UCRL-MA--110662-Pt.2

DE93 005826

EQPT, A Data File Preprocessor for the EQ3/6 Software Package: User's Guide and Documentation (Version 7.0)

Stephanie A. Daveler,

Thomas J. Wolery

MASTER

Preface

This report is the first in a set of documenting version 7.0 (version 3245.1090 under the old numbering system) of the EQ3/6 software package. This set includes:

I. The EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

II. The EQPT User's Guide (this report).

III. The EQ3NR Theoretical Manual and User's Guide (Wolery, 1992b).

IV. The EQ6 Theoretical Manual and User's Guide (Wolery and Daveler, 1992).

EQ3NR is the speciation-solubility code in the EQ3/6 package. EQ6 is a reaction path code and hence deals with the evolution of a water/rock system as reaction progress or time advances. EQPT is the EQ3/6 data file preprocessor.

The development of EQ3/6 has been supported by a number of programs concerned with geologic disposal of high level nuclear waste, including the Office of Nuclear Waste Isolation, the Salt Repository Project Office, the Waste Isolation Pilot Plant (through Sandia National Laboratory), the Nevada Nuclear Waste Storage Investigations, and the Yucca Mountain Site Characterization Project. Documentation for the package is aimed at satisfying the requirements of the U.S. Nuclear Regulatory Commission for software used for this purpose (Silling, 1983).

The Lawrence Livermore National Laboratory has not certified that EQ3/6 constitutes approved code for the conduct of quality affecting work for the Yucca Mountain Project.

No source codes or data files are reproduced in this report, nor are any computer media containing such items a part of this report or any of the other reports documenting this version of EQ3/6. The software itself must be obtained as described below.

The examples presented in this series of reports correspond to version 7.0 of the software and the R10 set of supporting thermodynamic data files. As of the date of publication of this report, the most recent version of the software is version 7.1 (containing bug fixes, but no enhancements), and the most recent set of data files is R16.

Agencies of the United States Government and their contractors may obtain copies of the software and its documentation from:

Energy Science and Technology Software Center
P. O. Box 1020
Oak Ridge, TN 37831-1020

Telephone: (615) 576-2606

Requests to obtain the software under a licensing agreement should be addressed to:

Technology Transfer Initiatives Program, L-795
Attn: Diana (Cookie) West
Lawrence Livermore National Laboratory
P.O. Box 808
Livermore, CA 94550

Telephone: (510) 423-7678
Fax: (510) 422-6416
Secretary: (510) 422-6416

Comments and questions concerning EQ3/6 exclusive of the thermodynamic data base should be addressed to the code custodian:

Thomas J. Wolery, L-219
Lawrence Livermore National Laboratory
P.O. Box 808
Livermore, CA 94550

E-mail: wolery1@llnl.gov
Telephone: (510) 422-5789
Fax: (510) 422-0208
Secretary: (510) 423-2970

Comments and questions which concern the EQ3/6 thermodynamic data base should be addressed to the data base custodian:

James W. Johnson, L-219
Lawrence Livermore National Laboratory
P.O. Box 808
Livermore, CA 94550

E-mail: johnson@s05.es.llnl.gov
Telephone: (510) 423-7352
Fax: (510) 422-0208
Secretary: (510) 423-2970

Contents

Glossary of Symbols

a, a'	Symbols used to represent cations in the notation of Harvie, Møller, and Weare (1984); see also X, X'.
a_i	Thermodynamic activity of the i-th aqueous solute species.
a_w	Thermodynamic activity of water.
$a_{\sigma\psi}$	Thermodynamic activity of the σ-th component of the ψ-th solid solution phase.
$\mathring{a}$	Generalized hard core diameter or "ion size" in aqueous solution.
$\mathring{a}_i$	Hard core diameter or "size" of the i-th aqueous solute species.
$A_{\gamma,10}$	Debye-Hückel A parameter used in writing expressions for $log_{10}\,\gamma_i$.
A_ϕ	Debye-Hückel A parameter used in writing expressions for $ln\,a_w$.
b_{sr}	Stoichiometric reaction coefficient, the number of moles of the s-th aqueous species appearing in the r-th aqueous reaction; it is negative for reactants and positive for products.
$b_{s\phi}$	Stoichiometric reaction coefficient, the number of moles of the s-th aqueous species appearing in the reaction for the dissolution of the ϕ-th pure mineral; it is negative for reactants and positive for products.
b_{sg}	Stoichiometric reaction coefficient, the number of moles of the s-th aqueous species appearing in the reaction for the dissolution of the g-th gas species; it is negative for reactants and positive for products.
b	A parameter theoretically equivalent to the product $\mathring{a}B_\gamma$ and appearing in Pitzer's equations with an fixed value of 1.2.
B_γ	Debye-Hückel B parameter used in writing expressions for $ln\,\gamma_i$ or $log_{10}\,\gamma_i$.
C^ϕ_{MX}	Third order interaction coefficient for cation M and anion X.
e^-	The electron. In common thermodynamic formalism, this is usually a hypothetical species, not a real one.
Eh	Redox potential, volts.Theoretical equilibrium electrical potential of a redox couple; $Eh = \frac{2.303RT}{4F}(log f_{O_2} - 4pH - 2 log a_w - log K_{\mathrm{Eh}})$, where f_{O_2} is understood to be the hypothetical equilibrium oxygen fugacity in aqueous solution.
$f(I)$	Debye-Hückel f function.
$f'(I)$	Debye-Hückel f' function; $f'(I) = df/dI$.
f_{O_2}	Oxygen fugacity.
F	The Faraday constant, 23062.3 cal/equiv-volt.
g	Subscript denoting a gas species.
$g(x)$	A function used to describe the ionic strength dependence of the second order interaction coefficient in Pitzer's equations.
I	Ionic strength.

K	Thermodynamic equilibrium constant.
K_{Eh}	Thermodynamic equilibrium constant for the half-reaction $2H_2O_{(l)} = O_{2(g)} + 4H^+ + 4e^-$
m_i	Molal concentration of the i-th aqueous solute species.
N, N'	Symbols denoting neutral species.
N_ψ	Site-mixing parameter for the ψ-th solid solution. If $N_\psi = 1$, the model is equivalent to a molecular-mixing model.
O_2	Oxygen gas; in aqueous solution, this refers to a hypothetical species similar to e^-; also symbolized as s_B.
$p_{k\psi}$	The k-th parameter used to compute the interaction coefficients W_ψ, $W_{i\psi}$, $W_{ij\psi}$, which in turn are used to compute the activity coefficients of end-member components in the ψ-th solid solution.
P	Pressure, bars.
pe	Logarithm of the hypothetical electron activity; $pe = F\,Eh/(2.303\,RT)$.
r	Subscript denoting an aqueous reaction.
R	The gas constant, 1.98726 cal/mol-°K.
s	Subscript denoting an aqueous species ($s = w$ implies $H_2O_{(l)}$).
s'	Subscript denoting s in the range from 1 to s_Q, excluding the cases $s = w$ and $s = s_B$.
s''	Subscript implying the species formally associated with the aqueous reaction designated by r ($s'' = r + s_B$).
s_B	Subscript denoting the hypothetical aqueous species $O_{2(g)}$.
s_Q	The total number of aqueous master species; depending on the problem at hand, s_Q is equal to or greater than s_B.
s_T	Total number of aqueous species.
T	Temperature, °K.
w	Subscript denoting water (e.g., a_w, the activity of water).
$W_\psi, W_{i\psi}, W_{ij\psi}$	Interaction coefficients used to compute the activity coefficients of end-member components in the ψ-th solid solution.
x	A general algebraic variable.
x_w	Mole fraction of water in aqueous solution.
$x_{\sigma\psi}$	Mole fraction of the σ-th end member of the ψ-th solid solution.
X, X'	Symbols denoting anions.
z_s	Electrical charge of the s-th aqueous species.

2.303	Symbol for and approximation of *ln* 10. As an approximation, this is not in general sufficiently accurate approximation; this constant should be computed to full machine accuracy in a computer code in order to avoid both inaccuracy and inconsistency.
α_1, α_2	Parameters appearing in Pitzer's equations.
$\beta^{(0)}_{MX}, \beta^{(1)}_{MX}, \beta^{(2)}_{MX}$	Observable second order interaction coefficient parameters for cation *M* and anion *X*.
γ_i	Molal activity coefficient of the *i*-th aqueous solute species.
ε	Subscript denoting a chemical element.
ε_T	Total number of chemical elements in a system.
ζ_{NMX}	Observable third order interaction coefficient for neutral species *N*, cation *M*, and anion *X*.
$\theta_{MM'}$	Harvie, Møller, and Weare's (1984) notation for $^S\theta_{MM'}$.
$^S\theta_{MM'}$	Observable short-range second order interaction coefficient for cations *M* and *M'*.
$\lambda_{ij}(I)$	Second-order interaction coefficient for the *i*-th and *j*-th aqueous solute species; in general, this is a function of the ionic strength.
$\lambda'_{ij}(I)$	The derivative of $\lambda_{ij}(I)$ with respect to ionic strength.
$\lambda^{(0)}_{MX}, \lambda^{(1)}_{MX}, \lambda^{(2)}_{MX}$	Second order interaction coefficient parameters for cation *M* and anion *X*.
λ_w	Rational (mole fraction) activity coefficient of water; $a_w = \lambda_w x_w$.
$\lambda_{\sigma\psi}$	Rational (mole fraction) activity coefficient of the σ-th end member of the ψ-th solid solution.
$^E\lambda_{MM'}(I)$	The electrostatic part of $\lambda_{MM'}(I)$.
$^S\lambda_{MM'}$	The short-range part of $\lambda_{MM'}(I)$; treated as a constant.
μ_{ijk}	Third-order interaction coefficient for the *i*-th, *j*-th, and *k*-th aqueous solute species.
σ, σ'	Symbols denoting end-member components of a solid solution.
$\sigma_{T,\psi}$	Total number of end members in the ψ-th solid solution.
ϕ	Subscript denoting a pure mineral.
ψ	Subscript denoting a solid solution.
$\psi_{MM'X}$	Observable third order interaction coefficient for cations *M* and *M'* and anion *X*.

EQPT, A Data File Preprocessor for the EQ3/6 Software Package: User's Guide and Related Documentation (Version 7.0)

Abstract

EQPT is a data file preprocessor for the EQ3/6 software package. EQ3/6 currently contains five primary data files, called **data0** files. These files comprise alternative data sets. These data files contain both standard state and activity coefficient-related data. Three (**com, sup,** and **nea**) support the use of the Davies or B-dot equations for the activity coefficients; the other two (**hmw** and **pit**) support the use of Pitzer's (1973, 1975) equations. The temperature range of the thermodynamic data on these data files varies from 25°C only to 0-300°C. The principal modeling codes in EQ3/6, EQ3NR and EQ6, do not read a **data0** file, however. Instead, these codes read an unformatted equivalent called a **data1** file. EQPT writes a **data1** file, using the corresponding **data0** file as input. In processing a **data0** file, EQPT checks the data for common errors, such as unbalanced reactions. It also conducts two kinds of data transformation. Interpolating polynomials are fit to data which are input on temperature grids. The coefficients of these polynomials are then written on the **data1** file in place of the original temperature grids. A second transformation pertains only to data files tied to Pitzer's equations. The commonly reported *observable* Pitzer coefficient parameters are mapped into a set of *primitive* parameters by means of a set of conventional relations. These primitive form parameters are then written onto the **data1** file in place of their observable counterparts. Usage of the primitive form parameters makes it easier to evaluate Pitzer's equations in EQ3NR and EQ6. EQPT and the other codes in the EQ3/6 package are written in FORTRAN 77 and have been developed to run under the UNIX operating system on computers ranging from workstations to supercomputers.

1. Introduction

EQPT is a data file preprocessor. It is part of the EQ3/6 software package (see Wolery, 1992a). It replaces the EQTL code (see Wolery, 1983). This report describes EQPT in version 7.0 (version 3245.1090 in the old numbering system) of this package (see the EQ3/6 Package Overview and Installation Guide, Wolery, 1992a). Other codes in the package include EQ3NR (Wolery, 1992b), a speciation-solubility code, and EQ6 (Wolery and Daveler, 1992), a reaction path code. The relationship of EQPT code to EQ3NR, EQ6, and the set of supporting thermodynamic data files is shown in Figure 1. This figure depicts the flow of information involving these codes. At present, there are five distinct data files, denoted by the suffixes **com**, **sup**, **nea**, **hmw**, and **pit**. These are provided in formatted ASCII and are called **data0** files. The full name of such a file ordinarily has a form exemplified by **data0.com.R10**, where the **R10** is a stage number (a configuration control identifier). On some systems, it is necessary to compress this to a form exemplified by **da0com.R10** (see Wolery, 1992a).

The user of EQ3NR or EQ6 must select which of the five data files is most appropriate to a given problem. Each data file corresponds to a general formalism for treating the activity coefficients of aqueous species and contains the relevant activity coefficient data as well as standard state thermodynamic data (e.g., dissociation constants). The **com**, **sup**, and **nea** data files are specific to a general extended Debye-Hückel formalism and can be used by EQ3NR and EQ6 with either the Davies (1962) equation or the B-dot equation (Helgeson, 1969). These equations are only

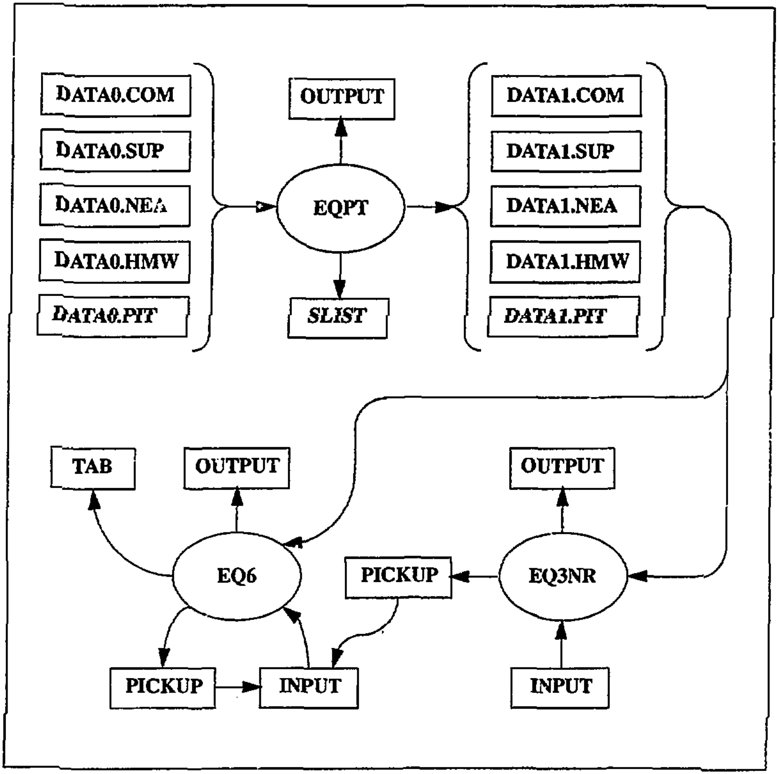

Figure 1. The flow of information among the computer codes EQPT, EQ3NR, and EQ6. Computer codes are represented by ovals, files by rectangles.

valid in relatively dilute solutions. The **hmw** and **pit** data files are specific to the formalism proposed by Pitzer (1973, 1975) and can be used to model solutions extending to high concentrations. However, the scope of chemical components covered is smaller. The temperature limits on the data files also vary, from 25°C only to 0-300°C.

Some important data file characteristics are given in Table 1. The **com** (for "composite") data file is the largest of the three data files specific to the extended Debye-Hückel formalism. It is a product of Lawrence Livermore National Laboratory (LLNL) drawing on many data sources, including those on which the other four data files are based. The **sup** data file is based entirely on SUPCRT92 (Johnson, Oelkers, and Helgeson, 1992), a software package and thermodynamic data base founded on the work of Helgeson and Kirkham (1974ab, 1976), Helgeson et al. (1978), Tanger and Helgeson (1988), Shock and Helgeson (1988, 1989, 1990), Shock, Helgeson, and Sverjensky (1989), Johnson and Norton (1991), and Shock et al. (1992). The **nea** data file is based entirely on Grenthe et al. (1989, draft report), a product of the Data Bank of the Nuclear Energy Agency of the European Community. This work has recently been published as Grenthe et al. (1992). The **hmw** data file is based on Harvie, Møller, and Weare (1984). The **pit** data file is based mostly on data summarized by Pitzer (1979). All five data files are maintained at LLNL in a relational data base described by Delany and Lundeen (1991). This relational data base is part of the Yucca Mountain Site Characterization Project's Technical Data Base.

The **sup** data file has a high level of internal consistency among the standard state thermodynamic data. In addition, the temperature-pressure dependence of these data are represented by a suite of equations of state for minerals, gases, and aqueous species that are well established in the geochemical literature (see references noted above). This data file covers a wide range of chemical elements and species of interest in the study of rock/water interactions (e.g., components which make up the major rock-forming and ore-forming minerals). It also includes a large number of organic species, mostly of small carbon number (C_2-C_8). The **nea** data file is something of a specialty item. Its strongest point is a thorough representation of the thermodynamics of uranium species.

The **com** (composite) data file encompasses a much broader range of chemical elements and species. It includes the data found on the **sup** and **nea** data files, with preference given to data from the former in cases of overlap. It also includes some data found in the **hmw** data file, as well as other data which do not appear in any of the other data files. Some of these data are estimates based on correlations or extrapolations (as to higher temperature), and are not tied directly to experimental measurements. The **com** data file thus represents a melange of data, which by its nature offers less assurance of internal consistency. However, this offers the only means presently available for modeling aqueous solutions with a high degree of compositional complexity, such as the fluids expected to be found in and about a facility for the geologic disposal of industrial or nuclear waste (e.g., the potential repository for high-level nuclear waste at Yucca Mountain, Nevada).

The **hmw** data file has the highest degree of internal consistency of any of the five data files, including mutual consistency of activity coefficient data and standard state thermodynamic data. It can be applied to dilute waters or concentrated brines. However, it only treats the set of components present in the "sea-salt" system (the major cations and anions present in seawater, including carbonate and bicarbonate). The geochemically important components aluminum and silica are not included. Also, this data file is limited to a temperature of 25°C. The **pit** data file can also be applied to concentrated brines. It covers a larger set of components, but these mostly involve other cations and anions of strong electrolytes. Examples include lithium and bromide. This data file nominally covers the temperature range of 0-100°C. However, it represents a melange of data, not a carefully crafted internally consistent set.

What one can do with EQ3NR or EQ6 depends to a high degree on what is on the supporting data file and if so how the species and reactions on the data file are organized. For example, iron does

Table 1. Major characteristics of the current five EQ3/6 data files ("R10" versions).

File Name (Suffix)	Source	Activity Coefficient Formalism	Temperature Limits	Number of Chemical Elements	Number of Basis Species	Number of Aqueous Species	Number of Pure Minerals	Number of Solid Solutions	Number of Gas Species
com	GEMBOCHS (LLNL)	Extended Debye-Hückel	0-300°C	78	147	852	886	12	76
sup	SUPCRT92	Extended Debye-Hückel	0-300°C	69	105	315	130	0	16
nea	NEA draft report	Extended Debye-Hückel	0-300°C	32	50	158	188	0	76
hmw	Harvie, Møller, and Weare (1984)	Pitzer's Equations	25°C only	9	13	17	51	0	3
pit	Pitzer (1979)	Pitzer's Equations	0-100°C	52	62	68	381	0	38

not appear on the **hmw** data file, so this file can not be used to model the behavior of iron in brine-mineral systems. Similarly, uranium does not appear on the **sup** data file. Even if a chemical element does appear on a given data file, the corresponding species required for a given problem must also appear on it.

EQPT processes these **data0** files one at a time (looking for a file named simply **data0**, though these files are normally stored under names which include the relevant suffixes) and writes a corresponding unformatted data file, which is called simply **data1**. These are also normally stored under names including the relevant suffixes (e.g., **data1.com.R10**). To run EQ3NR or EQ6, the user must provide one of these files, which is known to each code simply as **data1**.

To process all five data files running EQPT directly thus requires the user to do a lot of renaming of the various files. This is not very convenient. The export package includes a UNIX shell script called **runeqpt** to make the job easier. This script and its usage are described in the EQ3/6 Package Overview and Installation Manual (Wolery, 1992a). Caution: this script may require local modification, as it needs data for the location within the local directory structure of both the **data0** files and the EQPT executable file The script is invoked by commands of the form:

```
runeqpt R10 all
```

(processes all **data0** files with stage number **R10**) or:

```
runeqpt R10 com
```

(processes only the data file **data0.com.R10**).

The **runeqpt** script renames all of the files produced, incorporating the data file key and stage number of each **data0** file processed. For example, the **data1** file for **data0.com.R10** will be named **data1.com.R10**, and the slist file will be named **slist.com.R10**. Naming the **data1** files in this manner facilitates running EQ3NR and EQ6 under the shell script **runeq36** (se the EQ3/6 Package Overview and Installation Manual, Wolery, 1992a).

Note that EQPT in its present form has no **input** file and no user options. In porting EQ3/6, the user need only run EQPT on each of the **data0** files provided. This should be a simple process. The actual purpose of this manual is to comply with the NUREG documentation requirements (Silling, 1983) and to provide information concerning the data file structure and its processing that might be useful to users who modify the original data files or make up data files of their own.

The data file preprocessor EQPT performs a number of functions. It checks the composition, charge, and reaction coefficient data on a **data0** file for internal consistency and fits interpolating polynomials to various temperature dependent data which are organized on the **data0** file on temperature grids. Such data include certain activity coefficient parameters, such as Debye-Hückel $A_{\gamma,10}$ and B_γ, and the equilibrium constants for the reactions represented on the data file. In addition, in the case of data files specific to the formalism of Pitzer's equations, observable interaction coefficients are mapped to a set of conventionally defined primitive interaction coefficients. EQPT then writes the **data1** file corresponding to the input **data0** file. It also writes a formatted equivalent, called **data1f**. The user may examine this if desired, but this file is not otherwise used for any purpose. In addition, EQPT writes to a screen file and an **output** file, both of which are generally significant only if an error condition is encountered. In addition, it writes an **slist** (species list) file. This is very useful to the user, as it lists the species that are represented on the data file and identifies which species are in the strict and auxiliary basis sets. If no errors are encountered, the **output** and **slist** files are nearly identical.

When processing data files corresponding to the Pitzer formalism, EQPT also writes two files called **dpt1** and **dpt2**. The former contains the original, observable Pitzer coefficient data. The latter contains the equivalent conventional primitive Pitzer coefficient data. These files are vestigial and may be discarded.

Chapter 2 describes the organization of species and reactions. This is centered on the concept of a set of basis species, including the concept of an auxiliary basis set. Chapter 3 describes the types of thermodynamic data present on the data files, how they are represented, and how they are transformed or mapped by EQPT when it writes the **data1** file. Chapter 4 describes the structure of the **data0** files and the corresponding **data1** files. Chapter 5 describes the code architecture. Appendix A contains a glossary of the major code variables. The source code modules are listed and briefly described in Appendix B (for a similar treatment of EQLIB modules, see Appendix B of the EQ3/6 Package Overview and Installation Guide, Wolery, 1992a). Appendix C contains a list of error messages generated by EQPT modules, along with related notes (see Appendix C of Wolery, 1992a, for a similar list for EQLIB modules). Appendix D contains notes pertaining to known bugs and such. Appendix E contains the **slist** files for the **com** and **hmw** data files.

