84\text{x}10^{-4} \quad . \quad (22)$$

Because the electrostatic and nonelectrostatic contributions to the entropy at 25°C always appear in summation, it is not necessary to calculate the two terms separately. Therefore, equation (20) is a function only of the total entropy and enthalpy of reaction at 25°C and of the dielectric constant of pure water.

4.4 Methods Used for Temperature Extrapolation of Thermodynamic Properties of Individual Species

The methods described in Section 4.3 pertain to calculating thermodynamic properties for reactions, but MCRT can also be used to compute $\Delta G^{\circ}_{f,T}$ and other thermodynamic values for individual species from 25°C data contained in the MDA data base. The three methods used in MCRT to describe the temperature dependence of thermodynamic values of individual species are outlined in Sections 4.4.1 through 4.4.3.

4.4.1 Criss and Cobble

The method of Criss and Cobble (1964a, 1964b) can be used to calculate the Gibbs free energies of formation of ionic species at elevated temperatures from their entropies and free energies of formation at 25°C. The foundation of this method is the entropy correspondence principle. This empirical relationship was first described by Criss and Cobble and states that the entropies of similar types of ions at two different temperatures can be related to each other in a simple linear fashion. The linear relationship between the entropy at an elevated temperature (S°_{T}) and the reference values ($S^{\circ}_{T_r}$) can be expressed as

$$S^{\circ}_{T} = a + b\, S^{\circ}_{T_r} \quad . \tag{23}$$

The constants (a and b) in equation (23) can be determined from available high-temperature data for groups of ions of a given type. The unknown entropy of an ion at some elevated temperature can then be calculated using its entropy value at 25°C. Based on available high-temperature data for ionic species, ions are conveniently classified into four types: simple cations, simple anions and OH^-, oxy-anions, and acid oxy-anions. Note that most simple oxy-cations (e.g., UO_2^{2+} and PuO_2^{+}) were observed to behave similarly to simple cations. Values of a and b in equation (23) for various ion types are given in Criss and Cobble (Table III in 1964a) for temperatures up to 200°C. The same data are given in Table IV in Criss and Cobble (1964b) for temperatures from 200-300°C.

It was observed that the correspondence principle was valid (i.e., the entropies fell on a straight line) only if a particular value for the entropy of H^+ was used, a value determined through regression of the entropy data set. This so called "absolute entropy" for the hydrogen ion differs from the common standard state convention for aqueous species that specifies $S^{\circ}_{H^+} = 0$. The absolute ionic entropy for the hydrogen ion is used when the Criss-Cobble

method is used to calculate high-temperature entropies. Standard entropies are converted to absolute entropies using the relationship

$$S^{\circ}_{abs} = S^{\circ}_{std} + ZS^{\circ}_{H^+} \quad , \tag{24}$$

where Z denotes the charge on the ion.

Values for high-temperature entropies are then used to calculate the averaged heat capacity function over the temperature range of interest using the relationship

$$\Delta C^{\circ}_{P,av} = (S^{\circ}_{T} - S^{\circ}_{T_r}) \; / \; \ln (T/T_r) \quad . \tag{25}$$

Finally, the free energy of formation of the ion at some elevated temperature is calculated from its free energy and entropy at 25°C and the averaged heat capacity (Criss and Cobble, 1964b):

$$\Delta G^{\circ}_{f} = \Delta G^{\circ}_{f,T_r} + \Delta C_{P,av} (T - T_r) - \Delta S^{\circ}_{T_r} (T - T_r) - T\Delta C_{P,av} \ln(T/T_r) \quad . \tag{26}$$

Note that in equation (26), $\Delta C^{\circ}_{P,av}$ values are calculated using equation (25) and entropy data for the elements involved in the reaction.

4.4.2 Heat Capacity Integration

For many of the solid and gaseous species in the EQ3/6 data base, heat capacity information is available at elevated temperatures. This data is expressed as a polynomial in the form of either equation (2) or (3), which are variations of the Maier-Kelley equation (Maier and Kelley, 1932). The temperature independent coefficients (a, b, c, and d) are obtained by fitting a polynomial of this form to the high-temperature heat capacity data. The free energy, enthalpy, and entropy of formation of the mineral or gas at any

temperature is computed by integrating the heat capacity polynomial in conjunction with equations (29), (30), and (31).

4.4.3 SUPCRT Equations of State

Thermodynamic properties for most of the common aluminosilicate minerals; several carbonate, oxide, sulfate and sulfide minerals; liquid H_2O; many of the aqueous basis species; and several gases in the EQ3/6 data base are calculated using the SUPCRT computer code in conjunction with its associated data base. The calculational method used by this code is based on equations of state proposed by Helgeson and Kirkham (1974) for liquid water and those by Helgeson and Kirkham (1976) and Helgeson et al. (1978, 1981) for the minerals, gases, and aqueous species. The conventions and equations used in these computations are discussed briefly as follows. The thermodynamic data base that supports these calculations is based on the data contained in Helgeson et al. (1978) and Helgeson (1982, 1985).

The standard state for minerals and liquid H_2O adopted for use in the SUPCRT code and data base specifies unit activity of the pure solid or liquid at any temperature and pressure, and the standard state for gases requires unit fugacity of the hypothetical perfect gas at 1 bar and any specified temperature. The standard state for aqueous species corresponds to unit activity of the species in a hypothetical one molal solution referenced to infinite dilution at any pressure and temperature. Activity coefficients of aqueous species approach unity at all temperatures and pressures as the activity of the solvent (relative to the liquid standard state) approaches unity.

The Gibbs free energies and enthalpies computed by SUPCRT for a given pressure (P) and temperature (T) are apparent standard molal Gibbs free energies ($\Delta G^{\circ}_{P,T}$) and enthalpies ($\Delta H^{\circ}_{P,T}$) of formation defined by Benson

(1968) and Helgeson and Kirkham (1974) as

$$\Delta G^{\circ}_{P,T} \equiv \Delta G^{\circ}_{f,P_r,T_r} + (G^{\circ}_{P,T} - G^{\circ}_{P_r,T_r}) \tag{27}$$

and

$$\Delta H^{\circ}_{P,T} \equiv \Delta H^{\circ}_{f,P_r,T_r} + (H^{\circ}_{P,T} - H^{\circ}_{P_r,T_r}) \quad , \tag{28}$$

where $\Delta G^{\circ}_{f,P_r,T_r}$ and $\Delta H^{\circ}_{f,P_r,T_r}$ represent the standard molal Gibbs free energy and enthalpy of formation of a given species from the elements at a reference pressure (P_r) and temperature (T_r) of 1 bar and 298.15 K. The parenthetical terms in equations (27) and (28) correspond to the difference in the values of the standard molal Gibbs free energy and enthalpy of the species at the pressure and temperature of interest and those at P_r and T_r. All thermodynamic properties of aqueous species correspond to conventional properties consistent with assigning a value of zero to the corresponding property of H^+.

The parenthetical terms in equations (27) and (28) can be expressed as

$$G^{\circ}_{P,T} - G^{\circ}_{P_r,T_r} = -S^{\circ}_{P_r,T_r}(T-T_r) + \int_{T_r}^{T} C^{\circ}_{P_r}\, dT - T\int_{T_r}^{T} C^{\circ}_{P_r}\, d \ln T + \int_{P_r}^{P} V^{\circ}_{T}\, dP \tag{29}$$

and

$$H^{\circ}_{P,T} - H^{\circ}_{P_r,T_r} = \int_{T_r}^{T} C^{\circ}_{P_r}\, dT + \int_{P_r}^{P} (V^{\circ} - T(\frac{\partial V^{\circ}}{\partial T})_P)_T\, dP \quad , \tag{30}$$

where T refers to temperature (in K); P stands for pressure (in bars); and $S^{\circ}_{P_r,T_r}$, $C^{\circ}_{P_r}$, and V°_{T} represent the standard molal entropy, heat capacity, and volume of the species at the subscripted pressure and/or temperature. The

corresponding expression for the standard molal entropy of the species at a given pressure and temperature ($S^{\circ}_{P,T}$) is given by

$$S^{\circ}_{P,T} - S^{\circ}_{P_r,T_r} = \int_{T_r}^{T} C^{\circ}_{P_r} \, d \ln T - \int_{P_r}^{P} \left(\left(\frac{\partial V^{\circ}}{\partial T}\right)_P\right)_T dP \quad . \tag{31}$$

Standard molal heat capacities of minerals at a pressure of one bar and for temperatures greater than or equal to 298.15 K can be represented by the Maier-Kelley (1932) power function, which can be written as

$$C^{\circ}_{P_r} = a + bT - cT^{-2} \tag{32}$$

and integrated to yield

$$\int_{T_r}^{T} C^{\circ}_{P_r} \, dT = a(T-T_r) + \frac{b(T^2-T_r^2)}{2} + c\left(\frac{1}{T} - \frac{1}{T_r}\right) \tag{33}$$

and

$$\int_{T_r}^{T} C^{\circ}_{P_r} \, d \ln T = a \ln\left(\frac{T}{T_r}\right) + b(T-T_r) + \frac{c}{2}\left(\frac{1}{T^2} - \frac{1}{T_r^2}\right) , \tag{34}$$

where a, b, and c stand for temperature- and pressure-independent coefficients characteristic of a given mineral. The $(\partial V^{\circ}/\partial P)_r$ and $(\partial V^{\circ}/\partial T)_P$ terms in equations (30) and (31) for minerals can be regarded as zero without introducing significant errors in the calculated values of the thermodynamic properties of minerals over the ranges of pressure and temperature considered in the EQ3/6 data base (Helgeson et al., 1978).

Equations representing $G^{\circ}_{P,T} - G^{\circ}_{P_r,T_r}$; $H^{\circ}_{P,T} - H^{\circ}_{P_r,T_r}$; $S^{\circ}_{P,T} - S^{\circ}_{P_r,T}$; V°; and C°_P for aqueous species can be written (Helgeson et al., 1981) as

$$G^{\circ}_{P,T} - G^{\circ}_{P_r,T_r} = - S^{\circ}_{P_r,T_r}(T-T_r) - c_1\Big(T \ln (T/T_r) \tag{35}$$

$$- T + T_r\Big) + c_2\left(T-T_r-(T-\theta) \ln \left(\frac{T-\theta}{T_r-\theta}\right)\right)$$

$$+ \frac{2(a_1(T-\theta)+a_3T)(P-P_r)+(a_2(T-\theta)+a_4T)(P^2-P_r^2)}{2(T-\theta)}$$

$$- \omega(Z_{P,T}-Z_{P_r,T_r}-Y_{P_r,T}(T-T_r)),$$

$$H^{\circ}_{P,T} - H^{\circ}_{P_r,T_r} = (c_1+c_2)(T-T_r) + c_2\theta \ln\left(\frac{T-\theta}{T_r-\theta}\right) + a_1(P-P_r) + \frac{a_2}{2}(P^2-P_r^2) \tag{36}$$

$$+ \frac{2a_3T(P-P_r)+a_4T(P^2-P_r^2)}{2(T-\theta)} + \frac{\theta(2a_3T(P-P_r)+a_4T(P^2-P^2))}{2(T-\theta)^2}$$

$$+ \omega(TY_{P,T} - T_rY_{P_r,T_r}-Z_{P,T}+Z_{P_r,T_r}),$$

$$S^{\circ}_{P,T} - S^{\circ}_{P_r,T_r} = c_1 \ln\left(\frac{T}{T_r}\right) + c_2 \ln\left(\frac{T-\theta}{T_r-\theta}\right) + \frac{\theta(2a_3(P-P_r)+a_4(P^2-P_r^2))}{2(T-\theta)^2} \tag{37}$$

$$+ \omega(Y_{P,T}-Y_{P_r,T_r}),$$

$$V^{\circ} = a_1 + a_2P + (a_3T + a_4PT)/(T-\theta) + \omega Q \quad . \tag{38}$$

and

$$C_p^\circ = c_1 + \left(\frac{c_2 T}{T-\theta}\right) - \frac{\theta T(2a_3(P-P_r)+a_4(P^2-P_r^2))}{(T-\theta)^3} + \omega T X_{P,T}, \tag{39}$$

where a_1, a_2, a_3, a_4, c_1, c_2, θ, and ω correspond to temperature- and pressure-independent coefficients characteristic of a given aqueous species. The Born functions ($Q_{P,T}$, $X_{P,T}$, $Y_{P,T}$, and $Z_{P,T}$) are defined by

$$Q_{P,T} \equiv \frac{1}{\varepsilon_{P,T}}\left(\frac{\partial \ln\varepsilon}{\partial P}\right)_T , \tag{40}$$

$$X_{P,T} \equiv \frac{1}{\varepsilon_{P,T}}\left(\frac{\partial^2 \ln\varepsilon}{\partial T^2}\right)_p - \left(\frac{\partial \ln\varepsilon}{\partial T}\right)_p^2 , \tag{41}$$

$$Y_{P,T} \equiv \frac{1}{\varepsilon_{P,T}}\left(\frac{\partial \ln\varepsilon}{\partial T}\right)_p , \tag{42}$$

and

$$Z_{P,T} \equiv -\frac{1}{\varepsilon_{P,T}} , \tag{43}$$

where $\varepsilon_{P,T}$ represents the dielectric constant of pure water at the subscripted pressure and temperature.