EQPT and the other codes in the EQ3/6 software package are written in FORTRAN 77 and have been developed to run under UNIX operating systems on computers ranging from workstations to supercomputers, including Sun SPARCstations, VAXes (ULTRIX operating system), Alliants (CONCENTRIX operating system), and Crays (UNICOS operating system). They are fairly readily portable to VAX computers running the non-UNIX VMS operating system. They may be portable as well to 386 and 486 PCs. Platforms used at LLNL include Sun SPARCstations and an Alliant FX/80. For details concerning platforms, see the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

2. Organization of Species and Reactions

The concept of a set of basis species is critical to the data base organization. EQ3/6 further utilizes the concept of a set of auxiliary basis species. The purpose of the present chapter is to present a brief description of these concepts as they pertain to the structure of the EQ3/6 data file. These concepts are discussed in more detail and from the viewpoint of the code user in Chapter 5 of the EQ3NR Theoretical Manual and User's Guide (Wolery, 1992b).

A *basis* species is a species used as a general "building block" for writing chemical reactions in a standardized format that is convenient for chemical modeling. Each species appearing in a reaction is a basis species, except for one non-basis species which is associated with the reaction itself. In the format used in EQ3/6, each reaction always destroys this associated non-basis species. This is illustrated by the reaction:

$$CaHCO_3^+ = Ca^{2+} + HCO_3^- \tag{1}$$

where the ion pair $CaHCO_3^+$ is the associated (non-basis) species and the other three species appearing in the reaction are basis species. Because it is a non-basis species, $CaHCO_3^+$ does not appear in any other reaction on the data file.

Each basis species on an EQ3/6 data file must be an aqueous species. In addition, it should usually be composed of no more than three chemical elements, no more than one of which may be other than oxygen or hydrogen. Thus, $H_2O_{(l)}$, H^+, Na^+, Ca^{2+}, Cl^-, UO_2^{2+}, SO_4^{2-}, and HCO_3^- are examples of species which can be and are used as basis species. Species such as $CaHCO_3^+$ and $UO_2CO_{3(aq)}$ should not appear as basis species on the data file, because they do not meet this requirement. However, they can be switched into the active basis set via basis switching options available in EQ3NR and EQ6 (See Wolery, 1992b, and Wolery and Daveler, 1992). These restrictions on basis species composition are employed in order to insure that the corresponding mass balance totals for an aqueous solution pertain to physically measurable quantities (see Chapter 5 of the EQ3NR Theoretical Manual and User's Guide, Wolery, 1992b). These are not hard and fast rules. An exception will be noted later in this chapter.

Each *strict* basis species is associated one-to-one with a a chemical element, with the exception of one which is associated with a redox parameter. The strict basis species used to write oxidation-reduction reactions in EQ3/6 is O_2, which is treated as a fictive aqueous species. The associated redox parameter is the oxygen fugacity. A strict basis set is a minimal basis set; it represents the smallest possible basis set for a given set of chemical components, and corresponds to the case of complete chemical equilibrium within the aqueous solution. A strict basis species has no associated reaction.

It is advantageous to allow for an *auxiliary* basis set. Its members are usually similar species, most often representing a chemical element in a different oxidation state. An auxiliary basis set permits consideration of disequilibrium between a species in this set and a related species in the strict basis set. They are related by a reaction that is associated with each member of the auxiliary basis set. For example, if Fe^{2+} is in the strict basis set and Fe^{3+} is in the auxiliary basis set, the reaction may be written as:

$$Fe^{3+} + \frac{1}{2}H_2O = Fe^{2+} + H^+ + \frac{1}{2}O_2 \qquad (2)$$

The auxiliary basis set is preserved in its original form by EQPT. In EQ3NR or EQ6, an auxiliary basis species may be eliminated from the *active* basis set by using the associated reaction to rewrite all other reactions originally written in terms of that species so that it no longer appears in them. For example, the reaction:

$$FeCl_3^o = Fe^{3+} + 3Cl^- \qquad (3)$$

is combined with eq (2) to obtain:

$$FeCl_3^o + \frac{1}{2}H_2O = Fe^{2+} + H^+ + \frac{1}{2}O_2 + 3Cl^- \qquad (4)$$

The ferric trichloride complex then appears to be a complex of the ferrous ion. The mass action equation corresponding to reaction (2) is activated as a constraint, so the ferric ion itself (in addition to its complexes) is treated as a "complex" of the ferrous ion.

In a geochemical modeling code such as EQ3NR or EQ6, the incorporation of an auxiliary basis set allows the code user to treat a species in this set as either a basis species or as a non-basis (dependent) species. If it is treated as a basis species, an additional mass balance relation is defined and the reaction relating the species to a corresponding basis species is allowed to be in disequilibrium (the degree of which can be calculated). Otherwise, this auxiliary basis species (and all of its dependent species) are treated as dependent species of that corresponding basis species. They are then folded into the mass balance for that species.

Each reaction is associated with a non-basis or auxiliary basis species, and each non-basis or auxiliary basis species has an associated reaction. If an auxiliary basis species is to be treated as a basis species in EQ3NR or EQ6, its associated reaction is ignored, except for the purpose of computing the degree of disequilibrium. If an auxiliary basis species is eliminated from the active basis set, it is treated as a non-basis species, and its reaction is utilized in the same manner as that of a non-basis species. Thus, one should place a species in the auxiliary basis set if one wishes to allow the possibility of treating the corresponding reaction in a state of disequilibrium.

As a general rule, reactions of non-basis on an EQ3/6 data file should be written so that the associated species is transformed into the chemically most similar basis species. This means that one should attempt to preserve such things as oxidation states or molecular moieties (structural groups), on the theory that the associated reactions are more likely to be in a state of equilibrium. For example, one would write on the data file reaction (3) for the ferric trichloride complex (yielding the ferric ion). If one wrote instead reaction (2) (yielding the ferrous ion), this complex would always be treated as falling under the mass balance for the ferrous ion. This would be erroneous in the case in which ferric-ferrous disequilibrium is assumed and a separate mass balance is employed for the ferric ion.

It is not always possible to satisfy this guideline. The currently existing data files include ferrous and ferric ions as basis species, but not a dissolved iron species in the zero oxidation state. Metallic iron (Fe) requires a reaction, but there is no corresponding basis species on these files in the zero oxidation state. The reaction is therefore written instead with the minimal amount of oxidation-reduction:

$$iron + \frac{1}{2}O_2 + 2H^+ = Fe^{2+} + H_2O_{(l)} \tag{5}$$

Note that if the data file did contain a dissolved iron species in the zero oxidation state, such a species should be placed in the basis set.

A number of organic species appear in the **sup** and **com** data files. HCO_3^- is the strict basis species corresponding to the element carbon. The following carbon-bearing species appear on these data files as auxiliary basis species:

- ortho-phthalate ('o-(phth)--'; **com** file only)
- acetic acid ('acetic acid(aq)')
- acetone(aq)
- benzene(aq)
- ethane(aq)
- glycine(aq)
- methanamine(aq)
- methane(aq)
- methanol(aq)

Each of these except dissolved methane ($CH_{4(aq)}$) is treated as the parent of other organic species. For example, acetic acid is ($CH_3COOH_{(aq)}$) taken as the parent of propanoic acid ($CH_3CH_2COOH_{(aq)}$), the reaction for the latter being:

$$propanoic\ \ acid(aq) + \frac{1}{2}O_2 = \frac{3}{2}acetic\ \ acid(aq) \tag{6}$$

Here there is an attempt to preserve organic moieties (in this case, the -$COOH$ group). Similarly, glycine (the simplest amino acid, $CH_2NH_3COOH_{(aq)}$) is treated as the parent of the other amino acids. Note that in dealing with organics, it is nearly impossible to avoid oxidation-reduction in writing reactions for the non-basis organic species. Also, methanamine ($CH_2NH_{3(aq)}$) violates the usual compositional guideline in that it is composed of both carbon and nitrogen.

The associated reaction for each of the above organic auxiliary basis species is written on the data files in the R7 and R10 sets so that the species is oxidized to bicarbonate. On data files in the R16 and higher sets, the species 'acetic acid(aq)' plays the role of parent to the others, with the exception of aqueous methane (i.e., their associated reactions yield acetic acid, not bicarbonate). Acetic acid then functions as a master organic species; aqueous methane is treated as "inorganic," an admittedly arbitrary choice. To illustrate the result, the user of EQ3NR can then avoid all organics in a calculation simply by specifying a zero concentration of acetic acid on the **input** file. To avoid aqueous methane as well, it must also be treated in this manner. Using data files from the earlier sets, to avoid all organics one must do this for each of the organic auxiliary basis species, and for aqueous methane as well, if it is not desired.

In the **sup** and **com** data files in the R16 set, the auxiliary basis species S_2^{2-} is similarly treated as the master polysulfide species (other polysulfides including S_3^{2-}, S_4^{2-}, and S_5^{2-}). Also, the species $S_2O_3^{2-}$ is treated as the master species for related partially oxidized sulfur species, including $S_2O_4^{2-}$, $S_2O_5^{2-}$, $S_2O_6^{2-}$, and $S_2O_8^{2-}$. Again, the rationale is to make it easy for the user to eliminate such species in model calculations when it is so desired.

All non-aqueous species (pure minerals, end-member components of solid solutions, non-aqueous liquids, and gases) are treated on the data files as non-basis species. Thus, all reactions for such species take the form of dissolution reactions.

3. Thermodynamic Data: Representations, Transformations, and Mappings

The purpose of this chapter is to note the types of thermodynamic data that appear on an EQ3/6 data file, and to discuss certain transformations and mappings made from these data by EQPT. The purpose of thermodynamic data is to allow evaluations of mass action equations. This is facilitated by the representations, transformations, and mappings described below.

There are fundamentally two different categories of thermodynamic data. This can be illustrated by the reaction for the dissolution of halite (*NaCl*):

$$NaCl = Na^{+} + Cl^{-} \tag{7}$$

The corresponding mass action equation can be written as:

$$\log K_{NaCl} = \log m_{Na^{+}} + \log \gamma_{Na^{+}} + \log m_{Cl^{-}} + \log \gamma_{Cl^{-}} \tag{8}$$

where K denotes the equilibrium constant, m the molality, and γ the molal activity coefficient. The equilibrium constant is an example of *standard state* thermodynamic data. The activity coefficients are examples of *excess* thermodynamic data. Although referred to as "data," these entities are perhaps more properly referred to as functions. They may in fact be calculated from other "data."There are other examples of kinds of thermodynamic data in each category, representing the temperature and pressure derivatives of these functions. For example, standard partial molar volumes are standard state data. However, these other kinds of thermodynamic data are not directly used in version 7 of EQ3/6.

Most "thermodynamic data bases" emphasize the standard state kind of data. However, the two kinds of data are closely linked. For example, reaction (8) allows computation of the solubility of halite in aqueous solutions. Conversely, measurements of halite solubility can be used to obtain the equilibrium constant, but not independently of the activity coefficients. In fact, one could (and in the most rigorous sense should) use such measurements to obtain both the equilibrium constants and the activity coefficients. This is true, despite the fact that the activity coefficients are obtainable in principle solely from measurements of the osmotic coefficient (cf. Pitzer, 1973).

In principle, a thermodynamic data base is internally consistent only if the combined set of standard state and excess thermodynamic data are mutually consistent. This has been achieved quite rarely; the work of Harvie, Møller, and Weare (1984) provides one of the few examples. It is difficult to provide a high level of internal consistency even among the standard state thermodynamic data (for an example of a large data base with such consistency, see the SUPCRT92 of Johnson, Oelkers, and Helgeson, 1992). To deal with the issue of mutual consistency among standard state and excess thermodynamic data, EQ3/6 data files are designed to contain both types on a given file. This by itself only permits mutual consistency; it does not guarantee it.

In the remainder of this chapter, we discuss first the standard state thermodynamic data, then the excess thermodynamic data. Representations and any transformations or mappings are described for each member of each category of data.

3.1. Standard State Thermodynamic Data

The only example of standard state thermodynamic data used in version 7 of EQ3/6 is the equilibrium constant, taken as log *K*. This is represented as a sequence of values on a temperature grid (0-25-60-100-150-200-250-300°C; see Chapter 4). The equilibrium constant is a function of temperature as well as pressure. However, the pressure is currently taken as a function of the temperature, with values defined on the same temperature grid. The pressure is 1.013 bar up to 100°C, and follows the steam/liquid water equilibrium pressure at higher temperature. Thus, log *K(T)* is really treated as log *K(T,P(T))*. EQ3/6 calculations are presently restricted to this pressure curve.

There is a log *K* grid for each reaction. There is one reaction for each aqueous species not in the strict basis set, one for each pure mineral, and one for each gas species. In addition, there is an equilibrium constant (log K_{Eh}) for the following special redox reaction:

$$2H_2O_{(l)} = O_{2\,(g)} + 4H^+ + 4e^- \tag{9}$$

where *e-* is the fictive aqueous electron. This reaction is built into EQ3/6. It is used to compute secondary redox variables (the redox potential *Eh* and the electron activity function *pe*) from the primary redox variable, the oxygen fugacity (f_{O_2}).

The grid representation is inconvenient for modeling code calculations, because it may be desired to make calculations for temperatures not corresponding to one of the grid points. EQPT transforms the gridded data, replacing it with a set of coefficients for interpolating polynomials. One interpolating polynomial is applied to the 0-25-60-100°C part, another to the 100-150-200-250-300°C. This division respects the discontinuity of the temperature dependence of the grid pressure. It also assures a polynomial of only moderate order.

For a detailed discussion of the subject of fitting interpolating polynomials, the reader is referred to Chapter 1 of Carnahan, Luther, and Wilkes (1969) (or the appropriate section of almost any introductory text dealing with numerical methods). The interpolating polynomials used by EQPT are particularly simple in that they are exact; that is, they pass through all of the data points used in the fitting (a given fitting is limited to a corresponding temperature range). The 0-25-60-100°C part of the grid offers at most four data points, the 100-150-200-250-300°C part, at most five. Thus, the maximum order of the interpolating polynomial is three and four, respectively. Continuity at 100°C is guaranteed if a valid value for this temperature is present on the data grid.

The actual order of the interpolating polynomial depends on the number of valid points. Some points on the grid may be empty due to lack of data. The lack of data condition is marked in the case of log *K* grids by entering a value of "500.0000." Only valid points are used in the fitting. If only a 25°C value is present in the lower temperature part of the grid, the code fits a zero-th order polynomial (i.e., a constant). In order words, the 25°C value is extrapolated over the entire range. If there are no valid points in a given range, the code fits a zero-th order polynomial with a value of "500.0000." The effect of this is to suppress the associated species.

3.2. Excess Thermodynamic Data

The only kind of excess thermodynamic "data" used in the present version of EQ3/6 is the activity coefficient. This is actually treated as a function of other, related data. We will first consider the activity coefficients of aqueous species, then the activity coefficients of components of solid solution phases. The present version of EQ3/6 does not address non-aqueous liquid phases (e.g., a mixture of liquid hydrocarbons), hence it has no provision for treating the activity coefficients of component species of such phases. Nor does it address a gas phase, which would require the consideration of fugacity coefficients.

3.2.1. Activity Coefficients of Aqueous Species

The present version of EQ3/6 offers two formalisms for treating the activity coefficients of aqueous species (for a detailed discussion, see Chapter 3 of the EQ3/6 Theoretical Manual and User's Guide, Wolery, 1992b). The first of these includes simple extensions of the standard Debye-Hückel model, and consists of options for the Davies (1962) equation and the B-dot equation (Helgeson, 1969). The second is based on Pitzer's (1973, 1975, 1979, 1987) equations. The data requirements for the two kinds of formalisms are quite different and will be discussed below. The **com**, **nea**, and **sup** data files correspond to the first formalism, the **hmw** and **pit** data files, to the second.

In the discussion which follows, we give the equation for the solute activity coefficient (γ_i) as a means of introducing the parameters. A complete model for activity coefficients in aqueous solution also requires a corresponding equation for the activity of water (a_w) or its mole fraction activity coefficient (λ_w). These equations are presented in Chapter 3 of Wolery (1992b). They introduce no additional parameters (thermodynamic consistency requires that they do not), hence are not reproduced here.

3.2.1.1. Extended Debye-Hückel Formalism

The extended Debye-Hückel formalism is represented in the present version of EQ3/6 by the Davies (1962) and the B-dot ($\dot{B}$) equation of Helgeson (1969). These are sufficiently accurate for geochemical applications only in relatively dilute solutions (having ionic strengths of at most 1 molal). Their chief advantage is that the data requirements posed by these models are quite minimal.

3.2.1.1.1. The Davies (1962) equation

The Davies (1962) equation is:

$$log\gamma_i = -A_{\gamma,10} z_i^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} + 0.2I \right) \quad (10)$$

This is a simple extended Debye-Hückel model, to which it reduces if the "$0.2I$" part is removed. The only data required is for the Debye-Hückel $A_{\gamma,10}$ parameter. This is here written with a subscript "10" to note consistency with the base ten logarithm on the left hand side of eq (10). The only species-specific data required is for the electrical charge, which is actually an intrinsic parameter.

The use of this option requires a supporting data file consistent with the use of a simple extended Debye-Hückel model (e.g., **com**, **nea**, or **sup**). The parameter $A_{\gamma,10}$ is represented on the data file by a data grid completely analogous to those used to represent log K values. EQPT transforms this data grid into interpolating polynomials in the same manner.

3.2.1.1.2. The B-dot equation

The B-dot equation (Helgeson, 1969) is:

$$log\gamma_i = -\frac{A_{\gamma,10} z_i^2 \sqrt{I}}{1 + \mathring{a}_i B_\gamma \sqrt{I}} + \dot{B}I \tag{11}$$

Here $A_{\gamma,10}$ is the Debye-Hückel A parameter discussed above, B_γ is the Debye-Hückel B parameter, $\dot{B}$ is the B-dot parameter, and $\mathring{a}_i$ is the hard core diameter of the species.

The use of this option requires a supporting data file consistent with the use of a simple extended Debye-Hückel model (e.g., **com**, **nea**, or **sup**). The parameters $A_{\gamma,10}$, B_γ, and $\dot{B}$ are represented on the data file by data grids completely analogous to those used to represent log K values. EQPT transforms these data grids into interpolating polynomials in the same manner. The hard core diameters ($\mathring{a}_i$) are species-specific. They are taken to be constants. Values are assigned in a section of the data file described in Chapter 4.

When the B-dot option is chosen, the B-dot equation itself is only applied to charged species. Other equations are actually used for uncharged species. Each species is also assigned an **insgfl** flag; this flag is ignored for charged species. It appears in the same section of the data file as the hard core diameter (see Chapter 4).

For dissolved gases and other neutral species not of a strongly polar nature, the practice is to assign the value of the activity coefficient of aqueous CO_2 in otherwise pure sodium chloride solutions of the same ionic strength (Garrels and Thompson, 1962; Helgeson, 1969). This is computed from the following expression after Drummond (1981, p. 19):

$$ln\gamma_i = \left(C + FT + \frac{G}{T}\right)I - (E + HT)\left(\frac{I}{I+1}\right) \tag{12}$$

(see Chapter 3 of Wolery, 1992b) where T is the absolute temperature and $C = -1.0312$, $F = 0.0012806$, $G = 255.9$, $E = 0.4445$, and $H = -0.001606$. The coefficients appearing in eq (12) appear directly on the data file, and are not transformed or mapped in any way by EQPT. This treatment is marked by an **insgfl** value of 0. Note that $log\ \gamma_i$ is computed from $ln\ \gamma_i$

Following the recommendation of Garrels and Christ (1965, p. 70), the activity coefficients neutral aqueous species of a polar nature are set to unity; i.e., the equation is:

$$log\gamma_i = 0 \tag{13}$$

This requires no additional data. This treatment is marked by an **insgfl** value of -1.

3.2.1.2. Pitzer's Equations

Pitzer's (1973, 1975, 1979, 1987) equations are based on a virial expansion theory and require a fairly large set of interaction coefficients to model systems of much complexity. Apart from that, they require one Debye-Hückel parameter, which is discussed below. The equations themselves may be written in more than one form, depending on the type of interaction coefficients one wishes to use. It is customary to report interaction coefficients of the *observable* type. Therefore, this type of interaction coefficient appears on the corresponding EQ3/6 data file (e.g., **hmw** or **pit**). However, EQ3/6 actually calculates the activity coefficients using interaction coefficients of the *primitive* type. EQPT maps observable interaction coefficients to a conventionally defined set of primitive interaction coefficients.

In the original theoretical form (Pitzer, 1973), the activity coefficient was written in term of the primitive interaction coefficients λ_{ij} and μ_{ijk}:

$$ln\,\gamma_i = \left(\frac{z_i^2}{2}\right)f'(I) + 2\sum_j \lambda_{ij}(I)\,m_j + \sum_{jk}\left(\left(\frac{z_i^2}{2}\right)\lambda'_{jk}(I) + 3\mu_{ijk}\right)m_j m_k \qquad (14)$$

Here $f(I)$ is a Debye-Hückel function, $f'(I)$ is its derivative df/dI, the λ_{ij} are second order interaction coefficients, $\lambda'_{ij}(I)$ is the derivative $d\lambda_{ij}/dI$, and the μ_{ijk} are third order interaction coefficients. As is implied, the λ_{ij} are treated as functions of the ionic strength. The sums in the interaction coefficient terms are actually double and triple sums. This is the form actually evaluated by EQ3NR and EQ6. Its main virtue is that it is simple and compact, but completely general. It applies to any mixture of cations, anions, and uncharged solute species

The Debye-Hückel model used in Pitzer's equations is not the usual Debye-Hückel-charging formulation exemplified in the Davies or B-dot equations, but a different one derived by Pitzer (1973) and called the Debye-Hückel-osmotic model. The function $f(I)$ is given by:

$$f(I) = -\left(\frac{4A_\phi I}{b}\right) ln\,\left(1 + b\sqrt{I}\right) \qquad (15)$$

Here A_ϕ is a Debye-Hückel parameter is related to the more familiar $A_{\gamma,10}$ by:

$$A_\phi = \frac{2.303A_{\gamma,\,10}}{3} \qquad (16)$$

The parameter b is assigned a constant value of 1.2 (Pitzer, 1973). Different values have been used for the A_ϕ parameter at 25°C. It is important to use the value 0.392 with the Harvie, Møller, and Weare (1984) model of the "sea salt" system, not the stated value of 0.39 (see Plummer et al., 1988, p. 3).

Following Pitzer (1973) and Pitzer and Mayorga (1974) (see Chapter 3 of Wolery, 1992b), the second order interaction coefficient for cation-anion interactions is described by:

$$\lambda_{MX}(I) = \lambda_{MX}^{(0)} + \lambda_{MX}^{(1)} g(\alpha_1 \sqrt{I}) + \lambda_{MX}^{(2)} g(\alpha_2 \sqrt{I}) \tag{17}$$

where the $\lambda_{MX}^{(n)}$ ($n = 0, 1, 2$) are the model coefficient parameters. The function $g(x)$ is given by:

$$g(x) = \left(\frac{2}{x^2}\right)(1 - (1 + x) e^{-x}) \tag{18}$$

In most cases, $\lambda_{MX}^{(2)}$ is set to zero and the parameter α_1 is assigned a value of 2.0 (Pitzer, 1973). When *MX* comprises a 2:2 aqueous neutral electrolyte (and sometimes in other circumstances), $\lambda_{MX}^{(2)}$ is not set to zero, and α_2 and α_2 and are fixed at respective values of 1.4 and 12.0. Other values of α_2 and α_2 have occasionally been proposed (see Pitzer, 1987).

The second order interaction coefficient in the case of cation-cation, anion-anion, neutral-neutral, neutral-cation, and neutral-anion interactions is generally taken to be a constant. Thus, for such combinations one may write:

$$\lambda_{ij} = \lambda_{ij}^{(0)} \tag{19}$$

Pitzer (1975) modified his original treatment by adding a theoretical description for higher order electrostatic interactions. In the context of primitive interaction coefficients, this took the form of redefining the following second order interaction coefficients for the cation-cation and anion-anion combinations as:

$$\lambda_{MM'}(I) = {}^{S}\lambda_{MM'} + {}^{E}\lambda_{MM'}(I) \tag{20}$$

$$\lambda_{XX'}(I) = {}^{S}\lambda_{XX'} + {}^{E}\lambda_{XX'}(I) \tag{21}$$

Here *M* and *M'* denote two cations and *X* and *X'* two anions. The description of the electrostatic term (${}^{E}\lambda_{MM'}(I)$ and ${}^{E}\lambda_{XX'}(I)$) are obtained from entirely from theoretical expressions; see Pitzer, 1975, and Chapter 3 of Wolery, 1992b). The original term (the "short range" term) can be written analogously to eq (19):

$${}^{S}\lambda_{MM'} = \lambda_{MM'}^{(0)} \tag{22}$$

$${}^{S}\lambda_{XX'} = \lambda_{XX'}^{(0)} \tag{23}$$

The temperature dependence of Pitzer interaction coefficients and interaction coefficient parameters (excluding b, α_1, and α_2, which are treated as constants) can be represented up to no more than 100°C by a Taylor's series truncated at first order, using the values of the coefficients and their first temperature derivatives at 25°C (see Silvester and Pitzer, 1978;Pitzer, 1978, 1987; Chapter 3 of Wolery, 1992b). Such a truncated Taylor's series has the general form:

$$x(T) = x_0 + \left(\frac{dx}{dT}\right)_{T_0}(T - T_0) \tag{24}$$

where x_0 is the value of the parameter at temperature T_0 (here 25°C). To obtain a better representation, one may use a Taylor's series truncated at second order. This has the general form:

$$x(T) = x_0 + \left(\frac{dx}{dT}\right)_{T_0}(T - T_0) + \frac{1}{2!}\left(\frac{d^2x}{dT^2}\right)_{T_0}(T - T_0)^2 \tag{25}$$

This is presently the only means built into EQ3/6 for treating the temperature dependence of interaction coefficients and interaction coefficient parameters. Some other proposed methods but not yet implemented in EQ3/6 are discussed later in this chapter.

The use of the Pitzer's equations option requires a supporting data file consistent with these equations (e.g., **hmw** or **pit**). The model parameters required by EQ3/6 are:

- The A_ϕ Debye-Hückel parameter.
- 25°C values of the second order interaction coefficient parameters $\lambda_{ij}^{(0)}$, $\lambda_{ij}^{(1)}$, and $\lambda_{ij}^{(2)}$, the corresponding α_1 and α_2 parameters for each ij pair, and the third order interaction coefficients μ_{ijk}. The parameter $\lambda_{ij}^{(2)}$ (and consequently α_2) is only used in certain cases; the parameter $\lambda_{ij}^{(1)}$ (and consequently α_1) is used in many, but not all cases.
- The first and second temperature derivatives of the interaction coefficient parameters $\lambda_{ij}^{(0)}$, $\lambda_{ij}^{(1)}$, and $\lambda_{ij}^{(2)}$, and the third order interaction coefficients μ_{ijk} (if calculations are to be made for temperatures other than 25°C). Derivatives are not required for $\lambda_{ij}^{(1)}$, and $\lambda_{ij}^{(2)}$ if these parameters themselves are not used for a given combination of solute species.

The A_ϕ parameter is represented in the usual grid format and is transformed into a set of interpolating polynomials by EQPT in the manner previously described for log K values and other kinds of Debye-Hückel parameters.

There are more of the $\lambda_{MX}^{(n)}$ and μ_{ijk} parameters than can be physically observed (Pitzer, 1973; see also Chapter 3 of Wolery, 1992b). These parameters can only be observed in certain combinations, which depend on the electrical charge types of the species. These combinations are equivalent to the observable interaction coefficients. There is a multiplicity of such coefficients, and the equation for the activity coefficient in complex mixtures becomes accordingly more complex (see Pitzer, 1979, 1987; Harvie, Møller, and Weare, 1984; and Felmy and Weare, 1986). However, relatively simple forms can be obtained for simple solutions, such as for a pure aqueous electrolyte (Pitzer, 1973, 1979, 1987), a mixture of two electrolytes with a common ion (Pitzer, 1973, 1975, 1979, 1987), and a mixture of an electrolyte and a neutral solute species (Pitzer, 1987). This facilitates much of the fitting of observed coefficients, and the data are consequently commonly reported in this form.

We consider first the parameters associated only with cations and anions. The parameters $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, $\beta_{MX}^{(2)}$, and C_{MX}^{ϕ}, are observable in a pure solution of the aqueous neutral electrolyte comprised of cation M and anion X. The parameters ${}^{S}\theta_{MM'}$ and $\psi_{MM'X}$ are observable in a mixture of two aqueous neutral electrolytes, one comprised of cation M and anion X, the other of cation M' and anion X. Similarly, the parameters ${}^{S}\theta_{XX'}$ and $\psi_{MXX'}$ are observable in a mixture of two aqueous neutral electrolytes, one comprised of cation M and anion X, the other of cation M and anion X'. Here ${}^{S}\theta_{ij}$ is θ_{ij} in the nomenclature of Harvie, Møller, and Weare (1984).

The relationship of these observable Pitzer parameters to the corresponding primitive Pitzer parameters is discussed in detail in Chapter 3 of Wolery (1992b). The observable parameters may be mapped to an equivalent set of primitive parameters by means of certain mapping relations. Those used by EQPT are the following:

$$\lambda_{MX}^{(n)} = \beta_{MX}^{(n)} \quad \text{for} \quad n = 0,\ 2 \tag{26}$$

$$\lambda_{MM}^{(n)} = 0 \quad \text{for} \quad n = 0,\ 2 \tag{27}$$

$$\lambda_{XX}^{(n)} = 0 \quad \text{for} \quad n = 0,\ 2 \tag{28}$$

$$\mu_{MMX} = \frac{1}{6}\left|\frac{z_M}{z_X}\right|^{\frac{1}{2}} C_{MX}^{\phi} \tag{29}$$

$$\mu_{MXX} = \frac{1}{6}\left|\frac{z_X}{z_M}\right|^{\frac{1}{2}} C_{MX}^{\phi} \tag{30}$$

$$\lambda_{MM'}^{(0)} = {}^{S}\theta_{MM'} \tag{31}$$

$$\lambda_{XX'}^{(0)} = {}^{S}\theta_{XX'} \tag{32}$$

$$\mu_{MM'X} = \frac{1}{6}\left(\psi_{MM'X} + \left(\frac{3z_{M'}}{z_M}\right)\mu_{MMX} + \left(\frac{3z_M}{z_{M'}}\right)\mu_{M'M'X}\right) \tag{33}$$

$$\mu_{MXX'} = \frac{1}{6}\left(\psi_{MXX'} + \left(\frac{3z_{X'}}{z_X}\right)\mu_{MXX} + \left(\frac{3z_X}{z_{X'}}\right)\mu_{MX'X'}\right) \tag{34}$$

The temperature derivatives of the observable Pitzer parameters may be mapped to the temperature derivatives of the corresponding conventional primitive parameters using the temperature derivatives of the mapping relations for the parameters themselves. For example, differentiation of eq (26) gives:

$$\frac{d\lambda_{MX}^{(n)}}{dT} = \frac{d\beta_{MX}^{(n)}}{dT} \quad \text{for} \quad n = 0,\ 2 \tag{35}$$

$$\frac{d^2\lambda_{MX}^{(n)}}{dT^2} = \frac{d^2\beta_{MX}^{(n)}}{dT^2} \quad \text{for} \quad n = 0,\ 2 \tag{36}$$

The mapping relations for the second derivatives are analogous.

Harvie, Møller, and Weare (1984) used Pitzer's equations to construct a model of all of the major components of seawater at 25°C. They modified the equations for electrolyte systems to include some provision for neutral species-ion interactions. Felmy and Weare (1986) took the equations further in this direction when they extended the Harvie, Møller, and Weare model to include borate as a component. These investigators introduced the following new observable parameters: λ_{NM} and λ_{NX}, and ζ_{NMX}. Here N denotes a neutral species. The terms in λ_{NM} and λ_{NX} were introduced by Harvie, Møller, and Weare (1984) in order to treat the species $CO_{2(aq)}$ in their model of the "sea salt" system. They are treated as constants. To deal with the fact that they are only observable in combination, Harvie, Møller, and Weare (1984) adopted the following convention:

$$\lambda_{N,H^+} = 0 \tag{37}$$

We note that Clegg and Brimblecombe (1989, 1990) use a different convention:

$$\lambda_{N,Cl^-} = 0 \tag{38}$$

It is important to follow a single convention in any data file. At the present time, that of Harvie, Møller, and Weare (1984) is used in the **hmw** data file. The present version of the **pit** data file contains no λ_{NM} or λ_{NX} parameters.

The ζ_{NMX} parameter is an observable third order coefficient. It was developed by Felmy and Weare (1986) in order to account for interactions involving the species $B(OH)_{3(aq)}$. This parameter can be mapped into primitive equivalents by means of the following mapping conventions (see Chapter 3 of Wolery, 1992b):

$$\mu_{NMX} = \frac{\zeta_{NMX}}{6} \tag{39}$$

$$\mu_{NMM} = 0 \tag{40}$$

$$\mu_{NXX} = 0 \tag{41}$$

There are additional possible Pitzer coefficients for solutions containing neutral solute species (see Chapter 3 of Wolery, 1992b). Among these, the most likely to be needed are the second order interaction coefficients λ_{NN} and $\lambda_{NN'}$ (here N' denotes a second neutral species). These coefficients are directly observable.

The temperature dependence of observable and conventional primitive coefficients involving neutral solute species can be handled analogously to that manner previously described for coefficients and coefficient parameters involving only cations and anions; e.g., using tabulated first and second derivatives. The mapping functions for the derivatives are again analogous to those for the coefficients themselves.

The relevant EQ3/6 data files contain two superblocks of observable Pitzer coefficient data (a superblock is a collection of similar data blocks). The first superblock consists of blocks containing the data observable in solutions of pure aqueous neutral electrolytes: $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, $\beta_{MX}^{(2)}$, and C_{MX}^{ϕ}. Each of these blocks also contains the corresponding values of α_1 and α_2. The second superblock consists of blocks containing the data observable in mixtures of two aqueous neutral electrolytes containing a common ion: ${}^{S}\theta_{MM'}$ and $\psi_{MM'X}$, or ${}^{S}\theta_{XX'}$ and $\psi_{MXX'}$. The data in either type of superblock in represented by the 25°C value of the relevant parameters, plus the first and second temperature derivatives of these parameters at the same temperature (note: α_1 and α_2 are taken to be independent of temperature).

We note a problem concerning ${}^{S}\theta_{MM'}$ and its temperature derivatives. A potentially different value can be obtained by fitting measurements on more than one mixture of two aqueous electrolytes containing the two cations M and M'. The same problem holds for ${}^{S}\theta_{XX'}$ and its temperature derivatives. This is particularly a problem in that potentially different values of the theta coefficients and their temperature derivatives may appear on the data file for each relevant mixture. EQPT deals with this by taking the average of such parameters. Strictly speaking, the data file should not contain the different values for the any given theta coefficient. The same rule applies to its first and second order temperature derivatives.

The relevant EQ3/6 data files also contain a flag string which alerts EQ3NR or EQ6 to use or ignore the higher order electrostatic model proposed by Pitzer (1975). This is also written on the **data1** file produced by EQPT. Note that the fitted values of the theta and psi parameters involving two cations not of the same charge or two anions not of the same charge change according to whether or not this model is included.

The present version of EQPT was actually designed to handle parameters involving only cations and anions. However, it can deal with λ_{NM} by composing a pure aqueous neutral electrolyte block for a fictive electrolyte. Here N and M are specified as the pair of "ions" composing the "electrolyte." The value of λ_{NM} is entered in the field for $\beta_{NM}^{(0)}$. The remaining parameter fields in this block should be left blank or filled with zeros. The λ_{NX} parameter can be treated likewise. Coefficients of the type λ_{NN} and $\lambda_{NN'}$ can be dealt with by using the same trick used to deal with λ_{NM}. In this case, the fictive electrolyte consists of two neutral species (N and N, or N and N'). However, no examples of such coefficients appear on the **hmw** data file or the existing **pit** data file. The present version of EQPT can not deal with the ζ_{NMX} parameter, however.

The two superblocks for observable Pitzer parameters and their temperature derivatives are mapped by EQPT to corresponding superblocks on the **data1** file containing the corresponding conventional primitive parameters and their temperature derivatives. EQ3NR and EQ6 then use these data to calculate values of the relevant conventional primitive parameters at the desired temperature. Note that if the derivatives are missing, no temperature correction is made.

The **hmw** data file has nominal lower and upper temperature limits which are both set to 25°C. It contains no temperature derivative data. It should not be used to make calculations at temperature other than 25°C. EQ3NR and EQ6 will write warnings if the nominal temperature limits are exceeded. This data file also employs the higher order electrostatic model proposed by Pitzer (1975).

The **pit** data file has nominal lower and upper temperature limits of 0°C and 100°C, respectively. It contains a fair amount of data for first temperature derivatives. This data file does not employ the higher order electrostatic model proposed by Pitzer (1975).

The temperature dependency has been expressed in various more recent studies by a variety of different temperature functions, most of which require only 5-7 parameters per observable interaction coefficient. Pabalan and Pitzer (1987) used such equations to develop a model for the system $Na\text{-}K\text{-}Mg\text{-}Cl\text{-}SO_4\text{-}OH\text{-}H_2O$ which appears to be generally valid up to about 200°C. Pabalan and Pitzer (1988) used equations of this type built a model for the system $Na\text{-}Cl\text{-}SO_4\text{-}OH\text{-}H_2O$ that extends to 300°C. Greenberg and Møller (1989), using an elaborate compound temperature function, have constructed a model for the $Na\text{-}K\text{-}Ca\text{-}Cl\text{-}SO_4\text{-}H_2O$ system that is valid from 0-250°C. More recently, Spencer, Møller, and Weare (1990) have used a more compact equation to develop a model for the $Na\text{-}K\text{-}Ca\text{-}Mg\text{-}Cl\text{-}SO_4\text{-}H_2O$ system at temperatures in the range -60-25°C. The present version of EQPT has no capability to deal with these kinds of representations of the temperature dependence.

3.2.2. Activity Coefficients of Solid Solution Components

In general, the activity coefficient of a solid solution component depends on the composition of the solid solution. This in turn is normally expressed in terms of the mole fractions of the end-member components (for example, calcite [$CaCO_3$] and magnesite [$MgCO_3$] in magnesian calcite [$(Ca,Mg)CO_3$]). There are two categories of activity coefficient models, molecular-mixing models and site-mixing models (cf. Chapter 4 of the EQ3NR Theoretical Manual and User's Guide, Wolery, 1992b).

In molecular-mixing models, the activity coefficient of an end-member component is unity in the ideal case. In the non-ideal case, one generally utilizes a model which describes the activity coefficient via a set of interaction coefficients similar to those employed in Pitzer's equations for the activity coefficients of aqueous species.

In site-mixing models, explicit account is taken of the fact that mixing of ions occurs on well-defined sites in the crystal structure (see for example Wood and Fraser, 1977, or Nordstrom and Munoz, 1985). Vacancies may be present on a site, and be created or destroyed by substitutions of one ion for another of different electrical charge. In site-mixing models, the concept of ideality is modified from that appropriate to molecular mixing, though still based on the mole fractions of components. It is possible to utilize as the components species such as ions, vacancies, and framework moieties instead of end members, but the more common practice is to continue using end-member components. This is followed in the present version of EQ3/6. However, the activity coefficient of an end-member component in an ideal site mixing model may have a value other than unity. A site-mixing model will appear to be ideal in this sense only if there is only one site, an ion substitutes for others of the same charge type, and vacancies are not present on the site. Site mixing then effectively reduces to molecular mixing.

Nearly all of the existing site-mixing models of solid solutions are ideal in the site-mixing sense (see for example Viani and Bruton, 1992). The only parameters of such models are site-mixing parameters. It is possible to consider site-mixing models which are non-ideal even in the site-mixing sense. These would be described by both site-mixing parameters and interaction coefficients. No models of this type are presently treated in EQ3/6.

In EQ3/6, all solid solution models are defined on the supporting data file (see Chapter 4). At present (through the R16 set of data 2files), only the **com** file contains any solid solutions. Most of these are treated with a simple ideal site-mixing model (the only exception concerns olivine, which is treated according to a regular solution model). The actual types of models used on the data file are defined by the **jsol** flag array. The corresponding parameters (site-mixing parameters, interaction coefficients, and parameters used to compute interaction coefficients) are stored on the data file in the **apx** array. The elements of this array are represented below as $p_{k\psi}$.

The various models presently treated in EQ3/6 are briefly discussed in the following sections. To avoid confusion, we will often write the activity, mole fraction, activity coefficient, and related parameters of a solid solution component with a "$\sigma\psi$" subscript in place of "i." Here σ will denote the component itself (takes the place of "i"), and ψ the solid solution (in order to be completely explicit about which solid solution is being addressed).

3.2.2.1. Ideal Solution, with One Optional Site-Mixing Parameter

The first activity coefficient model for solid solutions in EQ3/6 is for an ideal solution in either the molecular-mixing sense or a limited site-mixing model in which mixing is confined to one site and vacancies are ignored. The former is a special case of the latter. This model corresponds to **jsol** = 1 and is characterized by the equation (Wood and Fraser, 1977; Viani and Bruton, 1992):

$$a_{\sigma\psi} = x_{\sigma\psi}^{N_\psi} \qquad (42)$$

where N_ψ is the site mixing parameter. This formulation is equivalent to:

$$log\lambda_{\sigma\psi} = (N_\psi - 1)\, logx_{\sigma\psi} \qquad (43)$$

If $N_\psi = 1$, the above model is mathematically equivalent to an ideal molecular-mixing model ($log\lambda_{\sigma\psi} = 0$).

The N_ψ parameter is stoichiometric in nature. In essence, it is the number of formula units of the site on which mixing occurs per formula unit of the solid solution framework. In principle, the formula for all the end-member components of a solid solution can be written so as to yield N_{ψ} $= 1$, hence $log\lambda_{\sigma\psi} = 0$.

In the case of heterovalent single-site solid solutions such as clays and zeolites, vacancies are involved. In order to simplify the solution model and preserve the simple relationship defined by eqs (42) and (43), Viani and Bruton (1992) have chosen to treat such solid solutions according to a model in which the mixing entities are ions or ion-vacancy complexes. Thus, two sodium ion entities might mix with a calcium ion-vacancy entity.

The N_{ψ} parameter is obtained from the parameters read from the data file according to:

$$N_{\psi} = p_{7\psi} \tag{44}$$

3.2.2.2. Third-Order Maclaurin Model for a Binary Solution

The third-order Maclaurin model for a binary solution corresponds to **jsol** = 2. It is taken from Helgeson et al. (1970). The activity coefficients of the two end-member components are given by:

$$log\lambda_{1\psi} = \frac{1}{2.303RT}\left[-\left(\frac{W_{2\psi}}{2}\right)x_2^2 - \left(\frac{W_{3\psi}}{3}\right)x_2^3\right] \tag{45}$$

$$log\lambda_{2\psi} = \frac{1}{2.303RT}\left[-\left(\frac{W_{2\psi}+W_{3\psi}}{2}\right)x_1^2 + \left(\frac{W_{3\psi}}{3}\right)x_1^3 + \left(W_{1\psi} + \frac{W_{2\psi}}{2} + \frac{W_{3\psi}}{6}\right)\right] \tag{46}$$

Here $W_{1\psi}$, $W_{2\psi}$, and $W_{3\psi}$ are interaction coefficients. There are no site-mixing parameters.

The formulation represented by eqs (45) and (46) is highly unsymmetrical. In order to satisfy the condition that $log\lambda_{2\psi} \rightarrow 0$ as $x_1 \rightarrow 0$, the interaction coefficients are required to satisfy the relation:

$$W_{1\psi} = -\frac{W_{2\psi}}{2} - \frac{W_{3\psi}}{6} \tag{47}$$

The interaction coefficients are obtained from the parameters read from the data file according to:

$$W_{1\psi} = p_{1\psi} \tag{48}$$

$$W_{2\psi} = p_{2\psi} \tag{49}$$

$$W_{3\psi} = p_{3\psi} \tag{50}$$

However, $W_{1\psi}$ is actually recalculated using eq (47).

3.2.2.3. Regular Solution Model for a Binary Solution

The regular solution model for a binary solution corresponds to **jsol** = 3. It is also called a parabolic Maclaurin model. For a discussion of this model, see Saxena (1973, p. 11-12). The activity coefficients of the two end-member components are given by:

$$log\lambda_{1\psi} = \frac{1}{2.303RT}W_{\psi}x_2^2 \quad (51)$$

$$log\lambda_{2\psi} = \frac{1}{2.303RT}W_{\psi}x_1^2 \quad (52)$$

Here W_{ψ} is the single interaction coefficient. There are no site-mixing parameters. This formulation is symmetrical.

The interaction coefficients are obtained from the parameters read from the data file according to:

$$W_{\psi} = p_{1\psi} + p_{2\psi}T + p_{3\psi}P \quad (53)$$

Thus, the interaction coefficient in this model can be treated as a function of temperature and pressure. On the **com** data file in the R10 and R16 sets, there is a regular solution model for the solid solution olivine. The $p_{2\psi}$ and $p_{3\psi}$ parameters are set to zero, so the interaction coefficient is actually treated as a constant. A non-unit site-mixing parameter is also given in the $p_{7\psi}$ parameter, but this is not used.

3.2.2.4. Cubic Maclaurin Model for a Binary Solution

The cubic Maclaurin model for a binary solution corresponds to **jsol** = 4. For a discussion of this model, see Saxena (1973, p. 16). The activity coefficients of the two end-member components are given by:

$$log\lambda_{1\psi} = \frac{1}{2.303RT}[(2W_{2\psi} - W_{1\psi})x_2^2 + 2(W_{1\psi} - W_{2\psi})x_2^3] \quad (54)$$

$$log\lambda_{2\psi} = \frac{1}{2.303RT}[(2W_{1\psi} - W_{2\psi})x_1^2 + 2(W_{2\psi} - W_{1\psi})x_1^3] \quad (55)$$

Here $W_{1\psi}$, and $W_{2\psi}$ are interaction coefficients. There are no site-mixing parameters. This formulation is asymmetrical.