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Table 1. List of data files and FORTRAN programs in the EQ3/6 data base preprocessing package.

MCRT - FORTRAN 77 code that calculates the thermodynamic properties of reactions between species present in MDAR, and extrapolates them to elevated temperatures. (Manipulation and Creation of Reaction Thermodynamics).

MDAP - FORTRAN 77 code used in conjunction with the MDA data base to interactively search, add, replace, and print data blocks and references (Master Data Analysis Program). MDAP can be used to output the following files:

File		Contents
BMDBF	-	Debugging information for random access file builder.
DADESC	-	Direct access file description.
HELPMN	-	Listing of MDAP help menus.
MDADR	-	Add/replace instructions.
MDAHDR	-	Header describing MDAR file structure.
MDADIRC	-	Complete directory of MDAR file.
MDADIRS	-	Directory summary of MDAR file.
MDAREF	-	Reference listing.
MDASPC	-	File containing retrieved species blocks.
MDRFIL	-	File containing species the user attempted to add which already existed.
MDCOM	-	Comments from MDAS file (includes format information).
MDELE	-	Listing of elements block.
MDOUT	-	Details of MDAR content.
MDKEY	-	Tally of key names in data blocks.
MDSUB	-	Tally of subset names in data blocks.
MDPFIL	-	Result of pattern search in reference blocks.
MDPSPC	-	Result of pattern search in species blocks.

REFERROR - File containing references the user attempted to add which already existed.

BDAR - FORTRAN 77 code used to convert DATAO (serial format) to direct access format (Build DATAO Random access file). Note: work is planned to incorporate this code into DARP as a menu option under a utility routines menu.

BDAS - FORTRAN 77 code to generate serial file DATAO from the direct access version DAOR.

DAOR - Direct access file of DATAO.

DARP - FORTRAN 77 code that allows user to add, replace, and print data blocks and references from the DATAO data file. DARP can produce the following files:

- DAOH - Header file describing file structure and format characteristics of the DAOR file.
- DAOUT - Detailed contents of DAOR.
- DAREF - Reference listing.
- DASPC - Add file containing items to be added to MDAR.
- DRDB - Debugging information from BDAR.
- DROUT - Output file from BDAR listing each reaction processed.
- DSOUT - Output file from BDAS listing each reaction processed.

DATAO - Thermodynamic data file in serial format containing data blocks to be used with DARP and EQPT.

DFILE - Output file from MCRT containing species blocks in a format for including them in DATAO. DFILE is set up in replace file format and can be used by DARP to update DATAO species blocks.

EQPT - FORTRAN 77 code that converts a DATA0 file into a DATA1 file that is read by EQ3NR and EQ6. EQPT previously produced DATA2 and DATA3 files in addition to DATA1, but they are no longer used by EQ6.

MDAR - MDA direct access format file containing data blocks for all aqueous, solid, and gaseous species (Master data Direct Access file).

MDAS - MDA serial format file containing data blocks for all aqueous, solid, and gaseous species (Master DAta Serial file).

OUTPUT - Output file from MCRT containing a detailed description of the thermodynamic data for each species considered in all the reactions processed by MCRT, a listing of all extrapolated thermodynamic data and the method of extrapolation, etc.

Table 2. Summary of MCRT input parameters.

UTITL1, UTITL2	Two lines of text for optional title.
IOPT1	Data Base control switch. = 0 Run only selected species sets and/or individual reactions listed below. = 1 Run entire MCRT master data base.
IOPT2	Control switch for aqueous species. = -2 Criss-Cobble method, will overwrite a SUPCRT grid input from MDAR if there is one [but will not for H^+, H_2O, and $O_2(g)$]. = -1 Criss-Cobble method, will not overwrite a SUPCRT grid if one exists. = 0 like IOPT2 = -1 if the first species in the reaction is electrically charged, otherwise like IOPT2 = 1 (default value). = 1 DQUANT method is used to extrapolate reaction properties to higher temperatures. = 2 constant enthalpy method is used to extrapolate reaction properties to higher temperatures. = 3 constant slope (d log K/d T) method is used to extrapolate reaction properties to higher temperatures.
IOPT3	Control switch for solids and gases. = 0 heat capacity integration. = 1 constant enthalpy method (reaction). = 2 constant slope (d log K/d T) method (reaction).

IOPT4 — Option switch to override built-in temperature extrapolation limits, if any.

- = 0 upper limits are in force (e.g., 200°C for DQUANT, constant enthalpy, and constant slope methods).
- = 1 upper limits are ignored.

IOPT5-8 — Option switches, not currently used.

IOPR1 — Option switch to print individual species data.

- = -2 no echo of base point data or data grid.
- = -1 echo base point data only.
- = 0 echo base point data and print the thermodynamic functions on the temperature-pressure grid.
- = 1 does the above and prints out information concerning the grid structure and the values of associated constants.

IOPR2 — Option switch to print individual species data grids if these are retrieved from storage arrays. This print is made only if IOPR1 .ge. 0, which implies that the grid was printed for a previous reaction.

- = 0 the grid is not printed.
- = 1 prints the projected data.

IOPR3 — Option switch to print projection of base point data to the 1 atm.-steam saturation curve. This print is made only if IOPR1 .ge. -1.

- = 0 does nothing.
- = 1 prints the projected data.

IOPR4	Option switch to display polynomial fits to the steam pressure curve, the Criss-Cobble parameters, and steam curve. = 0 do not print. = 1 print.
IOPR5-8	Print option switches; not currently used.
UKEY	Key names (see Appendix 1).
USUB	Subset labels (see Appendix 1).
USPEC	Species name for the following DATAO reaction, input overrides the MDAS DATAO reaction.
NSP	Number of species in DATAO reaction to follow.
CDRS	Reaction coefficient corresponding to associated UDRS species.
UDRS	Species names in reaction.

Appendix 1. LIST OF SPECIES IN DATAOR53, INCLUDING SPECIES FROM THE MDAS DATA FILE AND SUPCRT.

Owing to the absence of a clear and convenient way of representing subscripts and superscripts using the limited number of characters available in a standard ASCII character set, there are several possible ambiguities encountered when trying to write aqueous species names as chemical formulae in a computer file. Adopting a set of naming conventions is necessary, in particular, to reduce potential confusion between numbers designating the number of charges on a given aqueous species and stoichiometric numbers. The naming conventions also eliminate potential confusion in distinguishing between neutral aqueous species and gas or solid phases having the same composition. Positively charged aqueous species with charges less than 5 are written using +, ++, +++, and ++++ to designate the charge (instead of +1, +2, +3 and +4) to avoid confusion with stoichiometric numbers describing the elemental composition of the species. Aqueous cations having charges greater than 4 are named using a numeral preceding the "+", both enclosed in parentheses. For example, the chromium hydroxide species ($Cr(OH)_2^{4+}$) is written as "cr(oh)2++++", rather than "cr(oh)24+". However, the species ($Cr_3(OH)_4^{5+}$) would be written cr3(oh)4(5+) because the charge is greater than 4. Analogous designations are used for anions. Complex ligands such as 'co3--', 'hpo3--', and 'oh-' are enclosed in parentheses only when two or more ligands are present. Therefore, aloh++ and al(oh)2+ are both correct, but neither al(oh)++ nor aloh2+ is correctly named according to these conventions. Uncharged aqueous species are not denoted with any special symbol. If a solid species has a name that is potentially identical to that of a neutral aqueous species, it is generally denoted with an abbreviation of its crystallographic state, such as (s), (c), or (am). An example is the neutral neptunium hydroxide species, $Np(OH)_4$, which might be either a solid or an aqueous hydroxide complex. It is listed in DATAO as np(oh)4 when it represents an aqueous species and as np(oh)4(s) when it describes a solid.

48 Basis Species

h2o	ag+	al+++
am+++	as(oh)4-	au+
b(oh)3	ba++	br-
ca++	cl-	co++
cr+++	cs+	cu+
eu+++	f-	fe++
h+	hco3-	hg++
hpo4--	i-	k+
li+	mg++	mn++
na+	np++++	ni++
no3-	pb++	puo2++
ra++	rb+	ru+++
sio2(aq)	seo3--	sn++++
so4--	sr++	th++++
ti(oh)4	tco4-	u++++
v+++	zn++	o2(g)

46 Auxiliary Basis Species

ch4(aq)	co2(aq)	o2(aq)
h2(aq)	au+++	am++++
amo2+	amo2++	aso4---
ch3coo-	clo4-	co+++
co3--	cr++	cro4--
cro4---	cu++	eu++
fe+++	hg2++	hs-
nh4+	no2-	np+++
(o-phth)--	oh-	pu+++
pu++++	puo2+	ru++
ruo4	ruo4-	ruo4--
ru(oh)2++	se--	seo4--
sn++	tc+++	tco++

tco4--	tco4---	u+++
uo2+	uo2++	vo++
vo4---		

592 Nonbasis Aqueous Species

agcl	agcl2-	agcl3--
agcl4---	agf	agso4-
ag(so4)2---	al13o4(oh)24(7+)	al2(oh)2++++
al3(oh)4(5+)	alch3coo++	alf++
alf2+	alf3	alf4-
alf5--	alf6---	alh2po4++
alhpo4+	al(o-phth)+	al(o-phth)2-
aloh++	al(oh)2+	al(oh)3
al(oh)4-	also4+	al(so4)2-
amcl++	amcl2+	amco3+
am(co3)2-	am(co3)3---	amf++
amf2+	amf3	amh2po4++
am(h2po4)2+	am(h2po4)3	am(h2po4)4-
amno3++	am(no3)2+	amo2hco3
amoh++	am(oh)2+	am(oh)3
amso4+	am(so4)2-	ash3(aq)
aso2oh--	aso3f--	as(oh)3
ass2-	aucl++	aucl2+
aucl2-	aucl3	aucl4-
b2o(oh)5-	b3o3(oh)4-	b3o3(oh)5--
b4o5(oh)4--	bab(oh)4+	bach3coo+
bacl+	baco3	baf+
bano3+	ba(o-phth)	baoh+
baso4	bf2(oh)2-	bf3oh-
bf4-	bh4-	b(oh)4-
cab(oh)4+	cach3coo+	cacl+
caco3	caf+	cah2po4+
cah2sio4	cah3sio4+	ca(h3sio4)2

cahco3+
cano3+
cap2o7--
co2(oh)3+
cocl+
co(hs)2
cono3+
co(oh)2
cos2o3
cr2o7--
crbr++
cro3cl-
cr(oh)3
csf
cucl2
cucl3--
cuh2po4+
cunh3++
cu(nh3)3++
cuoh+
eubr++
eucl++
eu(co3)2-
eu1o3++
eu(oh)2+
fe2(oh)2++++
fe(b(oh)4)2+
fe(ch3coo)2+
fecl++
fecl3
feco3
fef++
feh2po4+
fehco3+
cahp2o7-
ca(o-phth)
capo4-
co4(oh)4++++
cocl2
cohso4+
co(no3)2
co(oh)3-
coseo4
cr2(oh)2++++
crcl++
croh++
cr(oh)4-
cucl
cucl2-
cucl4--
cuhpo4
cu(nh3)2+
cuno2+
cupo4-
eubr2+
eucl2+
euf++
euno3++
euso4+
fe3(oh)4(5+)
fech3coo+
fe(ch3coo)3
fecl2
fecl4-
feco3+
fef2+
feh2po4++
fehpo4
cahpo4
caoh+
caso4
cobr2
cohs+
coi2
cooh+
co(oh)4--
coso4
cr3(oh)4(5+)
crcl2+
cr(oh)2+
cscl
cucl+
cucl3-
cuf+
cunh3+
cu(nh3)2++
cu(no2)2
cuso4
eubro3++
euco3+
euf2+
euoh++
eu(so4)2-
feb(oh)4++
fech3coo++
fecl+
fecl2+
fecl4--
fef+
fef3
feh3sio4++
fehpo4+

fehseo3
feno3++
fe(oh)2
fe(oh)3-
feso4
h2aso4-
h2f2
h2po3f
h2s(aq)
h2sio4--
h3p2o7-
h4(h2sio4)4----
haso3f-
hch3coo
hcro4-
hg2so4
hgcl2
hgso4
h(o-phth)-
hruo5-
hseo4-
kco3-
kp2o7---
liso4-
mg4(oh)4++++
mgcl+
mgh2po4+
mg(h3sio4)2
mghpo4
mgpo4-
mn2(oh)3+
mncl3-
mnh2po4+
mnnh3++
fehso4++
feoh+
fe(oh)2+
fe(oh)4-
feso4+
h2b4o7
h2(o-phth)
h2po4-
h2se
h2so4
h3po4
h4p2o7
haso4--
hcl
hf
hg2(so4)2--
hgcl3-
hg(so4)2--
hp2o7---
hse-
hso4-
khpo4-
kso4-
mg2co3++
mgb(oh)4+
mgco3
mgh2sio4
mghco3+
mgoh+
mgso4
mncl+
mnco3
mnhco3+
mn(nh3)2++
feno2++
feoh++
fe(oh)3
fepo4-
fe(so4)2-
h2cro4
h2p2o7--
h2ruo5
h2seo3
h3aso4
h3sio4-
h6(h2sio4)4--
hass2
hcoo2-
hf2-
hgcl+
hgcl4--
hno2
hpo3f-
hseo3-
kcl
koh
lioh
mg2oh+++
mgch3coo+
mgf+
mgh3sio4+
mghp2o7-
mgp2o7--
mn2oh+++
mncl2
mnf+
mnhpo4
mn(nh3)3++