The interaction coefficients are obtained from the parameters read from the data file according to:

$$W_{1\psi} = p_{1\psi} + p_{2\psi}T + p_{3\psi}P \quad (56)$$

$$W_{2\psi} = p_{4\psi} + p_{5\psi}T + p_{6\psi}P \quad (57)$$

3.2.2.5. Guggenheim Polynomial Model for a Binary Solution

The Guggenheim polynomial model for a binary solution corresponds to **jsol** = 5. For a discussion of this model, see Saxena (1973, p. 14-15). The activity coefficients of the two end-member components are given by:

$$log\lambda_{1\psi} = \frac{1}{2.303RT}\left[(W_{1\psi}+3W_{2\psi}+5W_{3\psi})x_2^2 + (-4W_{2\psi}-16W_{3\psi})x_2^3 + 12W_{3\psi}x_2^4 \right] \quad (58)$$

$$log\lambda_{2\psi} = \frac{1}{2.303RT}\left[(W_{1\psi}-3W_{2\psi}+5W_{3\psi})x_1^2 + (4W_{2\psi}-16W_{3\psi})x_1^3 + 12W_{3\psi}x_1^4 \right] \quad (59)$$

Here $W_{1\psi}$, $W_{2\psi}$, and $W_{3\psi}$ are interaction coefficients. There are no site-mixing parameters. This formulation is asymmetrical.

The interaction coefficients are obtained from the parameters read from the data file according to:

$$W_{1\psi} = p_{1\psi} + p_{2\psi}T + p_{3\psi}T^2 \quad (60)$$

$$W_{2\psi} = p_{4\psi} + p_{5\psi}T + p_{6\psi}T^2 \quad (61)$$

$$W_{3\psi} = p_{7\psi} + p_{8\psi}T + p_{9\psi}T^2 \quad (62)$$

The full form of this model can be used in the present version of EQ3/6, although the parameters $p_{k\psi}$ for $k \geq 7$ are now intended to be reserved for site-mixing parameters.

3.2.2.6. Regular Solution Model for a Ternary Solution

The regular solution model for a ternary solution corresponds to **jsol** = 6. For a discussion of this model, see Prigogine and Defay (1954, p. 257). The activity coefficients of the three end-member components are given by:

$$log\lambda_{1\psi} = \frac{1}{2.303RT}[W_{12\psi}x_2^2 + W_{13\psi}x_3^2 + (W_{12\psi} - W_{23\psi} + W_{13\psi})x_2x_3] \quad (63)$$

$$log\lambda_{2\psi} = \frac{1}{2.303RT}[W_{12\psi}x_1^2 + W_{23\psi}x_3^2 + (W_{12\psi} - W_{13\psi} + W_{23\psi})x_1x_3] \quad (64)$$

$$log\lambda_{3\psi} = \frac{1}{2.303RT}[W_{13\psi}x_1^2 + W_{23\psi}x_2^2 + (W_{13\psi} - W_{12\psi} + W_{23\psi})x_1x_2] \quad (65)$$

Here $W_{1\psi}$, $W_{2\psi}$, and $W_{3\psi}$ are interaction coefficients. There are no site-mixing parameters. This formulation is symmetrical.

The interaction coefficients are obtained from the parameters read from the data file according to:

$$W_{12\psi} = p_{1\psi} \quad (66)$$

$$W_{13\psi} = p_{2\psi} \tag{67}$$

$$W_{23\psi} = p_{3\psi} \tag{68}$$

4. Data File Contents and Structures

The **data0** data files are represented by two archetypes. The first, called the **com** archetype is used for data files intended to support calculations using simple extended Debye-Hückel models for the activity coefficients of the aqueous species. This archetype pertains to the **com**, **sup**, and **nea** data files. The **hmw** archetype is used for data files intended to support calculations using Pitzer's (1973, 1975, 1979, 1987) equations. It pertains to the **hmw** and **pit** data files. The two archetypes differ in the types of parameters for computing activity coefficients of aqueous species. Otherwise, they are essentially the same.

Archetypes for the **data1** file structures closely parallel those for the corresponding **data0** files. The **data1** file is an unformatted file, so no formats (in the usual sense) are involved, and the file can not be printed or displayed in any meaningful fashion. To assist debugging, EQPT writes a corresponding data file called **data1f**, which is a formatted equivalent of **data1**.

The contents of **data1** are identical to those of **data0**, with the following exceptions. Data given on a standard temperature grid are replaced by the coefficients of interpolating polynomials which EQPT fits to such data grids. Also, in the case of data files of the **hmw** archetype, observable Pitzer coefficient parameters are mapped to an equivalent set of conventional primitive parameters. The temperature derivatives of these observable parameters are mapped similarly to those of the conventional primitive equivalents. All of these data transformations were discussed in detail in Chapter 3.

4.1. The com Archetype for the data0 File

The basic structure of the **com** archetype for **data0** file is given in Figure 2. The data file begins with a one-line header of the form:

```
data0.com.R10
```

The first five letters on this line must be **data0**. If they are not EQPT will terminate with an error message. Letters 7-9 must contain the three letter data file key string (**com**, **nea**, **sup**, **hmw**, or **pit**). The stage number (**R10** in the above example) is optional as far as EQPT is concerned. However, it should appear to assist in configuration management, as it will be written on the **data1** file by EQPT, and thence by EQ3NR and EQ6 on their **output** files.

The header is followed by a title, which may consist of up to 70 lines (see **ntitpa** in Appendix A) of descriptive text. The title on the **data0.com.R10** data file is:

```
THERMODYNAMIC DATABASE
generated by gembochs/INGRES  15-apr-91
+-----------------------------------------------------------------------
```

The "+-------" in the final line in this example is a block terminator used throughout the data file. EQPT writes the data file title on the **data1** file. EQ3NR and EQ6 read this title and write it on their **output** files. Any changes to the data file made by users may be noted or cited in this title. Users outside the LLNL Data Base Development Task who make any such changes are requested to make some kind of notation on modified data files so as to distinguish them from those supplied by LLNL.

Header (**data0**, data file key, stage number)

Title

"data0" parameters block:
- Temperature limits (°C)
- Temperature (°C), standard grid
- Pressure (bars), standard grid
- $A_{\gamma,10}$, standard grid
- B_{γ}, standard grid
- $\dot{B}$, standard grid
- Drummond (1981) C, F, G, E, and H coefficients
- $\log K_{Eh}$, standard grid

"bdot" parameters block:
- Aqueous species name, $\mathring{a}_i$, insgfl flag

Chemical elements block:
- Elements, atomic weights

Aqueous species superblock:
- Strict basis species
- Auxiliary basis species, with $\log K$ on the standard grid
- Non-basis species, with $\log K$ on the standard grid

Pure minerals superblock:
- Pure minerals, with $\log K$ on the standard grid

Pure liquids superblock:
- Pure liquids, with $\log K$ on the standard grid

Gas species superblock:
- Gas species, with $\log K$ on the standard grid

Solid solutions superblock:
- Solid solutions

References block:
- References

Figure 2. The basic structure of the data0 file for the com archetype.

The title is followed by a block of data for "data0" parameters. These include the nominal temperature limits (°C) for the application of the data file, the temperatures (°C) on the standard grid, the pressure (bars) on the standard temperature grid, the $A_{\gamma,10}$ and B_{γ} Debye-Hückel parameters on the standard temperature grid, the extended Debye-Hückel $\dot{B}$ on the standard temperature grid, the five Drummond 1981 coefficients (C, F, G, E, and H) needed to compute the activity coefficient of aqueous CO_2 (see Chapter 3 of Wolery, 1992b), and $log\ K_{Eh}$ on the standard temperature grid. The parameter $log\ K_{Eh}$ is the equilibrium constant of the special reaction (9) used in EQ3NR and EQ6 to relate seondary redox variables (Eh, pe) from the primary redox variable, teh oxygen fugacity. This reaction itself is not written on the data file. It is hard-wired into EQ3NR and EQ6.

The "data0" parameters block in **data0.com.R10** is as follows:

```
data0 parameters
+---------------------------------------------------------------------
temperature limits                                                    (a)
         0.0000  300.0000                                             (5x,2f10.4)
temperatures
         0.0100   25.0000   60.0000  100.0000                         (5x,4f10.4)
       150.0000  200.0000  250.0000  300.0000
pressures
         1.0132    1.0132    1.0132    1.0132
         4.7572   15.5365   39.7365   85.8378
debye huckel a (adh)
         0.4939    0.5114    0.5465    0.5995
         0.6855    0.7994    0.9593    1.2180
debye huckel b (bdh)
         0.3253    0.3288    0.3346    0.3421
         0.3525    0.3639    0.3766    0.3925
bdot
         0.0174    0.0410    0.0440    0.0460
         0.0470    0.0470    0.0340    0.0000
cco2   (coefficients for the Drummond (1981) polynomial)
        -1.0312               0.0012806                           (5x,f10.4,11x,f12.7)
          255.9                  0.4445                           (10x.f5.1,11x,f12.4)
      -0.001606                                                       (5x,f10.6)
log k for eh reaction
       -91.0448  -83.1049  -74.0534  -65.8641                         (5x,4f10.4)
       -57.8929  -51.6848  -46.7256  -42.6828
+---------------------------------------------------------------------
```

The "`data0 parameters`" on the first line is a block header flag. EQPT actually uses the "`temperature limits`" string to position the data file for reading this block. The other individual header strings are not read. The formats for reading the data are superimposed to the right in the above example where they appear in bold italic. These format strings do not appear in the data file itself. Formats which obviously repeat are not marked. We will continue this practice of giving formats in this manner in the examples to follow. Note the usage here of the standard pressure grid. The pressure of "`4.7572`" bars is the pressure at "`150.0000`" degrees (C).

This is followed by the "bdot" parameters block. This block consists of its own header and a list of the hard core diameter ($\mathring{a}_i$) and **insgfl** flag switch. This block in **data0.com.R10** is as follows:

```
bdot parameters                                                              (a)
+-------------------------------------------------------------------------
*  species name                     azer0  neutral ion type
(uo2)3(co3)6(6-)                  4.0000     0
np(co3)5(6-)                      4.0000     0                                 (a24,7x,f7.4,4x,i2)
u(co3)5(6-)                       4.0000     0
                         .
                         .
                         .
           (Material Deleted)
                         .
                         .
                         .
th6(oh)15(9+)                     6.0000     0
+-------------------------------------------------------------------------
```

Here "`azer0`" is the hard core diameter, and the "`neutral ion type`" is the **insgfl** flag. The former is given in units of cubic angstroms. The latter is meaningful only in the case of neutral species. If **insgfl** = -1, the activity coefficient of the species is taken to be the value for aqueous CO_2 in pure aqueous $NaCl$, as computed from eq (12) (see Chapter 3). This is appropriate for nonpolar species, such as most of the dissolved gas species. If **insgfl** = 0, the activity coefficient is set to unity. This is more appropriate for polar species, such as the $MgSO_{4(aq)}$ ion pair. The name of an aqueous species appearing in this block must be identical to its name in the corresponding species block, which appears below this block. EQPT writes the data in this block as-is onto the **data1** file. The line beginning with "`*  species name`" is a comment line. Comment lines begin with an asterisk in column one. EQPT actually reads a copy of the **data0** file from which the comment lines have been stripped.

Next is the chemical elements block,. It consists of a block header followed by the names of the chemical elements (represented by the standard symbols) and their atomic weights (grams per mole). It is illustrated below by the block from **data0.com.R10**:

```
elements      (a)
+-------------------------------------------------------------------------
o          15.99940
ag        107.86820                                                        (a8,f10.5)
al         26.98154
                         .
                         .
                         .
          (Material Deleted)
                         .
                         .
                         .
zr         91.22400
+-------------------------------------------------------------------------
```

This is followed by the aqueous species superblock. This is comprised of a data block for each aqueous species. The structure of this superblock is complicated somewhat in that these data blocks are organized into three "sub-superblocks," the first for strict basis species, the second for auxiliary basis species, and the third for non-basis aqueous species. Furthermore, water ("`h2o`") must be the first strict basis species. The fictive aqueous redox species "`o2(g)`" must be the last strict basis species. Each strict basis species except "`o2(g)`" must correspond to a chemical element in the chemical elements block. They should also appear in corresponding order. Note that water corresponds to the element oxygen. The strict basis species sub-superblock is terminated by a short block containing the string "`auxiliary basis species`" in place of a species name. The auxiliary basis species sub-superblock is similarly terminated by a short block containing the string “`aqueous species`”.

The aqueous species superblock is illustrated by the following, taken from **data0.com.R10**:

```
basis species                                                         (a)
+---------------------------------------------------------------------
h2o                                                                   (a24)
    date last revised =  13-jul-1990                                  (not read)
 keys    = basis           active                                     (not read)
    charge =     0.0                                                  (14x,5.1)
     2 chemical elements =                                            (4x,i2)
     1.0000 o              2.0000 h                              (4x,3(f8.4,1x,a8,5x))
* Extrapolation algorithm:  supcrt91
* gflag = 4  (supcrt91 equations and data used)
* basic source = supcrt91
* delG0f =      -56.688 kcal/mol
* delH0f =      -68.317 kcal/mol
* S0PrTr =       16.712 cal/(mol*K)
+---------------------------------------------------------------------
                                    .
                                    .
                                    .
            (Material Deleted)
                                    .
                                    .
                                    .
+---------------------------------------------------------------------
auxiliary basis species                                               (a24)
+---------------------------------------------------------------------
                                    .
                                    .
                                    .
            (Material Deleted)
                                    .
                                    .
                                    .
+---------------------------------------------------------------------
acetic acid(aq)         ch3cooh                                       (a24)
    date last revised =  08-mar-1990                                  (not read)
 keys    = aux             active                                     (not read)
    charge =     0.0                                                  (14x,5.1)
     3 chemical elements =                                            (4x,i2)
     2.0000 c              2.0000 o              4.0000 h        (4x,3(f8.4,1x,a8,5x))
     4 species in reaction =                                          (4x,i2)
   -1.0000  acetic acid(aq)                -2.0000  o2(g)         (2(1x,f10.4,2x,a24))
    2.0000  h+                              2.0000  hco3-
*    log k grid (0-25-60-100/150-200-250-300 C) =
       150.4618  136.1956  119.6467  104.3573                         (5x,4f10.4)
        89.0810   76.7815   66.5395   57.6542
* Extrapolation algorithm:  supcrt91
* gflag = 4  (supcrt91 equations and data used)
* basic source = supcrt91
* delG0f =      -94.760 kcal/mol
* delH0f =     -116.100 kcal/mol
* S0PrTr =       42.700 cal/(mol*K)
+---------------------------------------------------------------------
                                    .
                                    .
                                    .
            (Material Deleted)
                                    .
                                    .
                                    .
+---------------------------------------------------------------------
aqueous species                                                       (a24)
+---------------------------------------------------------------------
(npo2)2(oh)2++                                                        (a24)
    date last revised =  21-jul-1986                                  (not read)
 keys    = aqueous         active                                     (not read)
```

```
    charge =    2.0                                                  (14x,5.1)
     3 chemical elements =                                           (4x,i2)
     2.0000 h               2.0000 np           6.0000 o         (4x,3(f8.4,1x,a8,5x))
     4 species in reaction =                                         (4x,i2)
   -1.0000  (npo2)2(oh)2++            -2.0000  h+                  (2(1x,f10.4,2x,a24))
    2.0000  h2o                        2.0000  npo2++
*    log k grid (0-25-60-100/150-200-250-300 C) =
       500.0000    6.4000    5.6000    5.0000                        (5x,4f10.4)
         4.6000  500.0000  500.0000  500.0000
* gflag = 3  (reported logk data used)
* logk source = 84lem
*   calculated g-h-s values:
* delG0f =      -485.046 kcal/mol
* delH0f =      -537.089 kcal/mol
* S0PrTr =        -3.346 cal/(mol*K)
+-------------------------------------------------------------------
                     .
                     .
                     .
           (Material Deleted)
                     .
                     .
                     .
+-------------------------------------------------------------------
```

Note that the species blocks illustrated here each contain a number of comment lines. Also, the blocks for non-basis aqueous species block and auxiliary basis species share the same format. Note that "`500.0000`" is used in the *log K* grid to mean "no data." This is illustrated in the data block for "`(npo2)2(oh)2++`".

The pure minerals superblock follows the aqueous species superblock. It is similar, but has no sub-superblocks and no special ordering restrictions. It is illustrated by the following, taken from **data0.com.R10**:

```
solids                                                               (a24)
+-------------------------------------------------------------------
(pb(oh)2)3.pbcl2        (pb(oh)2)3.pblcl2                            (a24)
   date last revised =  24-aug-1989                                  (not read)
 keys   = solid             active                                   (not read)
      V0PrTr =     0.000 cm**3/mol  (source =                  )     (16x,f9.3)
     4 chemical elements =                                           (4x,i2)
     2.0000 cl              4.0000 pb           6.0000 h         (4x,3(f8.4,1x,a8,5x))
      6.0000 o
     5 species in data0 reaction                                     (4x,i2)
   -1.0000  (pb(oh)2)3.pbcl2          -6.0000  h+                  (2(1x,f10.4,2x,a24))
    2.0000  cl-                        4.0000  pb++
     6.0000  h2o
*    log k grid (0-25-60-100/150-200-250-300 C) =
       500.0000   17.2793  500.0000  500.0000                        (5x,4f10.4)
       500.0000  500.0000  500.0000  500.0000
* gflag = 1    (reported delG0f used)
* basic source = 82wag/eva
* delG0f =    -1682.600 kj/mol
* delH0f =     2092.000 kj/mol
* S0PrTr =     2092.000 j/(mol*K)
+-------------------------------------------------------------------
                     .
                     .
                     .
           (Material Deleted)
                     .
                     .
                     .
+-------------------------------------------------------------------
```

The pure liquids superblock follows. The format of a pure liquid block is identical to that in a pure mineral block. The pure liquids superblock is read by EQPT, but no corresponding data are written on the **data1** file. This is because EQ3NR and EQ6 have no capability for handling pure liquid species. Note that water does not appear in this superblock. This superblock is illustrated by the following, taken from **data0.com.R10**:

```
liquids
+-----------------------------------------------------------------------
br2
   date last revised =  18-may-1990                                (see above for formats)
 keys    = liquid           refstate        active
       V0PrTr =     0.000 cm**3/mol  (source =                      )
     1 chemical elements =
      2.0000 br
     5 species in data0 reaction
    -1.0000  br2                            -1.0000  h2o
     0.5000  o2(g)                           2.0000  br-
     2.0000  h+
*    log k grid (0-25-60-100/150-200-250-300 C) =
        -5.8592   -5.0927   -4.4059   -3.9728
        -3.7893   -3.9054   -4.2985   -5.0485
* Extrapolation algorithm: cp integration
* gflag = 1    (reported delG0f used)
* basic source = 89cox/wag
* delG0f =        0.000 kj/mol
* delH0f =        0.000 kj/mol
* S0PrTr =      152.210 j/(mol*K)
* cp source = 79rob/hem                     units = jou
*   T**0      0.36060000E+02
* cp source = 79rob/hem                     units = jou
*   T**0      0.38426000E+02
*   T**-0.5  -0.22423000E+02
*   T**-2    -0.95885000E+05
*   T**2      0.13663000E-06
* Tlimit    =  1526.850 C
+-----------------------------------------------------------------------
                          .
                          .
                          .
            (Material Deleted)
                          .
                          .
                          .
+-----------------------------------------------------------------------
```

The gas species superblock follows. The format of a gas species block is identical to that in a pure mineral block. This superblock is illustrated by the following, taken from **data0.com.R10**:

```
gases
+-----------------------------------------------------------------------
ag(g)
   date last revised =  05-apr-1988                                (see above for formats)
 keys    = gas              active
       V0PrTr =     0.000 cm**3/mol  (source =                      )
     1 chemical elements =
      1.0000 ag
     5 species in data0 reaction
    -1.0000  ag(g)                          -1.0000  h+
    -0.2500  o2(g)                           0.5000  h2o
     1.0000  ag+
*    log k grid (0-25-60-100/150-200-250-300 C) =
        55.5477   50.3736   44.4663   39.1150
        33.8983   29.8254  500.0000  500.0000
* Extrapolation algorithm: constant enthalpy approximation
* gflag = 2    (calculated delG0f(delH0f,S0PrTr) used)
* basic source = 89cox/wag
* delG0f =      246.040 kj/mol
```

```
* delHOf =       284.900 kj/mol
* SOPrTr =       172.888 j/(mol*K)
+-----------------------------------------------------------------------
                         .
                         .
                         .
            (Material Deleted)
                         .
                         .
                         .
+-----------------------------------------------------------------------
```

The solid solutions superblock follows the gas species superblock. A solid solution block consists of the name of the solid solution phase, a list of end-member component species, a mixing law to define the activity coefficients of these species, and a set of parameters for this mixing law. A set of site parameters may also be specified. Each end-member component must be represented on the data file as a pure mineral. For each end member, there is also specified an upper limit to its mole fraction in the solid solution. This superblock is illustrated by the following, taken from **data0.com.R10**:

```
solid solutions                                                       (a24)
+-----------------------------------------------------------------------
                         .
                         .
                         .
            (Material Deleted)
                         .
                         .
                         .
+-----------------------------------------------------------------------
carbonate-calcite      (ca,mn,zn,mg,fe,sr)co3                         (a24)
   date last revised = 22-dec-1987                                    (not read)
 keys   = ss                ideal              active                 (not read)
  6 end members                                                       (i3)
    1.0000  calcite                     1.0000  magnesite        (5x,2(f6.3,2x,a24,5x))
    1.0000  rhodochrosite               1.0000  siderite
    1.0000  smithsonite                 1.0000  strontianite
 type   = 1                                                           (10x,i1)
  0 model parameters                                                  (i3)
  1 site parameters                                                   (i3)
  1.000     0.000     0.000     0.000     0.000     0.000             (6f6.3)
+-----------------------------------------------------------------------
                         .
                         .
                         .
            (Material Deleted)
                         .
                         .
                         .
+-----------------------------------------------------------------------
```

Of the present five data files, only the **com** file contains any solid solutions. These are all ideal ("`type    = 1`"), except for olivine, which is treated as a binary regular solution ("`type    = 3`"). The "`model parameters`" are the set of interaction coefficient parameters. For an ideal solution, there are none. If there were any such parameters, they would be entered below "`model parameters`" using the format illustrated for "`site parameters`". Both kinds of parameters are currently stored in different parts of the same array (**apx**, see Chapter 3). In current practice, one site parameter is declared for each solid solution, regardless of type. This is stored as **apx(7,nx)** for the **nx**-th solid solution. If the solution is not ideal, however, the number given as a site parameter is not used as such (ion most cases is simply not used). It and other members in the site parameter range of the **apx** array may be used instead to store additional interaction coefficient parameters.

The references block is the last part of the data file. It contains references. It is terminated by a line beginning with "`stop.`". It is illustrated by the following, taken from **data0.com.R10**:

```
references
+--------------------------------------------------------------------
Abrahams, s.c., bernstein, j.l., and nassau, k., (1976) transition me
  tal iodates. vii. crystallographic and nonlinear optic survey of the
   4f-iodates journal of solid state chemistry 16, 173-184.
   76abr/ber
                    •
                    •
                    •
            (Material Deleted)
                    •
                    •
                    •
stop.
```

EQPT does not write the contents of this block onto the **data1** file. This block is present only to provide a means of documenting the data present on the data file.

4.2. The hmw Archetype for the data0 File

The basic structure of the **hmw** archetype is illustrated in Figure 3 (compare with Figure 2). This is identical to the **com** archetype, except for two differences. The "data0" parameters block has a slightly different content, and the "bdot" parameters block is replaced by two superblocks, one for Pitzer coefficient data pertaining to pure aqueous neutral electrolytes, the other to such data pertaining to mixtures of two aqueous neutral electrolytes containing a common ion.

The "data0" parameters block in **data0.hmw.R10** is as follows:

```
data0 parameters
+--------------------------------------------------------------------
temperature limits                                                   (a)
        25.0000   25.0000                                            (5x,2f10.4)
temperatures
         0.0100   25.0000   60.0000  100.0000                        (5x,4f10.4)
       150.0000  200.0000  250.0000  300.0000
pressures
         1.0132    1.0132    1.0132    1.0132
         4.7572   15.5365   39.7365   85.8378
debye huckel aphi
         0.3770    0.3920    0.4190    0.4610
         0.5300    0.6230    0.7540    0.9600
log k for eh reaction
       -91.0448  -83.1049  -74.0534  -65.8641
       -57.8929  -51.6848  -46.7256  -42.6828
+--------------------------------------------------------------------
```

Note that A_{ϕ} appears in place of $A_{\gamma,10}$. B_{γ}, $\dot{B}$, and the C, F, G, E, and H coefficients from Drummond (1981) do not appear in this block in this archetype. Although A_{ϕ} and $A_{\gamma,10}$ are related by theory, the former should not be calculated from the latter, as slight but significant differences in the value of Debye-Hückel parameters occur from model to model (see Chapter 3), hence also from data file to data file. This is also why the values of the Debye-Hückel parameters are written on the data files instead of being hard-wired into EQ3NR and EQ6.

Header (data0, data file key, stage number)

Title

"data0" parameters block:

- Temperature limits (°C)
- Temperature (°C), standard grid
- Pressure (bars), standard grid
- A_{ϕ}, standard grid
- $log\ K_{Eh}$, standard grid

Pure electrolyte parameters superblock:

- Species pairs; $\beta^{(n)}_{MX}$, $n = 1,2$ and C^{ϕ}_{MX}

Electrolyte mixtures parameters superblock:

- Species triplets; ${}^{S}\theta_{MM'}$ and $\psi_{MM'X'}$ or ${}^{S}\theta_{XX'}$ and $\psi_{MXX'}$

Chemical elements block:

- Elements, atomic weights

Aqueous species superblock:

- Strict basis species
- Auxiliary basis species, with *log K* on the standard grid
- Non-basis species, with *log K* on the standard grid

Pure minerals superblock:

- Pure minerals, with *log K* on the standard grid

Pure liquids superblock:

- Pure liquids, with *log K* on the standard grid

Gas species superblock:

- Gas species, with *log K* on the standard grid

Solid solutions superblock:

- Solid solutions

References block:

- References

Figure 3. The basic structure of the data0 file for the hmw archetype.

The superblock for Pitzer parameters for pure aqueous neutral electrolytes is illustrated by the following, which is taken from **data0.hmw.R10**. This superblock begins with the header "`single-salt parameters`". The contents of a typical block, illustrated by that for the species pair "`na+          cl-`", is obvious. A block can also be entered for a species pair consisting of one or more neutral species. This is illustrated below by the block for the species pair "`so4--  co2(aq)`". Note that here the "`beta`" parameters are really lambda parameters. EQPT maps the observable Pitzer parameters and their corresponding temperature derivatives in this superblock into corresponding conventional primitive equivalents. The conventional primitive equivalents are then written onto the **data1** file. The mapping relations are given in Chapter 3. Note that the standard temperature grid is not used to deal with the temperature dependence of any of the parameters of Pitzer's (1973, 1975, 1979, 1987) equations, with the exception of the A_ϕ Debye-Hückel parameter (which is not unique to these equations).

```
single-salt parameters                                               (a12)
+--------------------------------------------------------------------
na+           cl-                                                    (a12,2x,a12)
  1            -1                                                    (f3.0,t15,f3.0)
*
     beta0 =   0.07650   beta1 =   0.26440   beta2 =   0.00000      (2x,3(11x,f9.5)
                        alpha1 =   2.0       alpha2 =  12.0         (18x,2(16x,f5.1))
*
      cphi =  0.00127                                              (13x,f9.5,12x,f5.1)
    source = 84har/mol                                               (13x,a18)
*
*
   db0/dt =  0.000E+00  d2b0/dt2 =  0.000E+00                     (13x,e10.3,13x,e10.3)
   db1/dt =  0.000E+00  d2b1/dt2 =  0.000E+00
   db2/dt =  0.000E+00  d2b2/dt2 =  0.000E+00
    dc/dt =  0.000E+00   d2c/dt2 =  0.000E+00
    source =                                                         (13x,a18)
+--------------------------------------------------------------------
                    .
                    .
                    .
           (Material Deleted)
                    .
                    .
                    .
+--------------------------------------------------------------------
```

The superblock for Pitzer parameters for mixtures of two aqueous neutral electrolytes is illustrated by the following, which is taken from **data0.hmw.R10**. This superblock begins with the header "`mixture term parameters`". The contents of a typical block, illustrated by that for the species triplet "`na+          k+          cl-`", is obvious. EQPT maps the observable Pitzer parameters and their corresponding temperature derivatives in this superblock into corresponding conventional primitive equivalents. The conventional primitive equivalents are then written onto the **data1** file. The mapping relations are given in Chapter 3.

```
mixture term parameters                                              (a)
+--------------------------------------------------------------------
na+           k+            cl-                                      (a12,2(2x,a12))
*
     theta = -0.01200       psi = -0.00180                        (13x,f8.5,13x,f8.5)
    source = 84har/mol                                               (13x,a18)
*
*
   dth/dt =   0.0000   d2th/dt2 =  0.000E+00                     (13x,e10.3,13x,e10.3)
  dpsi/dt =   0.0000   d2ps/dt2 =  0.000E+00
    source =                                                         (13x,a18)
+--------------------------------------------------------------------
```

```
                        .
                        .
                        .
          (Material Deleted)
                        .
                        .
                        .
+-----------------------------------------------------------------------
```

4.3. The com Archetype for the data1/data1f Files

The **data1** file, being unformatted, can not be printed or displayed in meaningful fashion. The **data1f** file is a formatted equivalent. It can be useful in debugging if there are problems with a **data0** file or with EQPT. It also suffices to illustrate the structure of the **data1** file. In essence, each line of data in **data1f** represents one logical record of data in **data1**. Some block terminator lines appear in **data1f** to assist readability. The string "`endit.`" is frequently used to mark the end of superblocks.

*The **data1f** file corresponding to **data0.com.R10** is presented below. Material has been deleted* where appropriate in order to present the essential facts, following the practice established earlier in presenting the major parts of the **data0** file structure. Some notes are superimposed on the material presented below. These are distinguished by the use of bold italic font.

Note that the structure of the **data1/data1f** files differs in some ways from that of the corresponding **data0** file. In particular, the superblocks containing activity coefficient data (here the "bdot" parameters) appear at the end of the file, instead of near the beginning. Also, the nominal temperature limits appear in a different location from that in which the data for the other "data0" parameters. The structure of the species blocks is also slightly different. EQPT computes the molecular weight of each species and puts this in the species block written on **data1/data1f.** Note that all data represented on the **data0** file on the standard temperature grid are replaced by the coefficients of interpolating polynomials. The first 5 coefficients represent a fit to the data in the range 0-100°C, the second five the data in the range 100-300°C. The first example of this in the material below occurs for the pressure "`press`".

A **data1/data1f** file begins with a record/line containing the string "`data1`". This is followed by one containing the key string "`stfipc`" (**com** archetype) or "`stpitz`" (**hmw** archetype). The third record/line contains the number of chemical elements and the number of basis species (strict plus auxiliary). The fourth record/line contains the name of the **data0** file used to generate the present **data1/data1f** file. This record/line is appended to the title as its first line.

```
data1
stfipc                        (key string for a file of the com archetype)
   78  147                    (number of chemical elements, number of basis species)
data0.com.R10
THERMODYNAMIC DATABASE
generated by gembochs/INGRES  15-apr-91
+-----------------------------------------------------------------------
    0.0000  300.0000                   (temperature limits)
+-----------------------------------------------------------------------
o        15.99940                     0.00000            (the zeros in the this block
ag      107.86820                     0.00000             represent the oxide factor,
al       26.98154                     0.00000             which is no longer used)
                        .
                        .
```

```
                        .
            (Material Deleted)
                        .
                        .
                        .
zr        91.22400                     0.00000
press
 1.013200000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
-4.345000000E-01 7.632333333E-03 5.514000000E-05-1.263733333E-06 1.396800000E-08
adh
 4.938943704E-01 5.628991135E-04 5.680199734E-06-7.486279129E-09 0.000000000E+00
 6.123000000E-01-2.559500000E-03 3.578166667E-05-1.378000000E-07 2.313333333E-10
bdh
 3.252987270E-01 1.272991554E-04 5.443822909E-07-1.372465408E-09 0.000000000E+00
 3.311000000E-01-2.133333333E-05 1.913333333E-06-7.066666667E-09 1.066666667E-11
bdot
 1.738490207E-02 1.510054148E-03-2.607766840E-05 1.383863672E-07 0.000000000E+00
 1.090000000E-01-1.483333333E-03 1.173333333E-05-3.466666667E-08 2.666666667E-11
cco2
-1.031200000E+00 1.280600000E-03 2.559000000E+02 4.445000000E-01-1.606000000E-03
xlkeh
-9.104826360E+01 3.463716921E-01-1.212214387E-03 2.669138257E-06 0.000000000E+00
-9.006110000E+01 3.154611667E-01-8.761516667E-04 1.533533333E-06-1.211333333E-09
aqueous
h2o                        2    0      (name, # of elements, # of species in reaction)
        18.015   0.                        (molecular weight, charge)
     1.0000  o             2.0000  h
                        .
                        .
                        .
            (Material Deleted)
                        .
                        .
                        .
o2(g)                      1    0      (name, # of elements, # of species in reaction)
        31.999   0.                        (molecular weight, charge)
     2.0000  o
                        .
                        .
                        .
            (Material Deleted)
                        .
                        .
                        .
acetic acid(aq)            3    4      (name, # of elements, # of species in reaction)
        60.053   0.                        (molecular weight, charge)
     2.0000  c             2.0000  o
     4.0000  h
    -1.0000  acetic acid(aq)            -2.0000  o2(g)
     2.0000  h+                          2.0000  hco3-
 1.504679814E+02-6.181568055E-01 1.997116069E-03-4.266161503E-06 0.000000000E+00
 1.486100000E+02-5.620795000E-01 1.405498333E-03-2.245400000E-06 1.456666667E-09
                        .
                        .
                        .
            (Material Deleted)
                        .
                        .
                        .
(npo2)2(oh)2++             3    4      (name, # of elements, # of species in reaction)
       572.108   2.                        (molecular weight, charge)
     2.0000  h             2.0000  np
     6.0000  o
    -1.0000  (npo2)2(oh)2++             -2.0000  h+
     2.0000  h2o                         2.0000  npo2++
 7.128571429E+00-3.176190476E-02 1.047619048E-04 0.000000000E+00 0.000000000E+00
 5.800000000E+00-8.000000000E-03 0.000000000E+00 0.000000000E+00 0.000000000E+00
                        .
                        .
                        .
            (Material Deleted)
                        .
                        .
```

```
endit.
minerals
(pb(oh)2)3.pbcl2          4    5      (name, # of elements, # of species in reaction)
        1001.749   0.    0.000            (molecular weight, charge, molar volume)
      2.0000  cl          4.0000  pb
      6.0000  h           6.0000  o
     -1.0000  (pb(oh)2)3.pbcl2           -6.0000  h+
      2.0000  cl-                         4.0000  pb++
      6.0000  h2o
 1.727930000E+01 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
 5.000000000E+02 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
                              .
                              .
                              .
             (Material Deleted)
                              .
                              .
                              .
endit.
gases
ag(g)                     1    5      (name, # of elements, # of species in reaction)
         107.868   0.    0.000            (molecular weight, charge, molar volume)
      1.0000  ag
     -1.0000  ag(g)                      -1.0000  h+
     -0.2500  o2(g)                       0.5000  h2o
      1.0000  ag+
 5.554995563E+01-2.255708754E-01 7.834836108E-04-1.712704203E-06 0.000000000E+00
 5.297980000E+01-1.615240000E-01 2.287600000E-04 0.000000000E+00 0.000000000E+00
                              .
                              .
                              .
             (Material Deleted)
                              .
                              .
                              .
endit.
solid solutions
                              .
                              .
                              .
             (Material Deleted)
                              .
                              .
                              .
carbonate-calcite         6    1      (name, # of end members, # of site parameters)
      1.000  calcite                   1.000  magnesite
      1.000  rhodochrosite             1.000  siderite
      1.000  smithsonite               1.000  strontianite
 0.000 0.000 0.000 0.000 0.000 0.000
 1.000 0.000 0.000 0.000 0.000 0.000
                              .
                              .
                              .
             (Material Deleted)
                              .
                              .
                              .
endit.
(uo2)3(co3)6(6-)            4.0    0       (name, hard core diameter, insgfl flag)
np(co3)5(6-)                4.0    0
u(co3)5(6-)                 4.0    0
                              .
                              .
                              .
             (Material Deleted)
                              .
                              .
                              .
th6(oh)15(9+)               6.0    0
endit.
```

4.4. The hmw Archetype for the data1/data1f Files

The **data1f** file corresponding to **data0.hmw.R10** is presented below. Material has been deleted where appropriate in order to present the essential facts, following the practice established in the previous example. The superblocks containing the Pitzer coefficient parameters appear at the end of the file. Note that the observable parameters have been mapped into conventional primitive equivalents.

```
data1
stpitz                        (key string for a file of the com archetype)
    9   13                    (number of chemical elements, number of basis species)
data0.hmw.R10
THERMODYNAMIC DATABASE
generated by gembochs/INGRES  16-apr-91
+-----------------------------------------------------------------------
   25.0000   25.0000                    (temperature limits)
+-----------------------------------------------------------------------
o          15.99940                       0.00000          (the zeros in the this block
ca         40.07800                       0.00000           represent the oxide factor,
cl         35.45270                       0.00000           which is no longer used)
h           1.00794                       0.00000
c          12.01100                       0.00000
k          39.09830                       0.00000
mg         24.30500                       0.00000
na         22.98977                       0.00000
s          32.06600                       0.00000
press
 1.013200000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
-4.345000000E-01 7.632333333E-03 5.514000000E-05-1.263733333E-06 1.396800000E-08
aphi
 3.769945819E-01 5.417897788E-04 2.121889093E-06 8.607549305E-09 0.000000000E+00
 4.540000000E-01-1.558333333E-03 2.361666667E-05-8.866666667E-08 1.533333333E-10
xlkeh
-9.104826360E+01 3.463716921E-01-1.212214387E-03 2.669138257E-06 0.000000000E+00
-9.006110000E+01 3.154611667E-01-8.761516667E-04 1.533533333E-06-1.211333333E-09
aqueous
h2o                         2    0        (name, # of elements, # of species in reaction)
         18.015    0.                         (molecular weight, charge)
     1.0000  o              2.0000   h
                      .
                      .
                      .
           (Material Deleted)
                      .
                      .
                      .
o2(g)                       1    0        (name, # of elements, # of species in reaction)
         31.999    0.                         (molecular weight, charge)
     2.0000  o
                      .
                      .
                      .
           (Material Deleted)
                      .
                      .
                      .
caco3(aq)                   3    4        (name, # of elements, # of species in reaction)
        100.087    0.                         (molecular weight, charge)
     1.0000  c              1.0000   ca
     3.0000  o
    -1.0000  caco3(aq)                   -1.0000   h+
     1.0000  ca++                         1.0000   hco3-
 7.188000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
 5.000000000E-02 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
                      .
                      .
                      .
           (Material Deleted)
                      .
```

```
                           .
                           .
endit.
minerals
anhydrite                       3    3       (name, # of elements, # of species in reaction)
        136.142    0.     0.000                  (molecular weight, charge, molar volume)
     1.0000  ca            1.0000  s
     4.0000  o
    -1.0000  anhydrite                     1.0000  ca++
     1.0000  so4--
-4.362100000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
 5.000000000E+02 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
                           .
                           .
                           .
            (Material Deleted)
                           .
                           .
                           .
endit.
gases
co2(g)                          2    4       (name, # of elements, # of species in reaction)
        44.010    0.     0.000                   (molecular weight, charge, molar volume)
     1.0000  c             2.0000  o
    -1.0000  co2(g)                       -1.0000  h2o
     1.0000  h+                            1.0000  hco3-
-7.819200000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
 5.000000000E+02 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
                           .
                           .
                           .
            (Material Deleted)
                           .
                           .
                           .
endit.
*
E-lambda flag = on         (off/on)  Do not change this flag.        (Eλ flag)
na+            cl-
   lambda0 =    0.07650    lambda1 =    0.26440    lambda2 =    0.00000
                           alpha1 =    2.0         alpha2 =  12.0
    d10/dt =  0.000E+00    d210/dt2 =  0.000E+00
    d11/dt =  0.000E+00    d211/dt2 =  0.000E+00
    d12/dt =  0.000E+00    d212/dt2 =  0.000E+00
+-----------------------------------------------------------------------
                           .
                           .
                           .
            (Material Deleted)
                           .
                           .
                           .
+-----------------------------------------------------------------------
endit.
na+            cl-            na+                     (species triplet for μMMX or μMXX)
        mu =    0.00021   dmmx/dt =   0.000E+00   d2mmx/dt2 =   0.000E+00
+-----------------------------------------------------------------------
                           .
                           .
                           .
            (Material Deleted)
                           .
                           .
                           .
+-----------------------------------------------------------------------
endit.
k+             na+            cl-                     (species triplet for μMM'X or μMXX')
        mu =  -0.00026    dmu/dt =   0.000E+00    d2mu/dt2 =   0.000E+00
+-----------------------------------------------------------------------
                           .
                           .
                           .
            (Material Deleted)
```

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

5. Code Architecture and Flow of Execution

The purpose of the present chapter is to provide a description of the structure of the software itself. This material is primarily included because it is required as part of the documentation to satisfy NUREG-0856 (Silling, 1983). It does not provide anything necessary for the typical code user. It may be helpful to those few users who desire to modify the code for whatever purpose.

In the present description, we will not make it a point to describe the role and function of every module in the source code. For such descriptions, the reader is referred to the relevant glossaries of modules. For EQPT modules, see Appendix B of the present report. For EQLIB modules, see Appendix A of the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a). The purpose here is to describe the main features and essential aspects of the structure of the code. The purpose is not to provide detailed design documentation. Readers who want more detailed information are invited to examine the source code itself, which is reasonably well-documented internally.

The basic structure of EQPT is illustrated in the simplified flow diagram given in Figure 4. This diagram shows the flow of execution from the perspective of the main program, module **eqpt.f**. This is a fairly simple one-pass structure. EQPT does not process more than one **data0** file in a single run. There is branching in this flow only to deal with differences in the kinds of activity coefficient parameters and their processing between the **com** and **hmw** data file archetypes.

The simplified flow diagram omits references to writes to the **data1f**, **dpt1**, and **dpt2** files. The code writes to the **data1f** file whenever it writes to the **data1** file, as the former is a formatted version of the latter. The **dpt1** and **dpt2** files are only produced in the case of the **hmw** archetype. The **dpt1** file is written by modules **pdpz2.f** and **rdpz3.f**, and contains essentially just an echo of the observable Pitzer coefficient data read from the **data0** file. The **dpt2** file is written by module **wrpz3.f** and contains the corresponding conventional primitive Pitzer coefficient data. The same data are also written on the **data1f** file. The **dpt1** and **dpt2** files are vestigial in the present version of EQPT.

The simplified flow diagram also omits references to writes to the **slist** file and to some writes to the **output** and screen files which occur as the title and the superblocks for aqueous species, pure minerals, pure liquids, gas species, and solid solutions are processed by the relevant modules called by **eqpt.f**. These writes generate lists of the species on the data file. In the case of the screen file, only an abbreviated list is produced.

Module **eqpt.f** directs the overall process of code execution. Its first function is to get the time and date, which it does by calling the EQLIB module **timdat.f**. This module contains UNIX-dependent code. The main program then writes the code name and version identification, the copyright notice, and the time and date information to the screen and **output** files. Its next step is to initialize the dimensioning variables which correspond to the dimensioning parameters. Dimensioning variables are used to pass dimensioning data in the calling sequences of called modules; FORTRAN does not generally allow parameters (in the special FORTRAN sense) to be so passed.

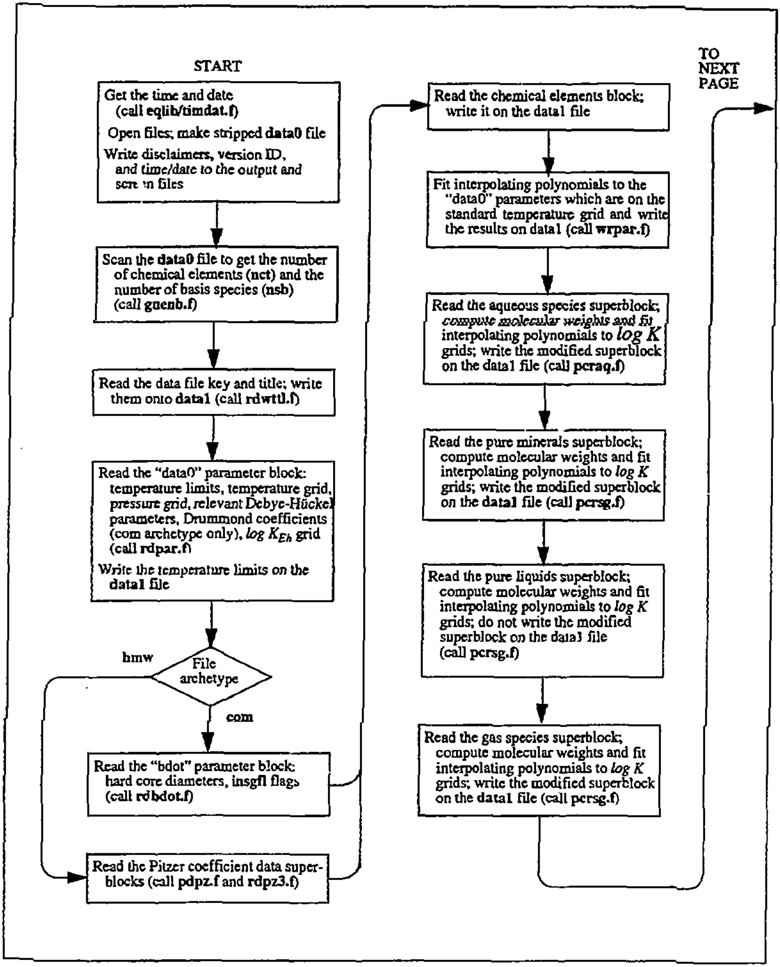

Figure 4. Simplified flow diagram of the EQPT code.