mnno3+
mno4--
mn(oh)3-
mnseo4
nab(oh)4
naco3-
nahco3
na(o-phth)-
naso4-
ni2oh+++
nihp2o7-
nino3+
ni(oh)2
nip2o7--
npcl+++
npf+++
np(h2po4)2+
np(hpo4)2
np(hpo4)5(6-)
(npo2)2(oh)2++
npo2cl+
npo2(co3)2---
npo2f
npo2h2po4
npo2hpo4-
npo2so4
npoh+++
np(oh)4
np(so4)2
pbcl2
pbco3
pbf3-
pbhpo4
pb(so4)2--

mn(no3)2
mnoh+
mn(oh)4--
mnso4
nach3coo
naf
nahp2o7--
naoh
nh3
ni4(oh)4++++
ni(nh3)2++
ni(no3)2
ni(oh)3-
niseo4
npcl2++
npf2++
np(h2po4)3
np(hpo4)3--
npo2+
(npo2)3(oh)5+
npo2co3-
npo2(co3)3----
npo2f+
npo2h2po4+
npo2oh
npo2so4-
np(oh)2++
np(oh)5-
p2o7----
pbcl3-
pbf+
pbf4--
pbpo4-
ph4+

mno4-
mn(oh)2
mnpo4-
na2p2o7--
nacl
nah3sio4
nahpo4-
nap2o7---
nh4so4-
nibr+
ni(nh3)6++
nioh+
ni(oh)4--
niso4
np(co3)5(6-)
nph2po4++
nphpo4++
np(hpo4)4----
npo2++
npo2cl
npo2(co3)2--
npo2(co3)3(5-)
npo2f2
npo2hpo4
npo2oh+
npoh++
np(oh)3+
npso4++
pbcl+
pbcl4--
pbf2
pbh2po4+
pbso4
po3f--

po4---
puco3++
puf3+
puhpo4++
pu(hpo4)4----
puo2cl+
puo2f2
puo2h2po4+
puo2(oh)2hco3-
puoh+++
pu(oh)4
puso4++
puso4hso4+
rucl++
rucl4-
ruoh++
ru(oh)2cl2
ru(oh)2so4
ru(so4)2-
s3--
s6--
snbr2
sncl2
snf+++
snf3+
snoh+
sn(oh)2++
sn(oh)4
srch3coo+
srh2po4+
srno3+
srpo4-
tcooh+
th2(oh)2(6+)
pucl++
puf+++
puf4
pu(hpo4)2
(puo2)2(oh)2++
puo2(co3)2--
puo2f3-
puo2oh
puo2so4
pu(oh)2++
pu(oh)5-
pu(so4)2
ru4(oh)12++++
ru(cl)2+
rucl5--
ru(oh)2+
ru(oh)2cl3-
ruso4
s--
s4--
sif6--
snbr3-
sncl3-
snf2
snf3-
snoh+++
sn(oh)3+
snso4++
srco3
srhco3+
sroh+
srso4
tco(oh)2
th4(oh)8(8+)
pucl+++
puf2++
puh2po4++
pu(hpo4)3--
(puo2)3(oh)5+
puo2f+
puo2f4--
puo2oh+
puoh++
pu(oh)3+
puso4+
pu(so4)2-
rucl+
ru(cl)3
rucl6---
ru(oh)2cl+
ru(oh)2cl4--
ruso4+
s2--
s5--
snbr+
sncl+
snf+
snf2++
snf4
sn(oh)2
sn(oh)3-
sn(so4)2
srf+
srhpo4
srp2o7--
tc++
[tco(oh)2]2
th6(oh)15(9+)

thcl+++
thcl4
thf3+
th(h2po4)2++
th(hpo4)2
th(oh)2++
thso4++
th(so4)4----
ucl4
uf3+
uf6--
u(hpo4)3--
(uo2)2(oh)2++
(uo2)3(oh)7-
uo2co3
uo2f+
uo2f4--
uo2(h2po4)h3po4+
uo2oh+
uo2(so4)2--
u(oh)3+
uso4++
vo2+
vo2f3--
vo2(hpo4)2---
(vo)2(oh)5-
vof+
vof4--
vooh+
vso4+
zncl3-
znh2po4+
znoh+
znso4

thcl2++
thf+++
thf4
thh3po4++++
th(hpo4)3--
th(oh)3+
th(so4)2
u6(oh)15(9+)
uf+++
uf4
uhpo4++
u(hpo4)4----
(uo2)3(oh)4++
(uo2)4(oh)7+
uo2(co3)2--
uo2f2
uo2h2po4+
uo2h3po4++
uo2sio(oh)3+
uoh+++
u(oh)4
u(so4)2
vo2f
vo2h2po4
(vo)2(oh)2++
vo2so4-
vof2
voh++
vo(oh)3
zncl+
zncl4--
znhco3+
znpo4-

thcl3+
thf2++
thh2po4+++
thhpo4++
thoh+++
th(oh)4
th(so4)3--
ucl+++
uf2++
uf5-
u(hpo4)2
(uo2)2(co3)(oh)3-
(uo2)3(oh)5+
uo2cl+
uo2(co3)3----
uo2f3-
uo2(h2po4)2
uo2(no3)2
uo2so4
u(oh)2++
u(oh)5-
v2(oh)2++++
vo2f2-
vo2hpo4-
vo2(oh)2-
vo3oh--
vof3-
v(oh)2+
voso4
zncl2
znf+
znhpo4
znseo4

716 Minerals

acanthite
akermanite
alabandite
albite high
alunite
am(oh)3(am)
amrph.silica
andalusite
anhydrite
antarcticite
aragonite
arsenopyrite
ashcroftite
ba3(aso4)2(c)
bacl2.2h2o
bacro4
bai2(c)
bao.(sio2)2(c)
(bao)2.sio2(c)
barite
baseo3
bassanite
beidellit-h
beidellit-na
birnessite
blockite
boltwood-na
boric acid
brewsterite-ca
brucite
ca-al pyroxene
ca2sio4.7/6h2o
ag2se
al2(so4)3
al(aso4)(c)
albite low
am2(co3)3(c)
am(oh)3(c)
analc-dehydr
andradite
annite
anthophyllite
arcanite
artinite
azurite
babr2.2h2o
bacl2.h2o
baf2(c)
bamno4(c)
bao.sio2(c)
bao(c)
barytocalcite
baseo4
bassetite
beidellit-k
berlinite
bischofite
bloedite
boltwoodite
bornite
brewsterite-sr
bunsenite
ca2cl2(oh)2.h2o
ca2sio4(gamma)
ag3po4(c)
al2(so4)3.6h2o
albite
alstonite
amesite-14a
amohco3(c)
analcime
anglesite
anorthite
antigorite
arsenolite
as2o5(c)
b2o3
babr2(c)
bacl2(c)
bahpo4(c)
ba(no3)2(c)
(bao)2.(sio2)3(c)
ba(oh)2.8h2o
bas(c)
basif6(c)
beidellit-ca
beidellit-mg
bieberite
bixbyite
boehmite
borax
brewsterite-ba
brezinaite
burkeite
ca2si3o8.5/2h2o
ca2v2o7(c)

ca3(aso4)2(c)
ca3v2o8(c)
ca5si6o17.11/2h2o
ca6si6o18.h2o
cacl2.h2o
calcium chloride
carnotite
casi2o5.2h2o
cav2o6(c)
chabazite
chalcopyrite
chloropyromorphite
claudetite
clinoptil-ca
clinoptil-na
co3(aso4)2
co3(po4)2
cocl2.6h2o
cof2
coffinite
co(no3)2(s)
copper
corundum
coseo3
coso4.h2o
cr2o3
crf4
cristobalite
cronstedt.-7a
cu3(po4)2.3h2o
cucr2o4
cuf(c)
cuse
cuseo3.2h2o
ca3si2o7.3h2o
ca4cl2(oh)6.13h2o
ca5si6o17.21/2h2o
cacl2.2h2o
cahpo4.2h2o
ca(oh)2(c)
caseo3.2h2o
caso4.1/2h2o(beta)
celestite
chalcedony
chamosite-7a
chrysotile
clinochl-14a
clinoptil-k
clinozoisite
co3(aso4)2.8h2o
cobr2(c)
cocl2(s)
cof3
cohpo4
coo
cordier.anhy
cos
coso4.3co(oh)2
coso4(s)
crcl3
cri3
cro2
crs
cu3(po4)2(c)
cuf2.2h2o
cufeo2(c)
cuse2
dachiardite-ca
ca3sio5
ca4si3o10.3/2h2o
ca5si6o17.3h2o
cacl2.4h2o
calcite
carnallite
caseo4
cattierite
cerussite
chalcocite
chloromagnesite
cinnabar
clinochl-7a
clinoptil-mg
co2sio4
co3o4
cocl2.2h2o
coco3
co(feo2)2
colemanite
co(oh)2(s)
cordier.hydr
cose
coso4.6h2o
covellite
crf3
crist.beta.amorph
cro3
cu3(aso4)2(c)
cu3se2
cuf2(c)
cuprite
cuseo3
dachiardite-k

dachiardite-na
dawsonite
dolomite
edingtonite
epidote-ord
erionite-ca
eu
eu2o3(monoclinic)
eubr3
eucl3.6h2o
eu(io3)3.2h2o
euocl
eu(oh)3
faujasite-ca
fe2(so4)3(c)
fecr2o4
feo(c)
ferrite-2-ca
ferrite-mg
fese
fev2o4(c)
forsterite
gaylussite
gismondine
gmelinite-ca
gold
grossular
h2(o-phth)(c)
harmotome
hematite
heulandite-ca
hg2seo3
hinsdalite
hydroboracite

daphnite-14a
diaspore
dolomite-dis
enstatite
epistilbite
erionite-k
eu2(co3)3.3h2o
eu2(so4)3.8h2o
eucl2
eucryptite
eu(no3)3.6h2o
eu(oh)2.5cl.5
eus
faujasite-na
fecl2.2h2o
fef2(c)
fe(oh)2(ppd)
ferrite-ca
ferrite-zn
fese2
fluorapatite
galena
gehlenite
glaserite
gmelinite-na
graphite
gummite
haiweeite
hausmannite
hercynite
heulandite-na
hgse
htco4(s)
hydromagnesite

daphnite-7a
diopside
dolomite-ord
epidote
epsomite
erionite-na
eu2o3(cubic)
eu3o4
eucl3
euf3.0.5h2o
euo
eu(oh)2cl
euso4
fayalite
fecl2.4h2o
fef3(c)
fe(oh)3(ppd)
ferrite-cu
ferrosilite
feso4(c)
fluorite
garronite
gibbsite
glauberite
goethite
greenalite
gypsum
halite
hedenbergite
heulandite
hexahydrite
hgseo3
huntite
hydrophilite

hydroxyapatite
jadeite
k-feldspar
k2cro4
k8h4(co3)6.3h2o
kalsilite
kaolinite
kieserite
knaco3.6h2o
kyanite
larnite
lawsonite
leonite
li2sio3
li(uo2)(aso4)(c)
magnetite
manganosite
maximum microcli
merwinite
metacinnabar
mg3(aso4)2(c)
mgcl2.2h2o
mgcr2o4
mgseo3
mgv2o6(c)
millerite
misenite
mncl2.2h2o
mnhpo4(c)
mnse
mnso4(c)
molysite
montmor-ca
montmor-na

hydroxypyromorphit
jarosite-k
k2co3.3/2h2o
k2mg(so4)2
kainite
kal(so4)2
kasolite
kmgcl3
ktco4(s)
labile salt
laumontite
leonhardite
levyne
lime
magnesite
malachite
margarite
melanterite
mesolite
mg2cl(oh)3.4h2o
mgbr2
mgcl2.4h2o
mgf2(c)
mgseo3.6h2o
mhsh(mgl.25)
minnesotaite
mn3(aso4)2(c)
mncl2.4h2o
mn(oh)2(am)
mnseo3
mnv2o6(c)
monohydrocalcite
montmor-k
mordenite

illite
jarosite-na
k2cr2o7
k2se
kalicinite
kal(so4)2.12h2o
kbr
kmgcl3.2h2o
k(uo2)(aso4)(c)
lansfordite
lawrencite
leonhardtite
li2se
linnaeite
magnesium oxychlor
manganite
matlockite
mercallite
mesolite-ss
mg2v2o7(c)
mgbr2.6h2o
mgcl2.h2o
mgohcl
mgso4(c)
mhsh(mgl.5)
mirabilite
mn3(po4)2(c)
mncl2.h2o
mn(oh)3(c)
mnseo3.2h2o
moderite
monticellite
montmor-mg
mordenite-k

mordenite-na
na2cr2o7
na2se
na2sio3
na2uo4(c)
na4sio4
nabr.2h2o
nanpo2co3.3.5h2o
natron
nh4hse
ni3(po4)2
ni3se4
nicl2.4h2o
nif2
ningyoite
nis
niseo3.2h2o
niso4(s)
nitrobarite
nontronit-mg
np2o5
npo2(oh)2
o-phth acid(c)
oxychloride-mg
pb3(aso4)2(c)
pbcro4
pbhpo4(c)
pbseo4
petalite
phillipsite-k
picomerite
polyhalite
potassium sesquica
przhevalskite
muscovite
na2cro4
na2se2
na2so4
na3h(so4)2
na6si2o7
nafeo2(c)
natco4(s)
nepheline
ni2p2o7
ni3s2
nicl2
nicl2.6h2o
nif2.4h2o
nio
nis2
niso4.6h2o
niter
nontronit-ca
nontronit-na
np(hpo4)2(s)
npo2(oh)(am)
orpiment
paragonite
pb3(po4)2(c)
pbf2(c)
pbse
pd-oxyannite
phengite
phillipsite-na
pirssonite
portlandite
potassium sodium c
pseudowollastonite
na2co3
na2mg(so4)2.2h2o
na2si2o5
na2u2o7(c)
na3uo4(c)
nabr
nahcolite
natrolite
nesquehonite
ni2sio4
ni3s4
nicl2.2h2o
nico3
nife2o4
ni(oh)2(s)
nise2
niso4.7h2o
nitratite
nontronit-k
np
npo2
np(oh)4(s)
oxychloride,a-ca
pargasite
pb4o(po4)2(c)
pb(h2po4)2(c)
pbseo3
pentahydrite
phillipsite-ca
phlogopite
plumbogummite
potassium carbonat
prehnite
pu2o3(c,beta)

puf3(c)
puf4(c)
pu(hpo4)2(c)
puo2
puo2(c)
puo2hpo4(c)
puo2(oh)2
puo2(oh)2(c)
puo2oh(am)
pu(oh)3
pu(oh)3(s)
pu(oh)4(am)
pu(oh)4(s)
pyrite
pyrolusite
pyrophyllite
pyrrhotite
quartz
quicksilver
ra(c)
racl2.2h2o
rankinite
ra(no3)2(c)
raso4
realgar
rhodochrosite
rhodonite
ripidolit-14a
ripidolit-7a
rubr3(s)
ru(c)
rucl3(s)
rui3(s)
ruo2.2h2o(am)
ruo2(s)
ruo4(s)
ru(oh)3.h2o(am)
rus2(s)
rutherfordine
safflorite
saleeite
sanidine high
saponite-ca
saponite-h
saponite-k
saponite-mg
saponite-na
s(c)
scacchite
schoepite
scolecite
scorodite
se2o5
se(black)
secl4
seo2
seo3
sepiolite
sesquipotassium su
sesquisodium sulfa
siderite
sillimanite
silver
sklodowskite
smectite-high-fe-m
smectite-low-fe-mg
smectite-reykjanes
smithsonite
sn2s3
sn3s4
snbr2(s)
snbr4
sncl2(s)
sno
sno2
sn(oh)2(s)
sns
snse
snse2
snso4
sn(so4)2(c)
soddyite
sphalerite
spinel
spodumene-a
sr-autunite
sr2sio4(c)
sr3(aso4)2(c)
sr3(po4)2(c)
srbr2.6h2o
srbr2.h2o
srbr2(c)
srcl2.2h2o
srcl2.6h2o
srcl2.h2o
srcl2(c)
srcro4
srf2(c)
srhpo4(c)
sri2(c)
sr(no3)2.4h2o
sr(no3)2(c)

sro(c)
srse
srsio3(c)
stilbite-na
sulfur-rhmb
tachyhydrite
tc2s7(s)
tc(c)
tc(oh)2(s)
tcs2(s)
tephroite
th7s12
thenardite
thf4(c)
tho2
ths2
torbernite
tridymite
tyuyamunite
u4o9(c)
uf4.2.5h2o
(uo2)3(po4)2(c)
uo2f2(c)
uo2(no3)2.3h2o
uo2(oh)2(c,bet)
uo2so4.3h2o
uo3(c,gamma)
uranocircite
u(so4)2.4h2o
v2o3(c)
v3o5(c)
(vo)3(po4)2(c)
whitlockite
wurtzite

sr(oh)2(c)
srseo3
stilbite-ca
strengite
sylvite
talc
tc3o4(s)
tco2.2h2o(am)
tc(oh)3(s)
tcs3(s)
th2s3
thbr4
thermonatrite
thi4
th(oh)4(c)
th(so4)2(c)
tremolite
troilite
u3o8(c,alph)
u(c,alph)
uf4(c)
uo2(am)
uo2hpo4(c)
uo2(no3)2.6h2o
uo2so4.(2.5h2o)
uo2so4.h2o
uof2.h2o
uranophane
u(so4)2.8h2o
v2o4(c)
v4o7(c)
wairakite
witherite
wustite

srs(c)
srseo4
stilbite-k
strontianite
syngenite
tc2o7(s)
tc4o7(s)
tco3(s)
tcoh(s)
tenorite
th2se3
thcl4(c)
thf4.2.5h2o
th(no3)4.5h2o
thorianite
todorokite
trevorite
tsumebite
u3se4
ucl4(c)
u(hpo4)2.4h2o
uo2cl2(c)
uo2(no3)2.2h2o
uo2(no3)2(c)
uo2so4.(3.5h2o)
uo2so4(c)
uraninite
use2
u(so4)2(c)
v2o5(c)
vivianite
weeksite
wollastonite
yugawaralite

zincite	zn3(aso4)2(c)	zn3(po4)2.4h2o
zncr2o4	znf2(c)	znse
znseo3.h2o	zoisite	

11 Gases

ch4(g)	co2(g)	h2(g)
h2s(g)	n2(g)	o2(g)
ru(g)	ruo4(g)	s2(g)
steam	tc2o7(g)	

16 Solid Solutions

biotite	carbonate-calcite	chlorite-ss
dachiardite-ss	epidote-ss	garnet-ss
glass	mordenite-ss	(na,k)-sanidine
olivine	orthopyroxene	phillipsite-ss
plagioclase	saponite-tri	smectite-di
stilbite-ss		

Subsets

Indexed by Element

americium	arsenic	boron	barium
cobalt	chromium	copper	europium
iron	iodine	lead	lithium
manganese	mercury	neptunium	nickel
plutonium	radium	ruthenium	selenium
tin	strontium	technicium	thorium
uranium	vanadium	zinc	zeolite

Keys

Indexed by Species

evap	organics	saltmin	tuffmin
uo_2sio_4			

Indexed by Data Type

alkalin	aqueous	aux	basis
element	gases	liquid	ref-state
solid			

Indexed by Data Information

active	cpdata	cptrans	data0
duplicate	logk_calc	notused	phasetr
proposed	t-pgrid	warning	

Indexed by Data Sets

codata	hdata	hmw	hmw84
pdata	supcrt		

APPENDIX 2. GLOSSARY OF IMPORTANT VARIABLES IN MCRT.

AA	'a' coefficient for heat capacity equation
ACNST	constant used in equation (16); ACNST = 0.01875
ACOB1	Criss-Cobble 'a' parameter in polynomial coefficient (0-100°C)
ACOB2	Criss-Cobble 'a' parameter in polynomial coefficient (100-300°C)
ACRISS	grid of 'a' parameters; input to Criss-Cobble method
AFCNST	variable having a value derived by (-0.001)*(A110)*(RCNST)
A110	natural log of 10 (approximately 2.302585)
ATWT	atomic weight of elements
AZERO	ion size parameter array for species in the reaction
BB	'b' coefficient for heat capacity equation
BCNST	constant used in equation (16); BCNST = -12.741
BCOB1	Criss-Cobble 'b' parameter in polynomial coefficient (0-100°C)
BCOB2	Criss-Cobble 'b' parameter in polynomial coefficient (100-300°C)
BCRISS	grid of 'b' parameters; input to Criss-Cobble method
CC	'c' coefficient for heat capacity equation
CCNST	exp(BCNST + ACNST*298.15)
CDRS	array of reaction coefficients for DATAO reaction (REAC file)
CDRS1	array of reaction coefficients for reference reaction (currently unused)
CESS	stoichiometric coefficient for elements in a given species
CP	array with partial molal heat capacities for species in DATAO reaction
DCNST	theta/omega
DD	'd' coefficient for heat capacity equation
DELGO	array of apparent molal Gibbs free energy
DELGOR	grid of Gibbs free energy of reaction for DATAO reaction
DELHO	array of apparent standard molal enthalpy for given species
DELHOR	grid of enthalpies of reaction (from REAC file)
DELHORB	enthalpy of reference reaction at base temperature/pressure
DELSOR	grid of entropies of reaction (from REAC file)
DELSORB	entropy of reference reaction at base temperature/pressure

ECNST	constant; ECNST = 1./THETA
EE	'e' coefficient for heat capacity equation
GBASE	apparent standard Gibbs free energy of species
GMIN	array of Gibbs free energy data for temperature grid points
HBASE	apparent standard enthalpy of species
HCOB1	polynomial coefficient used in calculating absolute entropy of H^+ 0-100°C
HCOB2	polynomial coefficient used in calculating absolute entropy of H^+ 100-300°C
HCRISS	grid of values for absolute entropy of H^+
HMIN	array of enthalpy data for temperature grid
HTR	enthalpy of transition for solids (kcal/mol)
HYDR	hydration number for aqueous species
ICRISS	ion type flag for Criss-Cobble extrapolation
IDATES	date species block was last modified
IERR	error counter -- after check for mass and charge balance
IFLN	first line in random directory for a set of species
IGRID	flag for type of temperature/pressure grid for apparent molal properties; each species in reaction has an IGRID flag = 0 no grid on INPUT = 1 grid calculations made by MCRT = 2 grid present in MDA and read as input
ILLN	last line in random directory for a set of species
IOPT 1-8	INPUT file option switches, see Table 2
IOPR 1-8	INPUT file print option switches, see Table 2
ISHIFT	see shift
ITMP	temperature range flag values of 0 and 1 indicate T = 0-100°C and T = 100-300°C, respectively
ITYP	species category (basis, nonbasis, solid, gas)
NCFLAG	elements flag; values of 0 and 1 indicate "element not in species" and "element in species", respectively; 0/1 = element not in species/element in species
NCODE	equation index for heat capacity equation but subroutine DLTSOL accepts only values of 0 and 1

NCPRT	total number of heat capacity ranges for solids
NCT	number of elements in elements file
NCTMAX	maximum number of elements per species
NCTS	number of elements in species for a reaction in DATAO
NESS	array of indexes to elements that are present in a species
NFBUF	dimension of first block in random file
NGRID	number of points on the standard temperature grid
NLBUF	dimension of buffer, UBBUF
NRST1	number of species in reference reaction
NSP	number of species in DATAO reaction (REAC file)
NSHIFT	number of additional temperature/pressure grid points
NSQ	maximum number of species in a given reaction
NSQMAX	maximum number of species in any reaction
NSSC	number of points on the steam saturation curve in the standard grid (5)
NTMPMX	maximum number of points on the full temperature grid (NTMPMX = NGRID + 1 + 2*NTRMX)
NTRANS	number of heat capacity transitions in a species
NTRMX	maximum number of transitions per phase (7)
NWARN	number of free energy-enthalpy-entropy inconsistencies found
OMEGA	1. + ACNST*CCNST*THETA
PBASE	pressure at base-point projected to 1.013 bar-ssc pressure
PCOF	polynomial coefficient for determining pressure values corresponding to the pressure grid (not including 1.013 bars)
PGRID	pressure grid values
PRESS	base pressure (1.103 if T < 373.15K; otherwise the value is calculated from the H_2O-steam saturation curve)
PSSC	input pressure grid in bars
RCNST	gas constant (1.98726 cal/mol/K)
SBASE	entropy at base point (cal/mol/K)
SE	electronic entropy (cal/mol/K)
SELEM	array of entropies of the elements
SLCNST	Clapeyron slope constant (SLCNST = 0.0239)
SLOPE	Clapeyron slope for minerals

SMIN	array of entropy data for temperature grid points
STR	entropy of transition for solids (cal/mol/K)
TBASE	temperature at base point projected to 1.013 bar-steam saturation curve pressure
TCGRID	temperature grid in °C
TEMPC	temperature in °C
TEMPK	temperature in K
TEMPTR	temperature limit for heat capacity range
THETA	constant used in equation 16 (= 219.0) from Helgeson (1969)
TITR	titration factor for aqueous species
TKGRDS	scaled temperature grid (K) from -1 to 1
TKGRID	temperature grid in K
TMAX	maximum temperature in temperature grid (K)
TSSC	input temperature grid
UBBUF	buffer for species blocks
UCODE	character array of subset and key codes in subroutine GDIRX
UDBUF	directory buffer
UDRSI	species name in DATAO reaction (REAC file)
UELEM	array with names of elements listed in elements file
UENTBY	person entering data; read from species block
UEQLRN	EQLIB release number
UEQLST	EQLIB stage number
UNAM	name of species or element of interest
URELNO	release number of MCRT code
USPEC	array of primary species names in a given reaction
USPEC2	array of secondary species names in a given reaction
USRC	source of data for species
USTAGE	stage number for code
VO	volume of species (cc/mol)
VBASE	volume at base point
VMIN	array of molar volume data for temperature grid points
VTR	volume of transition for solids (cc/mol)
XLKS	log K grid calculated by MCRT
XLKSB	log K of reference reaction at reference T and P
Z	charge of species

Appendix 3. GLOSSARY OF SUBROUTINES CALLED IN MCRT.