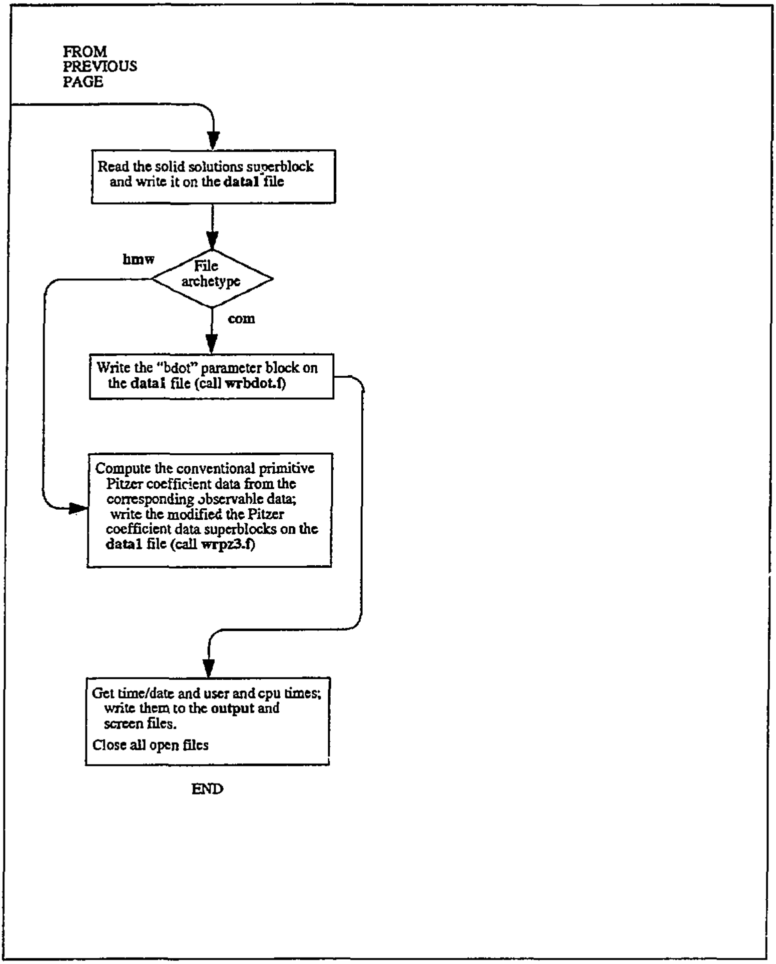

Figure 4 (continued). Simplified flow diagram of the EQPT code.

A seeming oddity in the flow of execution depicted in Figure 4 is that some block or superblocks are read from the **data0** file, processed, and written (sometimes in modified form) on the **data1** file in one continuous action, whereas in other cases some or all of the processing, and the writing of these blocks or superblocks on the **data1** file, does not occur until after succeeding blocks or superblocks have been read. This occurs because the succession of blocks and superblocks in the **data1** files differs somewhat from that of the corresponding **data0** files (see Chapter 4). There is no reason why this succession could not be the same for both kinds of files. However, if this were to be done, the activity coefficient superblocks should follow the species superblocks as in the **data1** files to facilitate processing of the data by EQ3NR and EQ6.

The main program module **eqpt.f** calls module **gnenb.f** to scan the **data0** file to determine the number of chemical elements (**nct**) and the number of basis species (**nsb**) on the data file. Module **eqpt.f** writes these data on the **data1** file, as well as the **output**, **slist**, and screen files.

Module **eqpt.f** *calls module* **rdwttl.f** *to read the* data file key (**com**, **nea**, **sup**, **hmw**, or **pit**) and the title. It validates the data file key against a set of known allowed possibilities and determines the code archetype. It then writes the data file key and the title on the **data1** file.

Module **eqpt.f** then calls module **rdpar.f** to read the "data0" parameter block. This includes the nominal temperature limits (°C) for the data file, the temperature values (°C) for the standard temperature grid, the pressure (bars) on the standard temperature grid, the relevant Debye-Hückel parameters on this grid ($A_{\gamma,10}$, B_{γ}, and $\dot{B}$ for the **com** archetype; A_{ϕ} for the hmw archetype), the coefficients for eq (12), which is used to compute the activity coefficient of aqueous CO_2 in $NaCl$ solutions (**com** archetype only), and $log\ K_{Eh}$ on the standard temperature grid. The temperature limits are written on the **data1** file at this point. However, processing and writing of data for other parameters on this block is deferred (carried out later by module **wrpar.f**).

The activity coefficient data are then read. In the case of the **com** archetype, **eqpt.f** calls module **rdbdot.f** to read the block of "bdot" parameters (species names, hard core diameters, **insgfl** flags). In the case of the **hmw** archetype, the main program calls module **pdpz.f** to read the superblock of observable Pitzer parameters *corresponding to solutions of pure aqueous neutral electrolytes (species pairs). It then calls module* **rdpz.f** *to read the superblock of observable* Pitzer parameters corresponding to mixtures of two aqueous neutral electrolytes.

Module **eqpt.f** then calls module **rdwele.f**. This reads the chemical elements block and writes it on the **data1** file. Following that, **eqpt.f** calls module **wrpar.f**. This module processes the remaining "data0" parameters and writes the corresponding data on the **data1** file. The parameters which were read from the **data0** file in the form of values on the standard temperature grid are processed as follows Module **wrpar.f** calls module **intrp.f** in each case to fit one interpolating polynomial to the part of the grid for the temperature range 0-100°C, and a second such polynomial to the part of the grid for the range 100-300°C. The interpolating polynomial coefficients replace the original grid values in the data written onto the **data1** file.

Module **eqpt.f** then processes four species superblocks. The aqueous species superblock is processed by a call to module **pcraq.f**. This module reads a data block for each species in the superblock, processes it, and writes a corresponding block onto the **data1** file. The $log\ K$ data for the associated reaction (all aqueous species but strict basis species have such a reaction) are read from the **data0** file as values on the standard temperature grid. Module **pcraq.f** calls module **rxnchk.f** to check each associated reaction for mass and charge balance. Module **pcraq.f** then calls module **intrp.f** to fit interpolating polynomials to these data in the same manner as it does for the "data0" parameters which are read as values on this grid. When the data block for the species is written onto the **data1** file, the interpolating polynomial coefficients replace the values on the grid. Module **pcraq.f** also computes the molecular weight of each species and includes this in the data block written on the **data1** file.

The superblocks for pure minerals, pure liquids, and gas species are handled similarly by a call in each case to module **pcrsg.f**. The pure liquids superblock is read, but this superblock is not written onto the **data1** file, as EQ3NR and EQ6 have not been developed to deal with pure nonaqueous liquids. Module **pcrsg.f** is closely analogous to module **pcraq.f**.

Module **eqpt.f** then calls module **pcrss.f**. This reads the solid solutions superblock and writes it onto the **data1** file. This superblock is not analogous to those for aqueous species, pure minerals, pure liquids, or gas species, as solid solutions are *phases*, not species. The data block for each solid solution includes a list of end-member components, which must correspond to pure minerals appearing in the pure minerals superblock.

The activity coefficient data are then processed and written to the **data1** file. In the case of the **com** archetype, the data require no processing. Module **eqpt.f** calls module **wrbdot.f** to write the "bdot" block onto the **data1** file. In the case of the **hmw** archetype, **eqpt.f** calls module **wrpz3.f**. This module processes the data, calculating conventional primitive Pitzer coefficient data from the set of corresponding observable coefficient data read from the **data0** file. Three superblocks of conventional primitive coefficient data are then written on the **data1** file: one for the λ coefficients corresponding to all types of species pairs, one for μ coefficients for species triplets in which one species appears twice, and one for μ coefficients for species triplets in which no species appears more than once. This contrasts with the two superblocks of observable coefficient data that are read from the **data0** file.

All data file processing is now complete. Module **eqpt.f** gets the time and date and user and cpu times and writes them to the **output** and screen files. It then closes all open files and terminates execution.

Acknowledgments

Thanks are due to many individuals for their contributions in one form or another to the development of EQ3/6. Among these are Roger Aines, Carol Bruton, Bill Bourcier, Manny Clinnick, Paul Cloke, Joan Delany, Don Emerson, Mandy Goldner, Bob Herrick, Dana Isherwood, Ken Jackson, Jim Johnson, Suzanne Lundeen, Bill McKenzie, Judith Moody, Miki Moore, Ignasi Puigdomenech, Larry Ramspott, Terry Steinborn, and Brian Viani. We thank Jim Johnson for his technical review of this report, which led to a number of improvements. We also thank Ardyth Simmons for her comments on the manuscript.

References

Carnahan, B., Luther, H. A., and Wilkes, J. O., 1969, Applied Numerical Methods: John Wiley & Sones, New York.

Clegg, S. L., and Brimblecombe, P., 1989, Solubility of ammonia in pure aqueous and multicomponent solutions: Journal of Physical Chemistry, v. 93, p. 7237-7248.

Clegg, S. L., and Brimblecombe, P., 1990, Solubility of volatile electrolytes in multicomponent solutions with atmospheric applications, *in* Melchior, D. C., and Bassett, R. L., editors, Chemical Modeling of Aqueous Systems II, American Chemical Society Symposium Series, v. 416, American Chemical Society, Washington, D. C., p. 58-73.

Davies, C. W., 1962, Ion Association: Butterworths, London.

Delany, J. M., and Lundeen, S. R., 1991, The LLNL Thermochemical Data Base- Revised Data and File Format for the EQ3/6 Package: UCID-21658, Lawrence Livermore National Laboratory, Livermore, California.

Drummond, S. E., Jr., 1981, Boiling and Mixing of Hydrothermal Fluids: Chemical Effects on Mineral Precipitation: Ph.D. thesis, The Pennsylvania State University, University Park, Pennsylvania.

Felmy, A. R., and Weare, J. H., 1986, The prediction of borate mineral equilibria in natural waters: Application to Searles Lake, California: Geochimica et Cosmochimica Acta, v. 50, p. 2771-2783.

Garrels, R. M., and Christ, C. L., 1965, Solutions, Minerals and Equilibria: Freeman, Cooper and Company, San Francisco.

Garrels, R. M., and Thompson, M. E., 1962, A chemical model for sea water at 25°C and one atmosphere total pressure: American Journal of Science, v. 260, p. 57-66.

Greenberg, J. P., and Møller, N., 1989, The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-K-Ca-Cl-SO_4-H_2O system to high concentration from 0 to 250°C: Geochimica et Cosmochimica Acta, v. 53, p. 2503-2518.

Grenthe, I., Lemire, R. J., Muller, A. B., Nguyen-Trung, C., and Wanner, H., 1989, NEA-TDB Chemical Thermodynamics of Uranium, OECD-Nuclear Energy Agency, Saclay, France (draft manuscript; NNA.900815.0013).

Grenthe, I., Fuger, J., Lemire, R. J., Muller, A. B., Nguyen-Trung, C., and Wanner, H., editors, 1992, Chemical Thermodynamics of Uranium: Elsevier Science Publishing Company, New York.

Harvie, C. E., Møller, N., and Weare, J. H., 1984, The prediction of mineral solubilities in natural waters: the Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O system to high ionic strengths at 25°C: Geochimica et Cosmochimica Acta, v. 48, p. 723-751.

Helgeson, H. C., 1969, Thermodynamics of hydrothermal systems at elevated temperatures and pressures: American Journal of Science, v. 267, p. 729-804.

Helgeson, H. C., Brown, T. H., Nigrini, A., and Jones, T. A., 1970, Calculation of mass transfer in geochemical processes involving aqueous solutions: Geochimica et Cosmochimica Acta, v. 34, p. 569-592-877.

Helgeson, H. C., Delaney, J. M., Nesbitt, H. W., and Bird, D. K., 1978, Summary and critique of the thermodynamic properties of rock-forming minerals: American Journal of Science, v. 278-A, p. 1-229.

Helgeson, H. C., and Kirkham, D. H., 1974a, Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: I. Summary of the thermodynamic/electrostatic properties of the solvent: American Journal of Science, v. 274, p. 1089-1198.

Helgeson, H. C., and Kirkham, D. H., 1974b, Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: II. Debye-Hückel parameters for activity coefficients and relative partial-molal properties: American Journal of Science, v. 274, p. 1199-1261.

Helgeson, H. C., and Kirkham, D. H., 1976, Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: IV. Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 600°C and 5 kb: American Journal of Science, v. 281, p. 1249-1516.

Helgeson, H. C., Kirkham, D. H., and Flowers, G. C., 1981, Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: III. Equation of state for aqueous species at infinite dilution: American Journal of Science, v. 276, p. 97-240.

Johnson, J. W., and Norton, D., 1991, Critical phenomena in hydrothermal systems: State, thermodynamic, electrostatic, and transport properties of H_2O in the critical region: American Journal of Science, v. 291, p. 541-648.

Johnson, J. W., Oelkers, E. H., and Helgeson, H. C., 1992, SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bars and 0° to 1000°C: Computers and Geosciences, v. 18, p. 899-947.

McKenzie, W. F., Wolery, T. J., Delany, J. M., Silva, R. J., Jackson, K. J., Bourcier, W. L., and Emerson, D. O., 1986, Geochemical Modeling (EQ3/6) Plan Office of Civilian Radioactive Waste Management Program: UCID-20864, Lawrence Livermore National Laboratory, Livermore, California.

Nordstrom, D. K. and Munoz, J. L., 1985, Geochemical Thermodynamics: Benjamin/Cummings Publishing Company, Inc., Menlo Park, California, 477 p.

Pabalan, R. T., and Pitzer, K. S., 1987, Thermodynamics of concentrated electrolyte mixtures and the prediction of mineral solubilities to high temperatures for mixtures in the system Na-K-Ca-Mg-Cl-SO_4-OH-H_2O: Geochimica et Cosmochimica Acta, v. 51, p. 2429-2443.

Pabalan, R. T., and Pitzer, K. S., 1988, Heat capacity and other thermodynamic properties of $Na_2SO_{4(aq)}$ in hydrothermal solutions and the solubilities of sodium sulfate minerals in the system Na-Cl-SO_4-OH-H_2O: Geochimica et Cosmochimica Acta, v. 52, p. 2393-2904.

Pitzer, K. S., 1973, Thermodynamics of electrolytes - I. Theoretical basis and general equations: Journal of Physical Chemistry, v. 77, p. 268-277.

Pitzer, K. S., 1975, Thermodynamics of electrolytes. V. Effects of higher-order electrostatic terms: Journal of Solution Chemistry, v. 4, p. 249-265.

Pitzer, K. S., 1979, Theory: ion interaction approach, *in* Pytkowicz, R. M., editor, Activity Coefficients in Electrolyte Solutions, CRC Press, Boca Raton, Florida, p. 157-208.

Pitzer, K. S., 1987, Thermodynamic model for aqueous solutions of liquid-like density, *in* Carmichael, I. S. E., and Eugster, H. P., editors, Thermodynamic Modeling of Geological Materials: Minerals, Fluids and Melts, Reviews in Mineralogy, v. 17, Mineralogical Society of America, Washington, D. C., p. 97-142

Plummer, L. N., Parkhurst, D. L., Fleming, G. W., and Dunkle, S. A., 1988, A Computer Program Incorporating Pitzer's Equations for Calculation of Geochemical Reactions in Brines: United States Geological Survey Water-Resources Investigations Report 88-4153, 310 p.

Prigogine, I., and Defay, R., 1954, Chemical Thermodynamics: Longmans, Green, and Company, London.

Saxena, S. R., 1973, Thermodynamics of Rock-Forming Crystalline Solutions: Springer-Verlag, New York.

Shock, E. L., and Helgeson, H. C., 1988, Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Correlation algorithms for ionic species and equation of state predictions to 5 kb and 1000°C: Geochimica et Cosmochimica Acta, v. 52, p. 2009-2036.

Shock, E. L., and Helgeson, H. C., 1989, Corrections to Shock and Helgeson (1988) *Geochimica et Cosmochimica Acta* 52, 2009-2036: Geochimica et Cosmochimica Acta, v. 53, p. 215.

Shock, E. L., and Helgeson, H. C., 1990, Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Standard partial molal properties of organic species: Geochimica et Cosmochimica Acta, v. 54, p. 915-945.

Shock, E. L., Helgeson, H. C., and Sverjensky, D. A., 1989, Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Standard partial molal properties of inorganic species: Geochimica et Cosmochimica Acta, v. 53, p. 2157-2183.

Shock, E. L., Oelkers, E. H., Johnson, J. W., Sverjensky, D. A., and Helgeson, H. C., 1992, Calculation of the thermodynamic properties of aqueous species at high pressures and temperatures: Effective electrostatic radii, dissociation constants and standard partial molal properties to 1000°C and 5 kbar: Journal of the Chemical Society Faraday Transactions, v. 88, p. 803-826.

Silling, S. A., 1983, Final Technical Position on Documentation of Computer Codes for High-Level Waste Management: NUREG-0856, United States Nuclear Regulatory Commission, Washington, D. C.

Spencer, R. J., Møller, N., and Weare, J. H., 1990, The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-K-Ca-Mg-Cl-SO_4-H_2O system at temperatures below 25°C: Geochimica et Cosmochimica Acta, v. 54, p. 575-590.

Tanger, J. C., and Helgeson, H. C., 1988, Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Revised equations of state for the standard partial molal properties of ions and electrolytes: American Journal of Science, v. 288, p. 19-98.

Viani, B. E., and Bruton, C. J., 1992, Modeling Fluid-Rock Interaction at Yucca Mountain, Nevada: A Progress Report: UCRL-ID-109921, Lawrence Livermore National Laboratory, Livermore, California.

Wolery, T. J., 1979, Calculation of Chemical Equilibrium between Aqueous Solutions and Minerals: The EQ3/6 Software Package: UCRL-52658, Lawrence Livermore National Laboratory, Livermore, California.

Wolery, T. J., 1983, EQ3NR, A Computer Program for Geochemical Aqueous Speciation-Solubility Calculations: User's Guide and Documentation: UCRL-53414, Lawrence Livermore National Laboratory, Livermore, California.

Wolery, T. J., 1992a, EQ3/6, A Software Package for Geochemical Modeling of Aqueous Systems: Package Overview and Installation Guide: UCRL-MA-110662-PT-I, Lawrence Livermore National Laboratory, Livermore, California.

Wolery, T. J., 1992b, EQ3NR, A Computer Program for Geochemical Aqueous Speciation-Solubility Calculations: Theoretical Manual, User's Guide, and Related Documentation (Version 7.0): UCRL-MA-110662-PT-III, Lawrence Livermore National Laboratory, Livermore, California.

Wolery, T. J., and Daveler, S. A., 1992, EQ6, A Computer Code for Reaction-Path Modeling of Aqueous Geochemical Systems: Theoretical Manual, User's Guide, and Related Documentation (Version 7.0): UCRL-MA-110662-PT-IV, Lawrence Livermore National Laboratory, Livermore, California.

Wolery, T. J., Jackson, K. J., Bourcier, W. L., Bruton, C. J., Viani, B. E., Knauss, K. G., and Delany, J. M., 1990, Current status of the EQ3/6 software package for geochemical modeling, *in* Melchior, D. C., and Bassett, R. L., editors, Chemical Modeling of Aqueous Systems II, American Chemical Society Symposium Series, v. 416, American Chemical Society, Washington, D. C., p. 104-116.

Wood, B. J., and Fraser, D. G., 1977, Elementary Thermodynamics for Geologists: Oxford University Press, Oxford, United Kingdom.

Appendix A: Glossary of Major Variables in EQPT

This glossary covers the major variables in EQPT. Most all of these are shared with EQ3NR (Wolery, 1992b) and EQ6 (Wolery and Daveler, 1992). Those which are unique to EQPT are so marked. This glossary does not include variables which are of a purely local nature, such as a floating point variable used to accumulate sums in a do loop. Logarithmic quantities are frequently used. All refer to base ten, unless otherwise specified.

The variable names may be preceded by the corresponding algebraic symbols used in this report, if any. Following the conventions used universally in the EQ3/6 package, variables beginning with **i**, **j**, **k** or **n** are integer, those beginning with **q** are logical, and those beginning with **u** are character variables. Variables beginning with any other letters, including **l** and **m**, should be **real*8**. On 32-bit machines, this corresponds to **double precision**; on 64-bit machines, this corresponds to **single precision.**

Most arrays in EQ3/6 are dimensioned using FORTRAN parameters. The value of a parameter is assigned once in a code (in a PARAMETER statement) and can not be changed elsewhere. Some FORTRAN compilers permit parameters to be passed through calling sequences, but others do not allow this, as a means of protecting the parameter's assigned value. A called module often requires the dimensions of passed arrays. This is handled in EQ3/6 by the use of "dimensioning variables," which are ordinary integer variables whose values have been set equal to the corresponding parameters. The names of the dimensioning parameters in EQ3/6 typically end in **par**, **pa**, or **pa1**. The names of the corresponding dimensioning variables end, respectively, in **max**, **mx**, and **mx1**. Thus, the dimension of the **uelem** matrix is given by the pair **nctpar/nctmax** (the maximum number of chemical elements. The parameter suffixes are used exclusively by dimensioning parameters. However, the corresponding variable suffixes are not used exclusively by dimensioning variables. For example, **itermx** is the number of Newton-Raphson iterations in EQ3NR and EQ6.