Variable or array names enclosed in parentheses at the beginning of the subroutine descriptions designate parameters passed in the calling sequence for that subroutine. Subroutines that originated with SUPCRT (Helgeson et al., 1978, 1981) and that correspond closely to SUBCRT versions of these routines (Flowers, 1986) are included in this list, and their origins are designated as such.

ADXTB (EX,ITBL,ITB) An index (IX) having either a positive or negative integer value is added to a table from the ITBL array if the index position is blank. If the position is already filled with the absolute value of IX, it is replaced by IX.

AFUNC This routine calculates one of the Criss-Cobble parameters (a) for an ion of the type specified by the IDUM setting.

BFUNC This routine calculates one of the Criss-Cobble parameters (b) for an ion of the type specified by the IDUM setting.

CCCRT (NS,ICC,QPGRID) This routine performs the Criss-Cobble extrapolation for the NSth aqueous species. ICC = 0 if the method worked in its usual sense. ICC = 1 if the method degenerated to the constant enthalpy method, and ICC = 2 if the base point data are insufficient to make an extrapolation.

CENTHR This routine extrapolates equilibrium constants, Gibbs energies, enthalpies, and entropies of reaction by means of the constant enthalpy assumption. The maximum temperature of extrapolation is 200°C.

CHEKRX (NERR). This routine checks to see if the reaction satisfies mass and charge balance relations. If it does not, the reaction might be unbalanced or bad data might be given for the component species

on the file MDAR. The CHEKRX routine returns a value of 0 for NERR if no error is found and a value greater than 1 if the reaction is found to be incorrectly balanced.

CPGRID (NS,NTEMPS,ICC) This routine copies the NTEMP version of the data grid for thermodynamic properties of a chemical species to the NGRID version.

CSLOPR Extrapolated equilibrium constants, Gibbs energies, enthalpies, and entropies of reactions are computed by CSLOPR by means of the constant slope (i.e., constant d log K/dT) assumption. The maximum temperature for which this extrapolation will be used is 200°C.

D1 (W,XU,FN,FW,FU,FFW,FFU,FUW) D1 is a SUBCRT routine that supports computations done in the KIRKW routine, which computes first, second, and cross derivatives.

DECOMP (QPGRID) This routine decomposes the thermodynamic properties of individual species in a reaction from the thermodynamic properties of the reaction itself.

DLPAQ1 (T2,P1,P2,NS,DELH,DELS,DELV) This routine estimates differences in the enthalpy (DELH), entropy (DELS), and volume (DELV) of an aqueous species (indexed by NS) as a function of pressure, going from P2 to P1.

DLPSOL (NCPR,T2,P1,P2,NS,DELH,DELS,DELV) The DLPSOL subroutine is designed to compute differences in the enthalpy (DELH), entropy (DELS), and volume (DELV) functions of a mineral (with index NS) for the states T2, P2 and T2, P1. Currently only DELH is assigned a nonzero value.

DLTAQ1 (T1,T2,S1,NS,DELH,DELS,DELV) This routine estimates differences in the enthalpy (DELH), entropy (DELS), and volume (DELV) functions of an aqueous species (indexed by NS) using the Criss-Cobble method for two different temperatures (T2 and T1) on the liquid vapor saturation curve for water.

DLTSOL (NCPR,T1,T2,NS,DELH,DELS,DELV,ICC,IER) This routine computes differences in the enthalpy (DELH), entropy (DELS), and volume (DELV) functions of a solid (indexed by NS) over a temperature internal defined by T1 and T2 at 1 bar pressure.

DQUANT This routine extrapolates equilibrium constants, Gibbs free energies, enthalpies, and entropies of reaction by means of the DQUANT approximation [equation (16) in Helgeson, 1969]. The upper temperature limit for this extrapolation is 200°C.

DRCALC This routine computes the log K, Gibbs free energy, enthalpy, and entropy functions according to the temperature-pressure grid.

FUNC (X,C,NPX) A polynomial of variable X of order NPX is evaluated by the FUNC function. C is an array containing the coefficients of the polynomial.

GDIRX (UCODE,NCODE,ICOL,NMAX,NSPEC,NOUTPT,IXSP,IDIRTB) GDIRX searches a directory for subset and key codes and/or adds to a directory index table.

GHSCLC (NS,NELE,TDUM,PDUM,GDUM,HDUM,SDUM,VDUM,SDUM1,QWARN,QPGRID,ILN) This routine calculates any one of the Gibbs energy, enthalpy, and entropy from the other two for the NS^{th} species. If there are data for all three from the data file (MDAR), then a consistency check is made by comparing the value of the Gibbs energy calculated from the enthalpy and entropy with the data file value.

GIONS (GZERO,HZERO,SZERO,VZERO) GIONS is a SUBCRT subroutine that calculates thermodynamic properties of an aqueous ion using the SUPCRT equations of state (Helgeson et al., 1981; Helgeson and Kirkham, 1976); GZERO is the apparent Gibbs free energy of formation, HZERO is the apparent enthalpy of formation, SZERO is the entropy, and VZERO is the partial molal volume of the ion as calculated using the SUPCRT equations of state.

GRAQS (NS,NMDAR,IFLN,ILLN,NAVB,IFLAG,ICC,NERR) This routine processes individual aqueous species data according to the following protocol:

1. Finds species
2. Gets species block information
3. Computes free energy, enthalpy, and entropy
4. Extrapolates species properties if the species is a nonbasis species or if IGRID is less than or equal to 1. (Properties of H_2O, H^+, and $O_2(g)$ are never extrapolated.)

GRSD (NS,NMDAR,IFLN,ILLN,NAVB,ITYP,IFLAG) This routine searches the directory for the species and strips the data block of all comment lines denoted with an asterisk in column one.

GRSOL (NS,NMDAR,IFLN,ILLN,NAVB,IFLAG,ICC,NERR) This routine reads the data for the NS^{th} species from the data file MDAR and, if necessary, calls a routine to extrapolate the base point data over the temperature-pressure grid.

GSKNM (ULINE,UBUF,NBUF) The INPUT file is read to obtain key/subset names. ULINE contains an 80 character ASCII line input to GSKNM. UBUF and NBUF contain 16 character ASCII arrays of key/subset names and the number of entries in UBUF, respectively.

HAAR (T,P,GT,HT,ST,RH,ALPH,BETT) HAAR is a SUBCRT subroutine that calculates the thermodynamic properties of water relative to their values at the triple point of water. The temperature (T) and pressure (P) are input, whereas the relative Gibbs free energy (GT), enthalpy (HT), entropy (ST), density (RH), expansivity (ALPH), and compressibility (BETT) are output.

HFUNC This routine calculates the absolute entropy of the hydrogen ion at temperature T1.

IDENT (UNAM,IWAT,IO2) IDENT is a SUBCRT routine that identifies whether the species named in UNAM is water (IWAT = 1), oxygen gas (IO2 = 1), or an ion. If it is an ion, the SUPCRT equation of state parameters (Helgeson et al., 1981) are loaded for subsequent use by subroutine GIONS.

INTERP (ITMP,B,C,NPX,NERR) Find interpolating polynomial coefficients for two temperature ranges (0-100°C, 100-300°C). The independent variable is scaled temperature (TKGRDS).

KIRKW (TC,R,ALPH,BET,DAT,DBP,EP,DLNDPT,DLNDTP,D2LDTP) KIRKW is a SUBCRT subroutine that calculates the electrostatic properties of water. The temperature (TC), density (R), expansivity (ALPH), compressibility (BET), derivative of ALPH with respect to temperature at constant pressure (DAT), and dielectric constant (EP) are passed to KIRKW as input. KIRKW computes the derivative of EP with respect to pressure at constant temperature (DLNDPT), the derivative of EP with respect to temperature at constant pressure (DLNDTP), and the second derivative of EP with respect to temperature at constant pressure.

LINEUP This subroutine is a SUBCRT subroutine that reads the SUPCRT data file (GMI).

O2PROP (P,T,VO2,SO2,HO2,GO2) This is a SUBCRT subroutine that calculates the molal volume (VO2), entropy (SO2), enthalpy (HO2), and Gibbs free energy (GO2) of oxygen gas as a function of pressure (P) and temperature (T).

PREAC This routine prints the DATAO reaction from the data file.

PRRXGR This subroutine prints the calculated thermodynamic properties of a reaction at conditions corresponding to the temperature-pressure grid.

PRSGNG (NS) Subroutine PRSGNG prints a grid of thermodynamic properties for the chemical species indexed by NS. The printed grid corresponds to NGRID, which includes only those P-T points required to write a DATAO data block. Routine PRSGNT prints the corresponding NTEMP arrays.

PRSGNT (NTEMPS) This subroutine prints a grid of thermodynamic properties of a chemical species. The printed arrays correspond to the NTEMP grid, which may contain T-P points in addition to those required to write a DATAO block. Routine PRSGNG prints the corresponding NGRID arrays.

PSAT (TC,DPDT) PSAT is a real*8 SUBCRT function that calculates the saturation pressure (at TC) along the liquid vaper saturation curve of water and the slope of this surface ($DPDT=\partial P_{SAT}/\partial T$).

RETRGR (NS) Whether or not an NGRID data grid has been saved from the processing of a previous reaction is checked. If so, this grid is retrieved, and the IGRID flag for this reaction is set = 2 (else it will remain = 1 or = 0). NS is the species index in the current reaction.

RHO (T,P) The real*8 SUBCRT function RHO calculates the density of water at a given temperature (T) and pressure (P).

READEL The MDELEM table that contains various data on the elements is read from the data file by READEL.

READRX (ULABEL,NRTAL) This routine reads the DATAO reaction for all active species from the data file.

RSKL (ILOC,NMDAR,NOUTPT,NAUB,UBAF,NL) A direct access file, identified by unit number NMDAR, containing a block of information located at ILOC is read and stored in UBUF. NL specifies the number of entries in UBUF and NOUTPT identifies the unit number of the output file.

SAVEGR (NS,IFLSV) SAVEGR saves an NGRID data grid for future use. The species index (NS) is input and IFLSV is output with a value = 0 if the grid is not saved and = 1 if it is saved.

SETGHS (NS,GB,HB,SB) The species indexed by NS has the SUBCRT value for free energy (GB), enthalpy (HB), and entropy (SB) reset to those values obtained from the MDAR data block.

SHIFT (NSHIFT,NTEMPS,ISHIFT) This routine shifts the temperature grid to create openings for new entries (the base temperature and the transition temperatures).

SOLCRT (NS,ICC,QPGRID) This routine calculates the thermodynamic properties of the NS^{th} solid or gas: ICC = 0 if the calculation was done by heat capacity integration, ICC = 1 if the method degenerated to the constant enthalpy method (no heat capacity data), and ICC = 2 if data were insufficient to extrapolate from the base point.

SSKCD (ILOC,NMDAR,NOUTPT,NTTYO,NAVB,UINBF,NIN,ICOL,NMAX,NSPEC,IXSP,IDIRTB) The SSKCD subroutine reads a direct access file list to find subset or key names and matches them with names read from an input file. SSKCD computes the index to the next available position (IXSP) in the IDIRTB array and also assembles information and inserts it into

IDIRTB, which serves as the array of directory indices. SSKCD uses the following information as input:

ILOC	direct access file location of key/subset data.
NMDAR	unit number for the direct access file.
NOUTPT	unit number for the output file.
NTTYO	unit number for the console device.
NAUB	direct access file index to the next available block.
UINBF	16 character subset/file name array read from INPUT.
NIN	number of names in UINBF.
ICOL	column position in the second directory line for the keys/subsets.
NMAX	maximum number of keys/subsets on the directory line.
NSPEC	number of species in the current directory.

SUBCRT (UNAM,NGRID,PGRID,TCGRID,VPT,SPT,HPT,GPT) The SUBCRT routine functions as a driver to call various routines to evaluate the SUPCRT equations of state. (For further discussion, see Flowers, 1986.)