$A_{\gamma,10}$	**adh**	Debye-Hückel A_γ parameter for computing the base ten logarithm of the molal activity coefficient of an aqueous species. Dimensioning: **adh(8)**. Usage: **adh(n)** is the Debye-Hückel A_γ parameter for the **n**-th point on the standard temperature grid. Note: dimensioning and usage differ from that in EQ3NR and EQ6.
α_1	**alph1**	The Pitzer α_1 parameter. Dimensioning: **alph1(npxpar)**. Usage: **alph1(npxp)** refers to the α_1 parameter.for the **npxp**-th neutral electrolyte (cation-anion pair). The arrays **alph1** and **alph2** are equivalent to the **palpha** array in EQ3NR and EQ6.
α_2	**alph2**	The Pitzer α_2 parameter. Dimensioning: **alph2(npxpar)**. Usage: **alph2(npxp)** refers to the α_2 parameter.for the **npxp**-th neutral electrolyte (cation-anion pair). The arrays **alph1** and **alph2** are equivalent to the **palpha** array in EQ3NR and EQ6.
A_ϕ	**aphi**	Debye-Hückel A_ϕ parameter. Dimensioning: **aphi(8)**. Usage: **aphi(n)** is the Debye-Hückel A_ϕ parameter for the **n**-th point on the standard temperature grid. Note: dimensioning and usage differ from that in EQ3NR and EQ6.
	apr	Work array for computing interpolating polynomial coefficients to fit the **xlks** array. Dimensioning: **apr(10)**. Usage: **apr(i)** refers to the **i**-th coefficient for the current

species. The **apr** array is copied into the part of the **ars** array corresponding to the current species. This array is unique to EQPT.

	apx	Solid solution activity coefficient model parameters. Dimensioning: **apx(12)**. Usage: **apx(i)** refers to the **i**-th parameter for the current solid solution. Note: dimensioning and usage differ from that in EQ3NR and EQ6.
	ars	Interpolating polynomial coefficients for computing the array of equilibrium constants **xlks**. Dimensioning: **ars(10,nsqpa1)**. Usage: **ars(i,ns)** refers to the **i**-th coefficient for the **ns**-th species. Note: dimensioning and usage differ from that in EQ3NR and EQ6.
$^S\theta_{MN}$, $^S\lambda^{(0)}_{MN}$	**atheta**	The Pitzer short range theta coefficient (25°C). Dimensioning: **atheta(npxpar)**. Usage: **atheta(k)** refers to the $^S\theta$ coefficient **k**-th cation-cation or anion-anion pair. Technically, this is the average $^S\theta$ value, as a different value may be fit to more than one mixture of two aqueous neutral electrolytes. Individual values for such mixtures are read from the **data0** file into the **theta** array, and **atheta** is computed from them. However, a common value should be specified on the data file for all such mixtures. This array is unique to EQPT. The coefficient $^S\theta_{MN}$ is mapped to the primitive Pitzer coefficient $^S\lambda_{MN}$ (the two are equal by the convention used in EQ3/6). There is no ionic strength dependence for this particular λ_{ij} coefficient, so $^S\lambda_{MN} = {}^S\lambda^{(0)}_{MN}$. In EQ3NR and EQ6, these and other $\lambda^{(n)}_{ij}$ coefficients are read into the **bslm** array.
	atwt	Atomic weight of a chemical element. Dimensioning: **atwt(nctpar)**. Usage: **atwt(nc)** refers to the **nc**-th chemical element.
B_γ	**bdh**	Debye-Hückel B_γ parameter. Dimensioning: **bdh(8)**. Usage: **bdh(n)** is the Debye-Hückel B_γ parameter for the **n**-th point on the standard temperature grid. Note: dimensioning and usage differ from that in EQ3NR and EQ6.
$\dot{B}$	**bdot**	Extended Debye-Hückel $\dot{B}$ parameter. Dimensioning: **bdot(8)**. Usage: **bdot(n)** is the extended Debye-Hückel $\dot{B}$ parameter for the **n**-th point on the standard temperature grid. Note: dimensioning and usage differ from that in EQ3NR and EQ6.
	cco2	Parameters of the Drummond (1981) equation for computing $log\gamma_{CO_{2(aq)}}$ as a function of temperature and ionic strength. Dimensioning: **cco2(5)**. Usage: **cco2(i)** refers to the **i**-th coefficient.
b_{sr}	**cdrs**	Reaction coefficient array. Dimensioning: **cdrs(nsqpa2,nsqpa1)**. Usage: **cdrs(nse,ns)** is the coefficient of the **nse**-th aqueous basis species appearing in the reaction for the **ns**-th species; **cdrg(nsq1,ns)** is the coefficient of the **ns**-th species itself. If the **ns**-th species is an auxiliary basis species then **cdrs(ns,ns)** = 0 and **cdrs(nsq1,nrs)** is the corresponding coefficient. Note: dimensioning and usage differ from that in EQ3NR and EQ6. The **cdrs** array of EQPT encompasses the **cdrs**, **cdrm**, and **cdrg** arrays of EQ3NR and EQ6.
	cdum1	Holding array used to read in the elemental composition coefficients of species listed on the data file. Dimensioning: **cdum1(nsqpa1)**. Usage: **cdum1(n)** is the **n**-th coefficient for the current species as it is written on the data file; it corresponds to the

element whose name is **unam8(n)**. This array is known as **cessd** in EQ3NR and EQ6.

$c_{\varepsilon s}$	cess	Array containing the elemental composition coefficients of aqueous species. Dimensioning: **cess(nctpar,nsqpal)**. Usage: **cess(nc,ns)** is the coefficient of the **nc**-th chemical element for the **ns**-th aqueous species. Note: dimensioning and usage differ from that in EQ3NR and EQ6. The **cess** array of EQPT encompasses the **cess**, **cemn**, and **cegs** arrays of EQ3NR and EQ6.
C^{ϕ}_{MX}	**cph**	The Pitzer coefficient C^{ϕ}_{MX} (25°C). Dimensioning: **cph(npxpar)**. Usage: **cph(npxp)** is the C^{ϕ} coefficient for the **npxp**-th pure aqueous neutral electrolyte. This array is unique to EQPT. This coefficient is used by EQPT to compute the primitive Pitzer coefficients μ_{MMX} and μ_{MXX}, which are respectively stored in the **mummx** and **mumxx** arrays. In EQ3NR and EQ6, these and other μ_{ijk} coefficients are read into the **bmu** array.
$\dfrac{d^2C^{\phi}_{MX}}{dT^2}$	**d2c**	The second temperature derivative of the Pitzer coefficient C^{ϕ}_{MX} (25°C). Dimensioning: **d2c(npxpar)**. Usage: **d2c(npxp)** is the second temperature derivative of the C^{ϕ} coefficient for the **npxp**-th pure aqueous neutral electrolyte. This array is unique to EQPT, which uses. $d^2C^{\phi}_{MX}/dT^2$ to compute $d^2\mu_{MMX}/dT^2$ and $d^2\mu_{MXX}/dT^2$, which are respectively stored in the **d2mmx** and **d2mxx** arrays In EQ3NR and EQ6, these and corresponding derivatives of other μ_{ijk} coefficients are read into the **dmu2** array.
$\dfrac{d^2\beta^{(0)}_{MX}}{dT^2}, \dfrac{d^2\lambda^{(0)}_{MX}}{dT^2}$	**d2l0**	The second temperature derivative of the primitive Pitzer coefficient parameter $\lambda^{(0)}_{MX}$ (25°C values). By convention, $\lambda^{(0)}_{MX}$ equals the Pitzer coefficient parameter $\beta^{(0)}_{MX}$, so the derivatives are also equal to one another. Dimensioning: **d2l0(npxpar)**. Usage: **d2l0(npxp)** is the second derivative for the **npxp**-th aqueous neutral electrolyte. This array is unique to EQPT. In EQ3NR and EQ6, these and the corresponding derivatives of other $\lambda^{(n)}_{ij}$ parameters are read into the **dslm2** array.
$\dfrac{d^2\beta^{(1)}_{MX}}{dT^2}, \dfrac{d^2\lambda^{(1)}_{MX}}{dT^2}$	**d2l1**	The second temperature derivative of the primitive Pitzer coefficient parameter $\lambda^{(1)}_{MX}$ (25°C values). By convention, $\lambda^{(1)}_{MX}$ equals the Pitzer coefficient parameter $\beta^{(1)}_{MX}$, so the derivatives are also equal to one another. Dimensioning: **d2l1(npxpar)**. Usage: **d2l1(npxp)** is the second derivative for the **npxp**-th aqueous neutral electrolyte. This array is unique to EQPT. In EQ3NR and EQ6, these and the corresponding derivatives of other $\lambda^{(n)}_{ij}$ parameters are read into the **dslm2** array.
$\dfrac{d^2\beta^{(2)}_{MX}}{dT^2}, \dfrac{d^2\lambda^{(2)}_{MX}}{dT^2}$	**d2l2**	The second temperature derivative of the primitive Pitzer coefficient parameter $\lambda^{(2)}_{MX}$ (25°C values). By convention, $\lambda^{(2)}_{MX}$ equals the Pitzer coefficient parameter

$\beta_{MX}^{(2)}$, so the derivatives are also equal to one another. Dimensioning: **d2l2(npxpar)**. Usage: **d2l2(npxp)** is the second derivative for the **npxp**-th aqueous neutral electrolyte. This array is unique to EQPT. In EQ3NR and EQ6, these and the corresponding derivatives of other $\lambda_{ij}^{(n)}$ parameters are read into the **dslm2** array.

$\frac{d^2\mu_{MMX}}{dT^2}$	d2mmx	The second temperature derivative of the primitive Pitzer coefficient μ_{MMX} (25°C). Dimensioning: **d2mmx(npxpar)**. Usage: **d2mmx(npxp)** is the second temperature derivative of the μ_{MMX} coefficient for the **npxp**-th pure aqueous neutral electrolyte. It is computed from the **d2c** array. This array is unique to EQPT. In EQ3NR and EQ6, these and corresponding derivatives of other μ_{ijk} coefficients are read into the **dmu2** array.
$\frac{d^2\mu_{MNX}}{dT^2}$	d2mu	The second temperature derivative of the primitive Pitzer coefficient μ_{MXX} (25°C). This is a local variable in module **rdpz3.f** computed from the **d2psi**, **d2mmx**, and **d2mxx** arrays. In EQ3NR and EQ6, these and corresponding derivatives of other μ_{ijk} coefficients are read into the **dmu2** array.
$\frac{d^2\mu_{MXX}}{dT^2}$	d2mxx	The second temperature derivative of the primitive Pitzer coefficient μ_{MXX} (25°C). *Dimensioning:* **d2mxx(npxpar)**. *Usage:* **d2mxx(npxp)** *is the second temperature* derivative of the μ_{MXX} coefficient for the **npxp**-th pure aqueous neutral electrolyte. It is computed from the **d2c** array. This array is unique to EQPT. In EQ3NR and EQ6, these and corresponding derivatives of other μ_{ijk} coefficients are read into the **dmu2** array.
$\frac{d^2\psi_{MNX}}{dT^2}$	d2psi	The second temperature derivative of the Pitzer coefficient ψ_{MNXZ} (25°C). Dimensioning: **d2psi(npxpar)**. Usage: **d2psi(nmpp)** is the second temperature derivative of the ψ coefficient for the **nmpp**-th mixture of two aqueous neutral electrolytes containing a common ion X. This array is unique to EQPT, which uses. $d^2\psi_{MNX}/dT^2$ to compute $d^2\mu_{MNX}/dT^2$ and $d^2\mu_{MNX}/dT^2$, which are respectively stored in the **d2mu** variable. In EQ3NR and EQ6, these and corresponding derivatives of other μ_{ijk} coefficients are read into the **dmu1** array.
$\frac{d^2\,{}^S\theta_{MN}}{dT^2}, \frac{d^2\lambda_{MN}^{(0)}}{dT^2}$	d2th	The second temperature derivative of the Pitzer short range theta coefficient (25°C). Dimensioning: **d2th(npxpar)**. Usage: **d2th(k)** refers to the second temperature derivative of the ${}^S\theta$ coefficient for the **k**-th cation-cation or anion-anion pair. Technically, this is an average value, as a different value may be fit to more than one mixture of two aqueous neutral electrolytes. Individual values for such mixtures are read from the **data0** file into the **d2thd** variable for each mixture, and **d2th** is computed as the average value. However, a common value should be specified on the

data file for all such mixtures. This array is unique to EQPT. The coefficient $d^{2S}\theta_{MN}/dT^2$ is mapped to the primitive Pitzer coefficient $d^{2S}\lambda_{MN}/T^2$ (the two are equal by the convention used in EQ3/6). There is no ionic strength dependence for this particular coefficient, so $d^{2\,S}\lambda_{MN}/dT^2 = d^2\lambda^{(0)}_{MN}/dT^2$. In EQ3NR and EQ6, these and corresponding derivatives of the $\lambda^{(n)}_{ij}$ parameters are read into the **dslm2** array.

$\frac{d^{2\,S}\theta_{MN}}{dT^2}$	**d2thd**	The second temperature derivative of the Pitzer short range theta coefficient (25°C). This is a local variable in module **rdpz3.f**used to read in the value of this derivative for the current mixture of two aqueous neutral electrolytes containing a common ion. See **d2thd.**
$\frac{dC^{\phi}_{MX}}{dT}$	**dc**	The first temperature derivative of the Pitzer coefficient C^{ϕ}_{MX} (25°C). Dimensioning: **dc(npxpar).** Usage: **dc(npxp)** is the first temperature derivative of the C^{ϕ} coefficient for the **npxp**-th neutral aqueous neutral electrolyte. This array is unique to EQPT, which uses. dC^{ϕ}_{MX}/dT to compute $d\mu_{MMX}/dT$ and $d\mu_{MXX}/dT$, which are respectively stored in the **dmmx** and **dmxx** arrays. In EQ3NK and EQ6, these and corresponding derivatives of other μ_{ijk} coefficients are read into the **dmu1** array.
$\frac{d\beta^{(0)}_{MX}}{dT}, \frac{d\lambda^{(0)}_{MX}}{dT}$	**dl0**	The first temperature derivative of the primitive Pitzer coefficient parameter $\lambda^{(0)}_{MX}$, (25°C values). By convention, $\lambda^{(0)}_{MX}$ equals the Pitzer coefficient parameter $\beta^{(0)}_{MX}$, so the derivatives are also equal to one another. Dimensioning: **dl0(npxpar).** Usage: **dl0(npxp)** is the first derivative for the **npxp**-th aqueous neutral electrolyte. This array is unique to EQPT. In EQ3NR and EQ6, these and the corresponding derivatives of other $\lambda^{(n)}_{ij}$ parameters are read into the **dslm1** array.
$\frac{d\beta^{(1)}_{MX}}{dT}, \frac{d\lambda^{(1)}_{MX}}{dT}$	**dl1**	The first temperature derivative of the primitive Pitzer coefficient parameter $\lambda^{(1)}_{MX}$ (25°C values). By convention, $\lambda^{(1)}_{MX}$ equals the Pitzer coefficient parameter $\beta^{(1)}_{MX}$, so the derivatives are also equal to one another. Dimensioning: **dl1(npxpar).** Usage: **dl1(npxp)** is the first derivative for the **npxp**-th aqueous neutral electrolyte. This array is unique to EQPT. In EQ3NR and EQ6, these and the corresponding derivatives of other $\lambda^{(n)}_{ij}$ parameters are read into the **dslm1** array.
$\frac{d\beta^{(2)}_{MX}}{dT}, \frac{d\lambda^{(2)}_{MX}}{dT}$	**dl2**	The first temperature derivative of the primitive Pitzer coefficient parameter $\lambda^{(2)}_{MX}$ (25°C values). By convention, $\lambda^{(2)}_{MX}$ equals the Pitzer coefficient parameter $\beta^{(2)}_{MX}$, so the derivatives are also equal to one another. Dimensioning: **dl2(npxpar).** Usage: **dl2(npxp)** is the first derivative for the **npxp**-th aqueous neutral electrolyte. This ar-

ray is unique to EQPT. In EQ3NR and EQ6, these and the corresponding derivatives of other $\lambda_{ij}^{(n)}$ parameters are read into the **dslm1** array.

$\frac{d\mu_{MMX}}{dT}$	**dmmx**	The first temperature derivative of the primitive Pitzer coefficient μ_{MMX} (25°C). Dimensioning: **dmmx(npxpar)**. Usage: **dmmx(npxp)** is the first temperature derivative of the μ_{MMX} coefficient for the **npxp**-th pure aqueous neutral electrolyte. It is computed from the **dc** array. This array is unique to EQPT. In EQ3NR and EQ6, these and corresponding derivatives of other μ_{ijk} coefficients are read into the **dmu1** array.
$\frac{d\mu_{MNX}}{dT}$	**dmu**	The first temperature derivative of the primitive Pitzer coefficient μ_{MXX} (25°C). This is a local variable in module **rdpz3.f** computed from the **dpsi**, **dmmx**, and **dmxx** arrays. In EQ3NR and EQ6, these and corresponding derivatives of other μ_{ijk} coefficients are read into the **dmu1** array.
$\frac{d\mu_{MXX}}{dT}$	**dmxx**	The first temperature derivative of the primitive Pitzer coefficient μ_{MXX} (25°C). Dimensioning: **dmxx(npxpar)**. Usage: **dmxx(npxp)** is the first temperature derivative of the μ_{MXX} coefficient for the **npxp**-th pure aqueous neutral electrolyte. It is computed from the **dc** array. This array is unique to EQPT. In EQ3NR and EQ6, these and corresponding derivatives of other μ_{ijk} coefficients are read into the **dmu1** array.
$\frac{d\psi_{MNX}}{dT}$	**dpsi**	The first temperature derivative of the Pitzer coefficient ψ_{MNXZ} (25°C). Dimensioning: **dpsi(npxpar)**. Usage: **dpsi(nmpp)** is the first temperature derivative of the ψ coefficient for the **nmpp**-th mixture of two aqueous neutral electrolytes containing a common ion X. This array is unique to EQPT, which uses. $d\psi_{MNX}/dT$ to compute $d\mu_{MNX}/dT$ and $d\mu_{MNX}/dT$, which are respectively stored in the **dmu** variable. In EQ3NR and EQ6, these and corresponding derivatives of other μ_{ijk} coefficients are read into the **dmu1** array.
$\frac{d^S\theta_{MN}}{dT}, \frac{d\lambda_{MN}^{(0)}}{dT}$	**dth**	The first temperature derivative of the Pitzer short range theta coefficient (25°C). Dimensioning: **dth(npxpar)**. Usage: **dth(k)** is the first temperature derivative of the $^S\theta$ coefficient for the k-th cation-cation or anion-anion pair. Technically, this is an average value, as a different value may be fit to more than one mixture of two neutral aqueous neutral electrolytes. Individual values for such mixtures are read from the **data0** file into the **dthd** variable for each mixture, and **dth** is computed as the average value. However, a common value should be specified on the data file for all such mixtures. This array is unique to EQPT. The coefficient $d^S\theta_{MN}/dT$ is mapped to the primitive Pitzer coefficient $d^S\lambda_{MN}/T$ (the two are equal by the convention used in EQ3/6). There is no ionic strength dependence for this particular coefficient, so

		$d^S\lambda_{MN}/dT = d\lambda^{(0)}_{MN}/dT$. In EQ3NR and EQ6, these and corresponding derivatives of the $\lambda^{(n)}_{ij}$ parameters are read into the **dslml** array.
$\frac{d^S\theta_{MN}}{dT}$	**dthd**	The first temperature derivative of the Pitzer short range theta coefficient (25°C). This is a local variable in module **rdpz3.f** used to read in the value of this derivative for the current mixture of two aqueous neutral electrolytes containing a common ion. See **dth**.
	eps100	One hundred times the **real*8** machine epsilon.
	gdum	A work array into which is copied the portion of the **xlks** array for a given species. Dimensioning: **gdum(8)**. Usage: **gdum(n) = xlks(n,ns)** for the species currently indicated by **ns**. This array is local to modules **pcraq.f** and **pcrsg.f**.
	ier	An error flag parameter commonly found in subroutine calling sequences. Values greater than zero mark error conditions. Values less than zero mark warning conditions. The significance of this flag is only that the subroutine did or may have failed to carry out its primary function. For example, a matrix solver may have found a matrix to be computationally singular. This situation may or may not equate to an error in the context of the larger code. For example, the larger code may not have a problem with the fact that a matrix is computationally singular.
	iktmax	The maximum number of end members in a solid solution. This is the variable which corresponds to the dimensioning parameter **iktpar**.
	iktpar	Dimensioning parameter: the maximum number of end members in a solid solution. See **iktmax**.
	iline	The maximum number of characters per line in the data file. This is currently set to 80.
	ineu	Flag variable for determining how to compute the activity coefficient of a neutral solute species in conjunction with the B-dot equation. This is a local variable in module **wrbdot.f**. Usage: **ineu** is the flag for the current aqueous species: = 0 Set $log\gamma_i = 0$ (polar species) = 1 Use the Drummond (1981) polynomial (non-polar species). This flag variable is stored in the **insgfl** array in EQ3NR and EQ6.
	insgfl	See **ineu**.
	ixs	The number of distinct Pitzer theta values read from the data file for a given pair of cations or anions. Dimension: **ixs(npxpar)**. Usage: **ixs(nmx)** is the number of such values for the **nmx**-th such pair.
$\beta^{(0)}_{MX}$, $\lambda^{(0)}_{MX}$	**l0**	The primitive Pitzer coefficient parameter $\lambda^{(0)}_{MX}$, taken by convention to be equal to the Pitzer coefficient parameter $\beta^{(0)}_{MX}$ (25°C values). Dimensioning: **l0(npxpar)**. Usage: **l0(npxp)** is the parameter for the **npxp**-th aqueous neutral electrolyte. This ar-

		ray is unique to EQPT. In EQ3NR and EQ6, these and other $\lambda_{ij}^{(n)}$ parameters are read into the **bslm** array.
$\beta_{MX}^{(1)}, \lambda_{MX}^{(1)}$	l1	The primitive Pitzer coefficient parameter $\lambda_{MX}^{(1)}$, taken by convention to be equal to the Pitzer coefficient parameter $\beta_{MX}^{(1)}$ (25°C values). Dimensioning: **l1(npxpar)**. Usage: **l1(npxp)** is the parameter for the **npxp**-th aqueous neutral electrolyte. This array is unique to EQPT. In EQ3NR and EQ6, these and other $\lambda_{ij}^{(n)}$ parameters are read into the **bslm** array.
$\beta_{MX}^{(2)}, \lambda_{MX}^{(2)}$	l2	The primitive Pitzer coefficient parameter $\lambda_{MX}^{(2)}$, taken by convention to be equal to the Pitzer coefficient parameter $\beta_{MX}^{(2)}$ (25°C values). Dimensioning: **l2(npxpar)**. Usage: **l2(npxp)** is the parameter for the **npxp**-th aqueous neutral electrolyte. This array is unique to EQPT. In EQ3NR and EQ6, these and other $\lambda_{ij}^{(n)}$ parameters are read into the **bslm** array.
μ_{MMX}	mummx	The primitive Pitzer coefficient μ_{MMX} (25°C). Dimensioning: **mummx(npxpar)**. Usage: **mummx(npxp)** is the μ_{MMX} coefficient for the **npxp**-th pure aqueous neutral electrolyte. It is computed from the C^{ϕ} coefficient. See **cph**. This array is unique to EQPT. In EQ3NR and EQ6, these and other μ_{ijk} coefficients are read into the **bmu** array.
μ_{MNX}	mumnx	The primitive Pitzer coefficient μ_{MNX} (25°C). This is a local variable in module **rdpz3.f**computed from the ψ coefficient. See **psi**. In EQ3NR and EQ6, these and other μ_{ijk} coefficients are read into the **bmu** array.
μ_{MXX}	mumxx	The primitive Pitzer coefficient μ_{MXX} (25°C). Dimensioning: **mumxx(npxpar)**. Usage: **mumxx(npxp)** is the μ_{MXX} coefficient for the **npxp**-th pure aqueous neutral electrolyte. It is computed from the C^{ϕ} coefficient. See **cph**. This array is unique to EQPT. In EQ3NR and EQ6, these and other μ_{ijk} coefficients are read into the **bmu** array.
M_i	mwtss	Molecular weight of a chemical species. This is a local variable in modules **pcraq.f** and **pcrsg.f**. The dimensioning and usage differ in EQ3NR and EQ6.
ε_T	nct	Total number of chemical elements.
	nctmax	The maximum number of chemical elements. This is a variable which corresponds to the parameter **nctpar**.
	nctpa1	Dimensioning parameter: the maximum number of chemical elements + 1. See **nctpar**. This is presently unused.
	nctpar	Dimensioning parameter: the maximum number of chemical elements. See **nctmax**.
	ncts	The number of chemical elements comprising a chemical species. This is a local variable in modules **pcraq.f** and **pcrsg.f**. It is unique to EQPT.