WATER (NGRID,IPT1,VW,SW,HW,GW) Subroutine WATER calculates the apparent thermodynamic properties (VW, SW, HW, and GW) of water at 1 bar and any specified temperature. NGRID and IPT1 (the number of P-T points on the pressure-temperature grid and the index of a particular ion, respectively) are used as input, and the volume (VW), entropy (SW), enthalpy (HW), and free energy (GW) of water are output from this routine.

In addition to the listed MCRT subroutines, the following subroutines are called by MCRT from the EQLIB (Wolery, 1983) software library:

EQLIB	READR
GETLU	RSCAL
LSQP	SCAL
OPENIN	STRIPL
OPENOU	TIMDAT

Appendix 4. FORTRAN CONVENTIONS USED IN MCRT.

To facilitate portability, the coding in MCRT has been written conforming to FORTRAN 77 standards and conventions (see ANSI X3.9-1978). All computation is done with single precision (real*8) and conforms to the FORTRAN naming conventions used throughout the EQ3/6 software package.* In addition to the various routines contained by MCRT, the code has to be linked to the EQ3/6 library (EQLIB) for several utility routines that are described elsewhere (Wolery, 1983). Except for the TIMDAT subroutine, which quizzes the operating system to determine the time and date and necessarily makes use of machine-dependent calls, there should be no machine dependencies built into MCRT.

Because most FORTRAN portability problems involve input and output functions, a short discussion of each of the subroutines that handle input and output and the processing involved with these files follows.

The primary data input file for MCRT (MDAR) is a standard formatted, direct access file. The MCRT driver reads from MDAR a directory and various other initializing information. Primary output from MCRT is written to a file called DFILE (Figure 1), which is a serial file in the format of a DATAO file. Subroutine READX searches a directory for the location of reactions. When a specific reaction is found, the information read from the reaction data block is used to determine subsequent calls to subroutines GRSD, GRAQS, GRSOL, and GHSCLC as needed and is the source of information that is passed to these routines. As briefly described in Appendix 3, subroutine GRSD reads the MDAR file for data blocks, and subroutines GRAQS and GRSOL extract data from aqueous and solid data blocks, respectively. All three subroutines also serve to process and verify data. Subroutine GHSCLC is called by GRAQS and GRSOL to compute and derive various requisite parameters from the data blocks.

---

*Variable names that begin with Q are logical variables. Variable names beginning with I, J, K, and N are integers; and names that start with U are character*8 variables. All others (names beginning with A-H, L, M, O, P, R-T, and V-Z) are real*8 variables or arrays.

Figure 1. Flowchart illustrating the relationships of the FORTRAN programs (in boxes) and data files of the EQ3/6 data base preprocessing package. More recent versions of the EQ6 code read the DATA1 file, not the DATA2 and DATA3 files as indicated in this figure. The DATA2 and DATA3 files are still produced by current versions of EQPT to allow the use of archival versions of EQ6 with current versions of the data base.

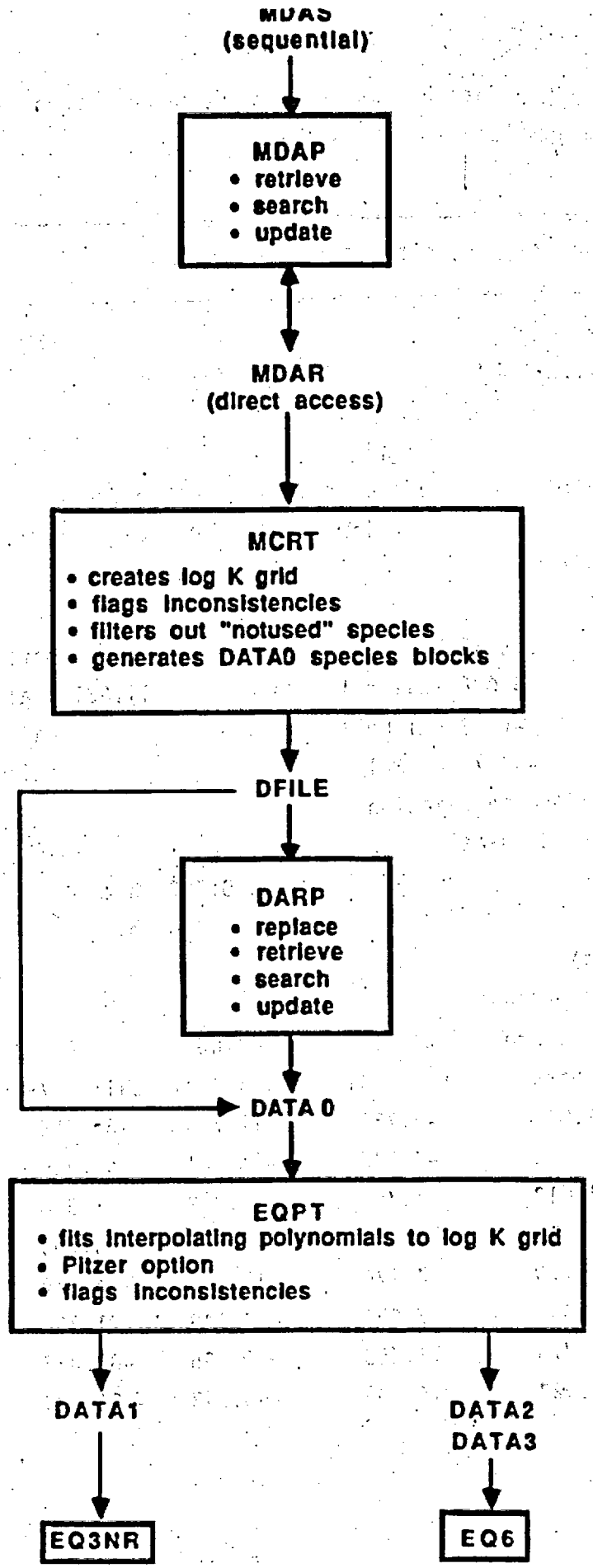
MDAS
(sequential)
MDAP
• retrieve
• search
• update
MDAR
(direct access)
MCRT
• creates log K grid
• flags inconsistencies
• filters out "notused" species
• generates DATA0 species blocks
DFILE
DARP
• replace
• retrieve
• search
• update
DATA 0
EQPT
• fits interpolating polynomials to log K grid
• Pitzer option
• flags inconsistencies
DATA1
DATA2
DATA3
EQ3NR
EQ6

Figure 2. Sample MDA data blocks for (a) an aqueous iron species and (b) a solid species.

```
+-----------------------------------------------------------------------
(a) Sample aqueous species data block
+-----------------------------------------------------------------------
fe+++                                                   date= 07/31/84
 entered by= d.l. axtell                 quality= good
 keys    = aux                 supcrt
 subsets= iron                 t-pgrid
     charge=    3.0             titr. factor=    0.0 eq/mol
   ion type=  1                    ion size=    9.0 a     hydr. no.=    0.0
  1 chemical elements
       1.000 fe
          temp=     298.15 k            press=      1.013 bars
         delg0=    -4.078 kcal/mol     delh0=    -11.821 kcal/mol
            s0=     -66.3 cal/mol/k      se=             cal/mol/k
            v0=    -43.78 cc/mol         cp=             cal/mol/k
  0 species in reference reaction
  5 species in data0 reaction
     -1.000  fe+++                          -0.500  h2o
      1.000  fe++                            1.000  h+
      0.250  o2(g)
 t-p data grid is present
*     temp      pressure     delg0       delh0       s0        v0
*      c         bars       kcal/mol    kcal/mol   cal/mol/k   cc/mol
     0.000      1.013       -5.733      -11.724    -65.955    -45.631
    25.000      1.013       -4.078      -11.821    -66.300    -43.780
    60.000      1.013       -1.762      -11.722    -65.990    -44.157
   100.000      1.013         .871      -11.641    -65.753    -47.500
   150.000      4.760        4.174      -12.122    -66.926    -57.190
   200.000     15.549        7.594      -14.149    -71.368    -79.327
   250.000     39.776       11.360      -20.495    -83.875   -137.057
   300.000     85.927       16.103      -43.243   -124.524   -346.963
```

```
source=[supcrt]
* base point data from [supcrt]
```

(b) sample solid species data block

```
+-----------------------------------------------------------------------
hematite                    fe2o3                    date= 06/15/84
 entered by= i.puigdomenech            quality= poor
 keys    = solid
 subsets= iron
  2 chemical elements
       2.000 fe              3.000 o
          temp=    298.150 k          press=      1.000 bars
         delg0=   -178.155 kcal/mol   delh0=    500.000 kcal/mol
            s0=     20.940 cal/mol/k     v0=      0.000 cc/mol
  1 heat capacity range(s) follow
      equation=                      cp or a=     23.490 cal/mol/k
             b=     18.600                c=     -3.550
             d=      0.000                e=      0.000
         limit=    950.000 k
  0 species in reference reaction
  4 species in data0 reaction
     -1.000  hematite                    -6.000  h+
      2.000  fe+++                        3.000  h2o
 t-p data grid is absent
 source=
 [supcrt] give delg0=-178.155, s0=20.94, cp=
                                a=23.49, b=18.6, c=-3.55  up to 950 k

 [wagman et al., 1982] give delg0=-177.39, s0=20.89, cp=24.821
 [robie et al., 1978] give delg0=-177.51, s0=20.89,
                                cp(298)=24.82, cp(600)=33.22
 [barin et al.] give s0=20.9, cp(298)=25.042, cp(600)=33.664
 [kubaschewski and alcock, 1979] give delg0=-176.73, s0=20.9
+-----------------------------------------------------------------------
```

Figure 3. Options available for MDAP program.

```
    ** MAIN **
1-end 2-prev menu 3-help
4-retrieve 5-add/replace 6-display 7-search
8-documentation 9- utilities

    main

end          stop execution
prev menu    redisplays this menu
help         display this page
retrieve     get specified species blocks and
              write to ascii file
add/replace  add new data or replace existing blocks
display      view data on terminal display
search       search for an arbitrary pattern
document     write serial output file -
              directory, references, or file description
utilities    allow stage number change,
              copy direct access file to serial file, or
              build direct access file from serial file


    ** RETRIEVE **
1-end 2-prev menu 3-help
4-subset 5-key 6-spec by el 7-spec by name 8-references 9-elements
10-comments

    retrieve

end          stop execution
```

prev menu	go back to previous menu
help	display this page
subset	select subset, write species blocks to serial file
key	select key, " " " " " "
spec by el	select element, " " " " " "
spec by name	input list of species names write species blocks to serial file
references	input list of reference citations write references to serial file
elements	write elements data block to serial file
comments	write comments block to serial file

** ADD/REPLACE **

1-end 2-prev menu 3-help

4-add data 5-replace data 6-instructions

add/replace

end	stop execution
prev menu	go back to main menu
help	display this page
add data	add new species or reference blocks
replace data	replace existing species, references, element, or comment blocks
instructions	output serial file showing structure of add/replace files

** DISPLAY **

1-end 2-prev menu 3-help

4-species 5-reference 6-subsets 7-keys

8-sub tally 9-key tally

display

end	stop execution
prev menu	go back to previous menu
help	display this page
species	display a species block
reference	display a reference block
subsets	list subsets in species blocks
keys	list keys in species blocks
sub tally	tally species per subset
key tally	tally species per key

** SEARCH **

1-end 2-prev menu 3-help
4-species 5-references

search

end	stop execution
prev menu	go back to previous menu
help	display this page
species	input a pattern, search selected species blocks, output blocks containing the pattern
references	input a pattern, search all references, output references containing the pattern

** DOCUMENTATION**

1-end 2-prev menu 3-help
4-dir. sum 5-dir. com 6-ref 7-d a file desc 8-help menus

documentation

end	stop execution
prev menu	go back to previous menu
help	display this page
dir. sum	write summary of directory to serial file
dir. com	write complete directory to serial file
references	write reference list to serial file
d a file desc	write direct access file description to serial file
help menus	write all help menus to a serial file

** UTILITIES **

1-end 2-prev menu 3-help

4-stage 5-d a to serial 6-serial to d a

utilities

end	stop execution
prev menu	go back to previous menu
help	display this page
stage	display current stage number, allow change
d a to serial	generate serial file mdas
serial to d a	build new direct access file from serial file

Figure 4. List of options available with DARP program.

help	display this message
header	write file header to file dahdr
direc	write directory to file dadir
sp look	requests species name, displays data block
sp get	requests species names writes species blocks to file daspc
add	requests file name, reads this file, adds species data blocks
replace	requests file name, replaces existing data with new data
stage	displays current stage number
params	writes data0 parameters to file dapar
refs	writes data0 references to file daref
end	exits this program

Figure 5. Flowchart for MCRT Program. MCRT expects an input file named INPUT and will produce an INPTS file which is equivalent to INPUT without any comment lines. MCRT also reads information from INPTS and from a random access input file named MDAR. If calculations that use the SUPCRT method are specified, MCRT requires a serial data file named GMI for the SUPCRT equation of state parameters. Output is written to serial files named OUTPUT and DFILE that contain run results and data, respectively.

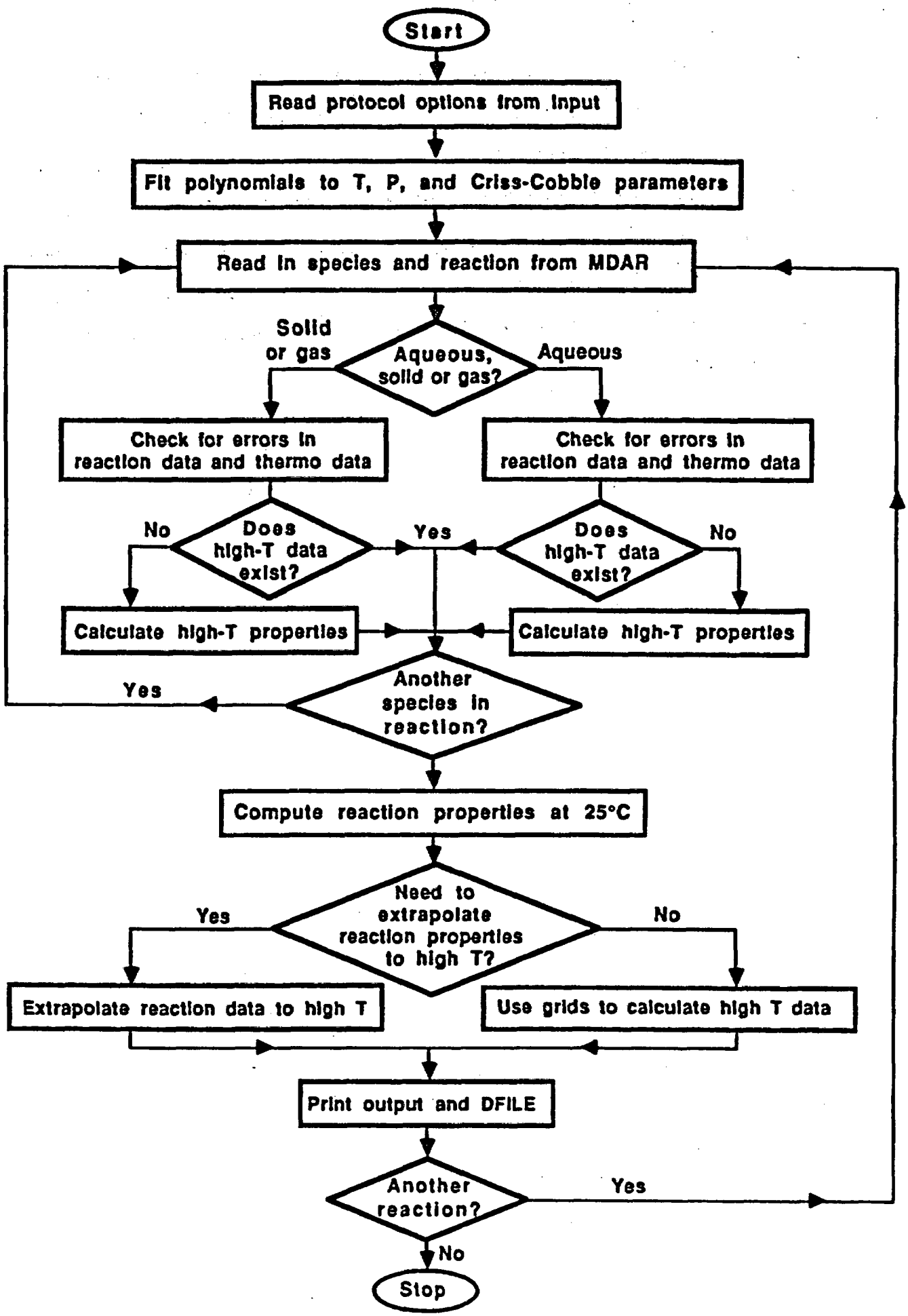
Start
Read protocol options from input
Fit polynomials to T, P, and Criss-Cobble parameters
Read in species and reaction from MDAR
Solid or gas
Aqueous, solid or gas?
Aqueous
Check for errors in reaction data and thermo data
Check for errors in reaction data and thermo data
No
Does high-T data exist?
Yes
Does high-T data exist?
No
Calculate high-T properties
Calculate high-T properties
Yes
Another species in reaction?
Compute reaction properties at 25°C
Yes
Need to extrapolate reaction properties to high T?
No
Extrapolate reaction data to high T
Use grids to calculate high T data
Print output and DFILE
Another reaction?
Yes
No
Stop

Figure 6. Sample input files for MCRT.

Example 1. Run entire MCRT master data base, generate DFILE output for elements, basis, auxiliary basis, solids, and gases.

```
 in.75       mcrt sample input file
  created 13oct87  mlc
*-----------------------------------------------------------
*                1    2    3    4    5    6    7    8
iopt1-8 =        1    0    0    0    0    0    0    0
iprn1-8 =        0    0    0    0    0    0    0    0
*
keys    =
subsets =
stop.
```

Example 2. Update elements table, run neptunium subset, and one alternate reaction for $NpO_2(s)$.

```
 in.75       mcrt sample input file
  created 13oct87  mlc
*-----------------------------------------------------------
*                1    2    3    4    5    6    7    8
iopt1-8 =        0    0    0    0    0    0    0    0
iprn1-8 =        0    0    0    0    0    0    0    0
*
keys    =
subsets = neptunium
+----------------------------------------------------------
npo2                        reaction = alternate
  5
    -1.0000  npo2                          1.0000  npo2++
     1.0000  h2o                          -2.0000  h+
    -0.5000  o2(g)
+----------------------------------------------------------
stop.
```

Example 3. Process only the four neptunium reactions below. The output for this MCRT job is listed in Figure 7.

```
 in.75      mcrt sample input file
  created 13oct87  mlc
*-----------------------------------------------------------------
*                1    2    3    4    5    6    7    8
iopt1-8 =        0    0    0    0    0    0    0    0
iprn1-8 =        0    0    0    0    0    0    0    0
*
keys    =
subsets =

+-----------------------------------------------------------------
npo2+                      reaction = alternate
  5
    -1.0000  npo2+                          1.0000  np++++
    -3.0000  h+                             1.5000  h2o
     0.2500  o2(g)
+-----------------------------------------------------------------
np(oh)4                    reaction = alternate
  4
    -1.0000  np(oh)4                        1.0000  np++++
    -4.0000  h+                             4.0000  h2o
+-----------------------------------------------------------------
npo2                       reaction = alternate
  4
    -1.0000  npo2                           1.0000  np++++
    -4.0000  h+                             2.0000  h2o
+-----------------------------------------------------------------
np(oh)4(s)                 reaction = alternate
  4
    -1.0000  np(oh)4(s)                     1.0000  np++++
    -4.0000  h+                             4.0000  h2o
+-----------------------------------------------------------------
stop.
```

Example 4. Run the DATA0 reaction for $NpO_2(s)$.

```
 in.75      mcrt sample input file
  created 13oct87  mlc
*-----------------------------------------------------------
*                1    2    3    4    5    6    7    8
iopt1-8 =        0    0    0    0    0    0    0    0
iprn1-8 =        0    0    0    0    0    0    0    0
*
keys    =
subsets =
+-----------------------------------------------------------
npo2
stop.
```

Figure 7. (a) OUTPUT file and (b) DFILE generated by processing the MCRT input file shown in the third example in Figure 6.

Figure 7(a).

```
 Supported by EQLIB, version 3245R141

   Copyright (c) 1987 The Regents of the University of California,
   Lawrence Livermore National Laboratory. All rights reserved.

 m     m   ccc   rrrr   tttttt
 m m m m  c      r   r     t
 m  m  m  c      rrrr      t
 m     m  c      r  r      t
 m     m   ccc   r   r     t

 mcrt.3245R75a
  supported by eqlib.3245R141

-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*
 in.75      mcrt sample input file
  created 13oct87  mlc
```

```
*-----------------------------------------------------------
*                1    2    3    4    5    6    7    8
iopt1-8 =        0    0    0    0    0    0    0    0
iprn1-8 =        0    0    0    0    0    0    0    0
*
keys    =
subsets =
+-----------------------------------------------------------
npo2+                      reaction = alternate
  5
    -1.0000  npo2+                          1.0000  np++++
    -3.0000  h+                             1.5000  h2o
     0.2500  o2(g)
+-----------------------------------------------------------
np(oh)4                    reaction = alternate
  4
    -1.0000  np(oh)4                        1.0000  np++++
    -4.0000  h+                             4.0000  h2o
+-----------------------------------------------------------
npo2                       reaction = alternate
  4
    -1.0000  npo2                           1.0000  np++++
    -4.0000  h+                             2.0000  h2o
+-----------------------------------------------------------
np(oh)4(s)                 reaction = alternate
  4
    -1.0000  np(oh)4(s)                     1.0000  np++++
    -4.0000  h+                             4.0000  h2o
+-----------------------------------------------------------
stop.
-*-*-*
```

temp c	press	delta g	delta h	entropy	volume
0.000	1.013	-218.828	-230.441	-6.054	0.000
25.000	1.013	-218.690	-230.145	-5.020	0.000
25.000	1.013	-218.690	-230.145	-5.020	0.000
60.000	1.013	-218.547	-229.562	-3.169	0.000
100.000	1.013	-218.475	-228.612	-0.478	0.000
150.000	4.760	-218.509	-227.721	1.764	0.000
200.000	15.549	-218.681	-226.238	5.076	0.000
250.000	39.776	-218.996	-225.038	7.487	0.000
300.000	85.927	-219.445	-223.438	10.409	0.000

base point data for np++++

tbase = 298.15 k, pbase = 1.013 bars
gbase = -120.200 kcal, hbase = -129.310 kcal
sbase = -92.970 cal/mol-k, sfbase = -30.556 cal/mol-k
se = 0.000 cal/mol-k, vbase = 0.000 cc

t-p data grid for np++++ calculated by criss-cobble method

temp c	press	delta g	delta h	entropy	volume
0.000	1.013	-122.525	-129.319	-93.001	0.000
25.000	1.013	-120.200	-129.310	-92.970	0.000
25.000	1.013	-120.200	-129.310	-92.970	0.000
60.000	1.013	-116.928	-129.631	-93.986	0.000
100.000	1.013	-113.114	-130.575	-96.662	0.000
150.000	4.760	-108.214	-131.613	-99.272	0.000
200.000	15.549	-103.196	-132.575	-101.422	0.000
250.000	39.776	-98.017	-134.690	-105.671	0.000
300.000	85.927	-92.671	-136.025	-108.108	0.000

base point data for h+

tbase = 298.15 k, pbase = 1.013 bars
gbase = 0.000 kcal, hbase = 0.000 kcal
sbase = 0.000 cal/mol-k, sfbase = 0.000 cal/mol-k
se = 0.000 cal/mol-k, vbase = 0.000 cc

t-p data grid for h+ calculated from the supcrt e-o-s

temp c	press	delta g	delta h	entropy	volume
0.000	1.013	0.000	0.000	0.000	0.000
25.000	1.013	0.000	0.000	0.000	0.000
60.000	1.013	0.000	0.000	0.000	0.000
100.000	1.013	0.000	0.000	0.000	0.000
150.000	4.760	0.000	0.000	0.000	0.000
200.000	15.549	0.000	0.000	0.000	0.000
250.000	39.776	0.000	0.000	0.000	0.000
300.000	85.927	0.000	0.000	0.000	0.000

base point data for h2o

tbase = 298.15 k, pbase = 1.013 bars

```
gbase =     -56.686 kcal,      hbase  =     -68.315 kcal
sbase =      16.714 cal/mol-k, sfbase =     -38.996 cal/mol-k
se    =       0.000 cal/mol-k, vbase  =      18.067 cc
```

t-p data grid for h2o calculated from the supcrt e-o-s

temp c	press	delta g	delta h	entropy	volume
0.000	1.013	-56.291	-68.766	15.138	18.018
25.000	1.013	-56.689	-68.315	16.718	18.068
60.000	1.013	-57.310	-67.684	18.717	18.323
100.000	1.013	-58.100	-66.962	20.766	18.797
150.000	4.760	-59.196	-66.044	23.070	19.645
200.000	15.549	-60.397	-65.096	25.174	20.833
250.000	39.776	-61.693	-64.093	27.163	22.545
300.000	85.927	-63.074	-62.979	29.147	25.287

base point data for o2(g)

```
tbase =     298.15 k,          pbase  =      1.013 bars
gbase =       0.000 kcal,      hbase  =      0.000 kcal
sbase =      49.003 cal/mol-k, sfbase =     -0.002 cal/mol-k
se    =       0.000 cal/mol-k, vbase  =      0.000 cc
```

t-p data grid for o2(g) calculated from the supcrt e-o-s

temp c	press	delta g	delta h	entropy	volume
0.000	1.013	1.218	-0.174	48.394	500.000
25.000	1.013	0.000	0.000	49.003	500.000
60.000	1.013	-1.729	0.248	49.788	500.000
100.000	1.013	-3.737	0.535	50.603	500.000
150.000	4.760	-6.291	0.900	51.522	500.000
200.000	15.549	-8.888	1.271	52.349	500.000
250.000	39.776	-11.524	1.646	53.102	500.000
300.000	85.927	-14.197	2.024	53.793	500.000

reaction properties by criss-cobble method

temp c	log k	delg0r	delh0r	dels0r	delv0r
0.	-9.74	12.17	-2.07	-52.14	500.00
25.	-9.86	13.46	-1.64	-50.62	500.00
60.	-9.99	15.22	-1.53	-50.29	500.00
100.	-10.12	17.28	-2.27	-52.38	500.00
150.	-10.29	19.93	-2.73	-53.55	500.00
200.	-10.47	22.67	-3.66	-55.65	500.00
250.	-10.68	25.56	-5.38	-59.14	500.00
300.	-10.91	28.61	-6.55	-61.35	500.00

udate is 16Nov87

- -

```
        1.000  np(oh)4
    +   4.000  h+
```

==

1.000 np++++
+ 4.000 h2o

base point data for np(oh)4

tbase =	298.15	k,	pbase =	1.013	bars
gbase =	-333.890	kcal,	hbase =	-376.375	kcal
sbase =	17.930	cal/mol-k,	sfbase =	-142.494	cal/mol-k
se =	0.000	cal/mol-k,	vbase =	0.000	cc

base point data for np++++

tbase =	298.15	k,	pbase =	1.013	bars
gbase =	-120.200	kcal,	hbase =	-129.310	kcal
sbase =	-92.970	cal/mol-k,	sfbase =	-30.556	cal/mol-k
se =	0.000	cal/mol-k,	vbase =	0.000	cc

t-p data grid for np++++ retrieved from previous calculation

base point data for h+

tbase =	298.15	k,	pbase =	1.013	bars
gbase =	0.000	kcal,	hbase =	0.000	kcal
sbase =	0.000	cal/mol-k,	sfbase =	0.000	cal/mol-k
se =	0.000	cal/mol-k,	vbase =	0.000	cc

t-p data grid for h+ retrieved from previous calculation

base point data for h2o

tbase =	298.15	k,	pbase =	1.013	bars
gbase =	-56.686	kcal,	hbase =	-68.315	kcal
sbase =	16.714	cal/mol-k,	sfbase =	-38.996	cal/mol-k
se =	0.000	cal/mol-k,	vbase =	18.067	cc

t-p data grid for h2o retrieved from previous calculation
t-p data grid for np(oh)4 calculated from reaction properties

temp c	press	delta g	delta h	entropy	volume
0.000	1.013	-333.580	-379.563	6.768	500.000
25.000	1.013	-333.890	-376.375	17.930	0.000
60.000	1.013	-334.773	-371.701	32.731	500.000
100.000	1.013	-336.405	-365.888	49.174	500.000
150.000	4.760	-339.451	-356.024	73.871	500.000
200.000	15.549	-343.909	-340.940	107.367	500.000
250.000	39.776	500.000	500.000	500.000	500.000
300.000	85.927	500.000	500.000	500.000	500.000

reaction properties by dquant method

temp c	log k	delg0r	delh0r	dels0r	delv0r
0.	11.29	-14.11	-24.82	-39.22	500.00
25.	9.58	-13.07	-26.19	-44.03	72.27

60.	7.47	-11.39	-28.67	-51.85	500.00
100.	5.34	-9.11	-32.53	-62.77	500.00
150.	2.86	-5.55	-39.76	-80.86	500.00
200.	0.40	-0.88	-52.02	-108.09	500.00
250.					
300.					

udate is 16Nov87

- -

```
      1.000  npo2
    + 4.000  h+

        ==

      1.000  np++++
    + 2.000  h2o
```

base point data for npo2

```
tbase =     298.15 k,          pbase  =      1.000 bars
gbase =    -244.220 kcal,      hbase  =   -253.109 kcal
sbase =      19.190 cal/mol-k, sfbase =    -29.815 cal/mol-k
se    =       0.000 cal/mol-k, vbase  =      0.000 cc
```

t-p data grid for npo2 calculated from heat capacity integration

temp c	press	delta g	delta h	entropy	volume
0.000	1.013	-243.811	-254.734	13.502	0.000
25.000	1.013	-244.220	-253.109	19.190	0.000
25.000	1.013	-244.220	-253.109	19.190	0.000
60.000	1.013	-245.025	-250.736	26.712	0.000
100.000	1.013	-246.256	-247.899	34.751	0.000
150.000	4.760	-248.230	-244.185	44.089	0.000
200.000	15.549	-250.654	-240.299	52.765	0.000
250.000	39.776	-253.497	-236.252	60.893	0.000
300.000	85.927	-256.735	-232.052	68.559	0.000

base point data for np++++

```
tbase =     298.15 k,          pbase  =      1.013 bars
gbase =    -120.200 kcal,      hbase  =   -129.310 kcal
sbase =     -92.970 cal/mol-k, sfbase =    -30.556 cal/mol-k
se    =       0.000 cal/mol-k, vbase  =      0.000 cc
```

t-p data grid for np++++ retrieved from previous calculation

base point data for h+

```
tbase =     298.15 k,          pbase  =      1.013 bars
gbase =       0.000 kcal,      hbase  =      0.000 kcal
sbase =       0.000 cal/mol-k, sfbase =      0.000 cal/mol-k
se    =       0.000 cal/mol-k, vbase  =      0.000 cc
```

t-p data grid for h+ retrieved from previous calculation

base point data for h2o

tbase =	298.15 k,	pbase =	1.013 bars
gbase =	-56.686 kcal,	hbase =	-68.315 kcal
sbase =	16.714 cal/mol-k,	sfbase =	-38.996 cal/mol-k
se =	0.000 cal/mol-k,	vbase =	18.067 cc

t-p data grid for h2o retrieved from previous calculation

reaction properties by heat capacity integration

temp c	log k	delg0r	delh0r	dels0r	delv0r
0.	-6.96	8.70	-12.12	-76.23	500.00
25.	-7.80	10.64	-12.83	-78.72	36.14
60.	-8.84	13.48	-14.26	-83.26	500.00
100.	-9.92	16.94	-16.60	-89.88	500.00
150.	-11.17	21.62	-19.52	-97.22	500.00
200.	-12.32	26.66	-22.47	-103.84	500.00
250.	-13.41	32.09	-26.62	-112.24	500.00
300.	-14.46	37.92	-29.93	-118.37	500.00

udate is 16Nov87

- -

1.000 np(oh)4(s)
+ 4.000 h+

==

1.000 np++++
+ 4.000 h2o

base point data for np(oh)4(s)

tbase =	298.15 k,	pbase =	1.000 bars
gbase =	-345.840 kcal,	hbase =	-383.766 kcal
sbase =	33.220 cal/mol-k,	sfbase =	-127.204 cal/mol-k
se =	0.000 cal/mol-k,	vbase =	0.000 cc

t-p data grid for np(oh)4(s) calculated from heat capacity integration

temp c	press	delta g	delta h	entropy	volume
0.000	1.013	-345.151	-387.041	21.748	0.000
25.000	1.013	-345.840	-383.766	33.220	0.000
25.000	1.013	-345.840	-383.766	33.220	0.000
60.000	1.013	-347.262	-379.181	47.760	0.000
100.000	1.013	-349.475	-373.941	62.614	0.000
150.000	4.760	-353.026	-367.391	79.087	0.000
200.000	15.549	-357.353	-360.841	93.718	0.000
250.000	39.776	-362.373	-354.291	106.878	0.000
300.000	85.927	-368.021	-347.741	118.835	0.000

base point data for np++++

tbase =	298.15 k,	pbase =	1.013 bars

```
    gbase =    -120.200 kcal,       hbase  =    -129.310 kcal
    sbase =     -92.970 cal/mol-k,  sfbase =     -30.556 cal/mol-k
    se    =       0.000 cal/mol-k,  vbase  =       0.000 cc

t-p data grid for np++++              retrieved from previous calculation

base point data for h+
    tbase =      298.15 k,           pbase  =       1.013 bars
    gbase =       0.000 kcal,        hbase  =       0.000 kcal
    sbase =       0.000 cal/mol-k,   sfbase =       0.000 cal/mol-k
    se    =       0.000 cal/mol-k,   vbase  =       0.000 cc

t-p data grid for h+                  retrieved from previous calculation

base point data for h2o
    tbase =      298.15 k,           pbase  =       1.013 bars
    gbase =     -56.686 kcal,        hbase  =     -68.315 kcal
    sbase =      16.714 cal/mol-k,   sfbase =     -38.996 cal/mol-k
    se    =       0.000 cal/mol-k,   vbase  =      18.067 cc

t-p data grid for h2o                 retrieved from previous calculation

              reaction properties by heat capacity integration

    temp c      log k      delgOr      delhOr      delsOr      delvOr

       0.        2.03      -2.54      -17.34      -54.20      500.00
      25.        0.82      -1.12      -18.80      -59.32       72.27
      60.       -0.72       1.09      -21.19      -66.88      500.00
     100.       -2.32       3.96      -24.48      -76.21      500.00
     150.       -4.15       8.03      -28.40      -86.08      500.00
     200.       -5.81      12.57      -32.12      -94.44      500.00
     250.       -7.35      17.58      -36.77     -103.90      500.00
     300.       -8.79      23.05      -40.20     -110.36      500.00
udate is            16Nov87

 there were
       0 reactions with errors
       0 errors encountered and
       0 warnings about g-h-s inconsistencies
```

Figure 7(b).

```
dfile
 mcrt.3245R75a
+-----------------------------------------------------------------------
npo2+
    entered by= mcrt (see below)        date= 16Nov87
        source= mcrt.3245R75a        quality= unspecified
        charge=   1.0            titr. factor=   0.0 eq/mol
     ion size=   4.0 a          hydr. number=   0.0
     2 chemical elements=
       1.000 np              2.000 o
     5 species in reaction=
      -1.000 npo2+           1.000 np++++          -3.000 h+
       1.500 h2o             0.250 o2(g)
*    log k grid (0-25-60-100/150-200-250-300 c) =
       -9.7384   -9.8632   -9.9854  -10.1182
      -10.2922  -10.4699  -10.6768  -10.9099
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000  500.0000  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* alternate reaction from input file  in.75
+-----------------------------------------------------------------------
np(oh)4
    entered by= mcrt (see below)        date= 16Nov87
        source= mcrt.3245R75a        quality= unspecified
```

```
      charge=   0.0          titr. factor=   0.0 eq/mol
    ion size=   4.0 a        hydr. number=   0.0
   3 chemical elements=
     1.000 np            4.000 h             4.000 o
   4 species in reaction=
    -1.000 np(oh)4        1.000 np++++        -4.000 h+
     4.000 h2o
*   log k grid (0-25-60-100/150-200-250-300 c) =
      11.2871    9.5778    7.4746    5.3355
       2.8639    0.4044  500.0000  500.0000
*   delvr grid (0-25-60-100/150-200-250-300 c) =
     500.0000   72.2736  500.0000  500.0000
     500.0000  500.0000  500.0000  500.0000
* alternate reaction from input file  in.75
+-----------------------------------------------------------------------
npo2              date= 18-jul-198
   entered by= mcrt (see below)        date= 16Nov87
      source= mcrt.3245R75a        quality= unspecified
      volume=     0.000 cc/mol
   2 chemical elements=
     1.000 np            2.000 o
   4 species in reaction=
    -1.000 npo2           1.000 np++++        -4.000 h+
     2.000 h2o
*   log k grid (0-25-60-100/150-200-250-300 c) =
      -6.9644   -7.8001   -8.8405   -9.9218
     -11.1682  -12.3155  -13.4069  -14.4570
*   delvr grid (0-25-60-100/150-200-250-300 c) =
     500.0000   36.1368  500.0000  500.0000
     500.0000  500.0000  500.0000  500.0000
* alternate reaction from input file  in.75
+-----------------------------------------------------------------------
np(oh)4(s)        date= 18-jul-198
   entered by= mcrt (see below)        date= 16Nov87
      source= mcrt.3245R75a        quality= unspecified
      volume=     0.000 cc/mol
   3 chemical elements=
     1.000 np            4.000 h             4.000 o
   4 species in reaction=
    -1.000 np(oh)4(s)     1.000 np++++        -4.000 h+
     4.000 h2o
*   log k grid (0-25-60-100/150-200-250-300 c) =
       2.0295    0.8186   -0.7176   -2.3190
      -4.1471   -5.8054   -7.3455   -8.7898
*   delvr grid (0-25-60-100/150-200-250-300 c) =
     500.0000   72.2736  500.0000  500.0000
     500.0000  500.0000  500.0000  500.0000
* alternate reaction from input file  in.75
```

```
+-----------------------------------------------------------------------
stop.

 there were
        0 reactions with errors
        0 errors encountered and
        0 warnings about g-h-s inconsistencies

              0 species in requested set which are not on data0
           (no data0 reaction/excluded set/error in species block)
```

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