	ndata0	The unit number of the stripped **data0** file. This is a scratch file that has been stripped of any comment lines. This variable is unique to EQPT.
	ndata1	The unit number of the **data1** file. This variable is unique to EQPT. In EQ3NR and EQ6, the unit number of this file is **nad1**.
	ndat1f	The unit number of the **data1f** file. This variable is unique to EQPT.
	ndpt1	The unit number of the **dpt1** file. This variable is unique to EQPT.
	ndpt2	The unit number of the **dpt2** file. This variable is unique to EQPT.
	ndrs	The number of species in a chemical reaction. This is a local variable in modules **pcraq.f** and **pcrsg.f**. It is unique to EQPT.
	nmpp	The number of mixtures of two aqueous neutral electrolytes for which Pitzer coefficients have been read from the data file. This variable is unique to EQPT.
	nmtp	The number of distinct cation-cation or anion-anion pairs corresponding to Pitzer coefficients for mixtures of aqueous neutral electrolytes containing a common (third) ion. This is used in analyzing data preparatory to computing the average Pitzer theta coefficient for such pairs of ions. See **atheta**.This variable is unique to EQPT.
	nout	*The unit number of the* **out** *file. This variable and the corresponding file are no longer used.*
	noutpt	The unit number of the **output** file.
	npxp	Counter for the number of blocks of Pitzer coefficient data read from either the superblock for pure aqueous neutral electrolytes or the superblock for mixtures of two such electrolytes.
	npxpar	Dimensioning parameter: the maximum number entries in the various Pitzer coefficient data arrays.
s_B	nsb	The number of strict basis species. Also the index denoting the aqueous redox species (currently O_2); **nsb** = **nct** + 1.
	nslist	The unit number of the **slist** file. This variable is unique to EQPT.
	nslt	The number of pure aqueous neutral electrolytes for which Pitzer coefficients have been read from the data file. This variable is unique to EQPT.
s_Q	nsq	Number of aqueous basis species.
	nsq1	The variable equivalent to **nsq** + 1. This is used in reaction coefficient arrays to mark the coefficient of the species formally associated with a given reaction. For example, **cdrs(nsq1,ns)** refers to the coefficient of the associated aqueous species destroyed in the reaction for the **ns**-th species. The first **nsq** species are the aqueous basis species. The **nsq1**-th species is the current non-basis species, which may be a species of any type of *phase*.
	nsq2	The variable equivalent to **nsq** + 2. This is unique to EQPT and is presently not used.

	nsqmax	The maximum number of aqueous basis species. This is the variable corresponding to the parameter **nsqpar**.
	nsqpa1	Dimensioning parameter: the equivalent of **nsqpar** + 1.
	nsqpa2	Dimensioning parameter: the equivalent of **nsqpar** + 2.
	nsqpar	Dimensioning parameter: the maximum number of aqueous basis species. See **nsqmax**.
	nssp	The number of aqueous species appearing in the set of pure aqueous neutral electrolytes for which Pitzer coefficients have been read from the data file. This variable is unique to EQPT. See **ussp**.
	nstpar	Dimensioning parameter: the maximum number of aqueous species.
	ntitld	The number of lines of the title on the **data1 file**.
	ntitpa	Dimensioning parameter: the maximum number of lines in a data file title.
	ntmps	The unit number of the **data0** file. This variable is unique to EQPT.
	nttyi	The unit number of the keyboard file.This variable is unique to EQPT and is currently not used.
	nttyo	The unit number of the screen file.
	nubdot	The number of aqueous species for which hard core diameters and **insgfl (ineu)** flags are specified on the data file. See **ubdotp**.
	oxfac	Stoichiometric oxide factor. Dimensioning: **oxfac(nctpar)**. Usage: **oxfac(nc)** is the oxide factor for the **nc**-th chemical element. See **uoxide**. Both arrays are currently vestigial, though they are processed by EQPT.
P	**press**	Pressure, bars, on the standard temperature grid. Dimensioning: **press(8)**. Usage: **press(n)** is the pressure for the **n**-th point on the grid. Note: dimensioning and usage differ from that in EQ3NR and EQ6.
ψ_{MNX}	**psi**	The Pitzer coefficient ψ_{MNX} (25°C). Dimensioning: **psi(npxpar)**. Usage: **psi(nmpp)** is the ψ coefficient for the **nmpp**-th mixture of two aqueous neutral electrolytes containing a common ion X. This array is unique to EQPT. This coefficient is used by EQPT to compute the primitive Pitzer coefficient μ_{MNX}, which is stored in the **mumnx** variable. In EQ3NR and EQ6, these and other μ_{ijk} coefficients are read into the **bmu** array.
	sumd2t	The sum of the distinct values read from the data file for the *second temperature* derivative of a given Pitzer theta coefficient. Dimensioning: **sumd2t(npxpar)**. Usage: **sumd2t(k)** is the sum for the **k**-th pair of cations or pair of anions. This array is used to compute the average values of the second temperature derivatives of the theta coefficients for such pairs (see **d2th**). This array is unique to EQPT.
	sumdt	The sum of the distinct values read from the data file for the first temperature derivative of a given Pitzer theta coefficient. Dimensioning: **sumdt(npxpar)**. Usage: **sumdt(k)** is the sum for the **k**-th pair of cations or pair of anions. This array is used

		to compute the average values of the first temperature derivatives of the theta coefficients for such pairs (see **dth**). This array is unique to EQPT.
	sumt	The sum of the distinct values read from the data file for a given Pitzer theta coefficient. Dimensioning: **sumt(npxpar)**. Usage: **sumt(k)** is the sum for the **k**-th pair of cations or pair of anions. This array is used to compute the average values of the theta coefficients for such pairs (see **atheta**). This array is unique to EQPT.
	summ	The number of distinct values read from the data file for a given Pitzer theta coefficient. Dimensioning: **summ(npxpar)**. Usage: **summ(k)** is the number of distinct values for the **k**-th pair of cations or pair of anions. This array is used to compute the average values of the theta coefficients and the average values of the first and second temperature derivatives for such pairs (see **atheta**, **dth**, and **d2th**). This array is unique to EQPT.
	tdamax	The nominal upper temperature limit of the data file, °C.
	tdamin	The nominal lower temperature limit of the data file, °C.
	tempc	Temperature, °C, on the standard temperature grid. Dimensioning: **tempc(8)**. Usage: **tempc(n)** is the temperature for the **n**-th point on the grid. Note: dimensioning and usage differ from that in EQ3NR and EQ6.
	tempcs	The scaled temperature on the standard temperature grid. Dimensioning: **tempcs(8)**. Usage: **tempcs(n)** is the scaled temperature for the **n**-th point on the grid. This is used in fitting interpolating polynomials to data on the standard grid. The scaled temperature array is computed from the **tempc** array by normalizing the values on each segment of the grid by dividing by the maximum value on that segment. This array is unique to EQPT.
$^{S}\theta_{MN}$	**thdum**	The Pitzer short range theta coefficient (25°C). This is a local variable in module **rdpz3.f** used to read in the value of this coefficient for the current mixture of two aqueous neutral electrolytes containing a common ion. See **theta** and **atheta**. This variable is unique to EQPT.
$^{S}\theta_{MN}$	**theta**	The Pitzer short range theta coefficient (25°C). This is an array in which is saved the theta coefficient for each mixture of two aqueous neutral electrolytes containing a common ion. Dimensioning: **theta(ixspar,npxpar)**. Usage: **theta(i,nmx)** is the **i**-th theta value read for the **nmx**-th cation-cation or anion-anion pair. This array is actually presently not used for anything. It could be used to summarize the situation when the theta values read for a given pair of cations or anions are not all identical. See **thdum** and **atheta**. This array is unique to EQPT.
	tmax	The max norm of the temperature on a range of the standard temperature grid. See **tempsc**.This variable is unique to EQPT.
	ubdotp	Array of lines read from the data file which specify hard core diameters and insgfl (ineu) flags for the aqueous species.
	ucode	A variable containing the name of the code.
	uelem	Array of names of chemical elements (their chemical symbols). Dimensioning: **uelem(nctpar)**. Usage: **uelem(nc)** is the name of the **nc**-th element.

uendit	The string 'endit.'.
ueqlrn	A string containing the release number of the supporting EQLIB library.
ueqlst	A string containing the stage number of the supporting EQLIB library.
uhead	Data file type key string: = 'stfipc' Simple extended Debye-Hückel formalism = 'stpitz' Pitzer formalism
ukey	Data file key string: The value read from the data file is the data file key, which is one of the following: = 'com' Composite = 'sup' SUPCRT92 = 'nea' NEA = 'hmw' Harvie-Møller-Weare (Harvie, Møller, and Weare, 1984) = 'pit' Pitzer (Pitzer, 1979) These are mapped to one of the following: = 'bdot' Simple extended Debye-Hückel formalism ('com', 'sup', "nea") = 'pitzer' Pitzer formalism ('hmw", 'pit') Functionally, these latter values duplicate the function of the **uhead** key string.
umsp	Array containing the names of the cations corresponding to pure aqueous neutral electrolytes read from the data file. The anions are stored in **uxsp**. Instead of a cation-anion pair, the code will also accept a pair of neutral species, in which case one will be stored in **umsp**, the other in **uxsp**. Dimensioning: **umsp(npxpar)**. Usage: **umsp(npxp)** is the cation (or one of two neutral species) in the **npxp**-th pure aqueous neutral electrolyte or pair of neutral species. This array is unique to EQPT.
unam24	Array containing the names of the species appearing in a chemical reaction given on the data file. Dimensioning: **unam24(nsqpa1)**. Usage: **unam24(n)** is the name of the species corresponding to the n-th coefficient in the current reaction as it is written on the data file. This array is known as **udrxd** in EQ3NR and EQ6.
unam8	Holding array of names of chemical elements. Dimensioning: **unam8(nctpar)**. Usage: **unam8(n)** is the name of the n-th element listed for the current species. See **cdum1**. This array is known as **uelemd** in EQ3NR and EQ6.
unone	The string 'none'.
uoxide	Array of names of oxides of the chemical elements. Dimensioning: **uoxide(nctpar)**. Usage: **uoxide(nc)** is the name of the oxide of the nc-th chemical element. This array is presently vestigial. See also **oxide**.
urelno	A string containing the release number of the code it is contained in.
ustage	A string containing the stage number of the code it is contained in.
utitld	The title (text) from the **data1** file. Dimensioning: **utitld(ntitpa)**. Usage: **utitld(n)** is the **n**-th line of this title.

uxsp	Array containing the names of the anions corresponding to pure aqueous neutral electrolytes read from the data file. The cations are stored in **umsp**. Instead of a cation-anion pair, the code will also accept a pair of neutral species, in which case one will be stored in **umsp**, the other in **uxsp**. Dimensioning: **uxsp(npxpar)**. Usage: **uxsp(npxp)** is the anion (or one of two neutral species) in the **npxp-th** pure aqueous neutral electrolyte or pair of neutral species. This array is unique to EQPT.
uref	Array of reference strings for the Pitzer theta coefficient for a pair of cations or a pair of anions. Dimensioning: **uref(npxpar)**. Usage: **uref(nmx)** is the reference string for the **nmx-th** such pair. This array is unique to EQPT. Note: **uref** is also used as a local variable with a slightly different meaning in module **pcrss.f**.(reference string for a solid solution).
urefp	Array of reference strings for the Pitzer coefficient data for mixtures of two aqueous neutral electrolytes. Dimensioning: **uref(npxpar)**. Usage: **uref(npxp)** is the reference string for the **npxp-th** such mixture.
usp1	Array of names of the first of a pair of ions of the same charge sign for which the data file contains a Pitzer theta coefficient. Dimensioning: **usp1(npxpar)**. Usage: **ups1(nmx)** is the name of the first species in the **nmx-th** such pair. See also **usp2**. This array is unique to EQPT. Note: **usp1** and **usp2** are also used as local variables for species names in module **pdpz2.f**.
usp2	Array of names of the second of a pair of ions of the same charge sign for which the data file contains a Pitzer theta coefficient. Dimensioning: **usp1(npxpar)**. Usage: **ups1(nmx)** is the name of the second species in the **nmx-th** such pair. See also **usp1**. This array is unique to EQPT. Note: **usp1** and **usp2** are also used as local variables for species names in module **pdpz2.f**.
uspcm	Array of names of the third of a triplet of ions composing two aqueous neutral electrolytes containing a common ion. This third ion has the opposite charge sign of the other two. Dimensioning: **uspcm(ixspar,npxpar)**. Usage: **uspcm(ixs(nmx),nmx)** is the name of the third species in the **ixs(nmx)-th** triplet containing the **nmx-th** distinct pair of the first two ions. See also **theta** and **ixs**. This array is unique to EQPT.
uspec	Array of names of species. Dimensioning: **uspec(nsqpa1)**. Usage: **uspec(ns)** is the name of the **ns-th** species. The first **nsq** species are the aqueous basis species. The **nsq1-th** species is the current non-basis species. This may be a species belonging to any type of phase. Dimensioning and usage differ in EQPT from that in EQ3NR and EQ6.
uspn	Holding array which contains the names of two consecutively read species of a given phase type. Dimensioning: **uspn(2)**. Usage: **uspn(1)** and **uspn(1)** are the names of two consecutive such species. This array is used to write species lists to the **output** and **slist** files. It is unique to EQPT.
uspp1	Array of names of the first of a triplet of ions composing two aqueous neutral electrolytes containing a common ion. This first ion is one of two having the same charge sign. Dimensioning: **uspp1(npxpar)**. Usage: **uspp1(nmpp)** is the name of the first species in the **nmpp-th** such triplet. See also **uspp2** and **usppc**. This array is unique to EQPT.
uspp2	Array of names of the second of a triplet of ions composing two aqueous neutral electrolytes containing a common ion. This second ion is one of two having the same

		charge sign. Dimensioning: **uspp2(npxpar)**. Usage: **uspp2(nmpp)** is the name of the second species in the **nmpp-th** such triplet. See also **uspp1** and **usppc**. This array is unique to EQPT.
	usppc	Array of names of the third of a triplet of ions composing two aqueous neutral electrolytes containing a common ion. This third ion has the opposite charge sign of the other two. Dimensioning: **usppc(npxpar)**. Usage: **usppc(nmpp)** is the name of the third species in the **nmpp-th** such triplet. See also **uspp1** and **uspp2**. This array is unique to EQPT.
	ussp	Array of names of the ions (or neutral species) defining an aqueous neutral electrolyte (or pair of neutral species) for which Pitzer coefficient data are read from the data file. This array contains no duplications. Dimensioning: **ussp(npxpar)**. Usage: **ussp(j)** is the name of the **j-th** species in this array. This array is created by extracting the species names from the **ussrs** array. See also **nssp**. This array is presently not used for anything. It array is unique to EQPT.
	ussrs	Array of pairs of names of the ions (or neutral species) defining an aqueous neutral electrolyte (or pair of neutral species) for which Pitzer coefficient data are read from the data file. The first ion is normally the cation. Dimensioning: **ussrs(2,npxpar)**. Usage: **ussrs(1,(npxp)** is the name of the first species in the **npxp-th** such pair; **ussrs(2,(npxp)** is the name of the second species. This array is unique to EQPT.
	xbarlm	Array of limits on the mole fractions of solid solution end-member components. Dimensioning: **xbarlm(iktpar)**. Usage: **xbarlm(ik)** is the limit on the mole fraction of the **ik-th** component of the current solid solution.
$log\ K_{Eh}$	**xlkeh**	Log equilibrium constant of the half reaction relating the hypothetical electron and $O_{2(g)}$. Dimensioning: **xlkeh(8)**. Usage: **xlkeh(n)** is the log equilibrium constant of this half reaction for the **n-th** point on the standard temperature grid. Note: dimensioning and usage differ from that in EQ3NR and EQ6.
$log\ K_r$	**xlks**	Array of log equilibrium constants of the dissociation/destruction reactions of aqueous species. Dimensioning: **xlks(8,nsqpa1)**. Usage: **xlks(n,ns)** is the log of the equilibrium constant for the **n-th** point on the standard temperature grid for the **ns-th** species. The first **nsq** species are the aqueous basis species. The **nsq1-th** species is *the current non-basis species and may be of any phase type. Note: dimensioning and* usage differ from that in EQ3NR and EQ6.
z_i	**z**	Array of electrical charges of the species on the data file. Dimensioning: **z(nsqpa1)**. Usage: **z(ns)** is the electrical charge of the **ns-th** species. The first **nsq** species are the aqueous basis species. The **nsq1-th** species is the current non-basis species and may be of any phase type. Dimensioning and usage differ in EQPT from that in EQ3NR and EQ6.
$\mathring{a}_i$	**zero**	Hard core diameter of the current aqueous species. See **ubdotp**. Note: the array **azero** is used to hold hard core diameters in EQ3NR and EQ6. Here 'zero' appears to be a corruption of **azero**.
	zm	Array of electrical charges of the first species (cation or neutral) in an aqueous neutral electrolyte (or pair of neutral species) for which Pitzer coefficient data are read from the data file. Dimensioning: **zm(npxpar)**. Usage: **zm(npxpar)** is the electrical charge of the first species in the **npxp-th** such aqueous neutral electrolyte or pair of neutral species. See also **zx**.

zx	Array of electrical charges of the second species (anion or neutral) in an aqueous neutral electrolyte (or pair of neutral species) for which Pitzer coefficient data are read from the data file. Dimensioning: **zx(npxpar)**. Usage: **zx(npxpar)** is the electrical charge of the second species in the **npxp**-th such aqueous neutral electrolyte or pair of neutral species. See also **zm**.

Appendix B. Glossary of EQPT Subroutines

EQPT is a medium-sized code. The source code consists of the main program and a number of subroutines. In addition, EQPT uses several modules from the EQLIB library. These are described in Appendix B of the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a). The modules are described as "**.f**" files, as this is how they are normally worked with under a UNIX operating system. For a description of the code architecture, see Chapter 5.

bldsp.f	This module is called by the EQPT module **eqpt.f**. It builds the array **ussp** from the **ussrs** array. The array **ussp** contains the names of all species which appear in connection with Pitzer coefficient data for pure aqueous neutral electrolytes (cation-anion pair) or pairs of neutral species. Names that are found more than once in **ussrs** are copied only once to **ussp**. The **ussp** array is presently not used for anything.
eqpt.f	This module is the main program of EQPT. It calls other modules to read the data file, process the data, and write the **data1** and other output files.
funcy.f	This module is called by the EQPT module **intrp.f**. It evaluates fitted interpolating polynomials at the points corresponding to the standard temperature grid. It expects one interpolating polynomial for the range 0-100°C, another for the range 100-300°C.
gnenb.f	This module is called by the EQPT module **eqpt.f**. It scans the data file, counting the number of chemical elements (**nct**) and the number of basis species (**nsq**). It the rewinds the data file.
gridpy.f	This module is called by the EQPT modules **pcraq.f** and **pcrsg.f**. It writes specified data on the standard temperature grid to a specified file.
intrp.f	This module is called by the EQPT modules **pcraq.f**, **pcrsg.f**, and **wrpar.f**. It fits interpolating polynomials to specified data on the standard temperature grid. It fits one interpolating polynomial for the range 0-100°C, another for the range 100-300°C.
ofiles.f	This module is called by the EQPT module **eqpt.f**. It opens all files, except for **output**, which is opened by **eqpt.f**.
pcraq.f	This module is called by the EQPT module **eqpt.f**. It reads the composition, reaction, and standard state thermodynamic data for all aqueous species. It checks the data for simple errors, such as unbalanced reactions.
pcrsg.f	This module is called by the EQPT module **eqpt.f**. It reads the composition, reaction, and standard state thermodynamic data for all pure mineral and gas species. It checks the data for simple errors, such as unbalanced reactions.
pcrss.f	This module is called by the EQPT module **eqpt.f**. It reads the data for all solid solutions.
pdpz2.f	This module is called by the EQPT module **eqpt.f**. It reads the data for all Pitzer coefficient parameters associated with pure aqueous neutral electrolytes or pairs of aqueous neutral species. It does limited processing of these data. It writes these data on the **dpt1** file.
preacy.f	This module is called by the EQPT modules **pcraq.f**, **pcrsg.f**, and **rxnchk.f**. It writes a specified chemical reaction onto a specified file.

rdpar.f This module is called by the EQPT module **eqpt.f**. It reads the data for the following data grids, as applicable:

tempc	standard temperature grid
press	pressure on the standard temperature grid
adh	Debye-Hückel A_γ parameter on the standard temperature grid
bdh	Debye-Hückel B_γ parameter on the standard temperature grid
bdot	extended Debye-Hückel $\dot{B}$ parameter on the standard temperature grid
cco2	coefficients of the Drummond (1981) polynomial for the log activity coefficient of dissolved CO_2
aphi	Debye-Hückel A_ϕ parameter on the standard temperature grid
xlkeh	$log\ K_{Eh}$ on the standard temperature grid

rdpz3.f This module is called by the EQPT module **eqpt.f**. It reads the data for all Pitzer coefficient parameters associated with mixtures of two aqueous neutral electrolytes It does limited processing of these data.

rdwele.f This module is called by the EQPT module **eqpt.f**. It reads the data for the chemical elements and *writes it on the* ***data1*** *file.*

rdwttl.f This module is called by the EQPT module **eqpt.f**. It reads the title of the data file and writes it on the **data1** file.

rdbdot.f This module is called by the EQPT module **eqpt.f**. It reads the lines of the data file which contain hard core diameters and **insgfl** flags for the aqueous species. These data are used in conjunction with the B-dot equation for the activity coefficients of aqueous species.

rxnchk.f This module is called by the EQPT modules **pcraq.f** and **pcrsg.f**. It checks a specified reaction for mass and charge balance. If an error is found, an error message is written to the **output** and screen files.

srch22.f This module is called by the EQPT module **wrpz3.f**. It searches to parallel arrays of species names to see if a common index exists which corresponds to an input pair of species names. If such an index exists, it is returned. It also returns information on which array each input species name was found in.

wrbdot.f *This module is called by the EQPT module* ***eqpt.f****. It writes the data for* the *hard core diameters and* **insgfl** flags for the aqueous species onto the **data1** file.The lines containing these data are read from the data file by module **rdbdot.f**.

wrpar.f This module is called by the EQPT module **eqpt.f**. It processes the data read from the data file by module **rdpar.f**. It then writes the corresponding data onto the **data1** file.

wrpz3.f This module is called by the EQPT module **eqpt.f**. It completes the processing of all Pitzer coefficient data and writes the results onto the **data1** file.

Appendix C. EQPT Error Messages

All EQ3/6 error messages fit into one of three categories: *error*, *warning*, and *note*. An *error* implies a fatal error. Execution of the current problem will cease without completion, immediately in some cases, later in others. Which is the case depends on whether it makes more sense to stop immediately or to continue checking for other errors before ceasing execution. A *warning* indicates a condition which may or may not represent a real error. A *note* indicates a condition knowledge of which may assist the user in determining or tracking down the cause of an error. An *error* message may be preceded or followed by one or more other *error*, *warning*, or *note* messages. These messages are written to both the screen file and the **output** file.

Each EQ3/6 error message has the following format:

* *msgtype* - (*source/module*) *Message.*

where *msgtype* = *error*, *warning*, or *note*, *source* is the root name of the source file (e.g., *eqlib*, *eqpt*, *eq3nr*, or *eq6*) containing the *module*, *module* is the name of the module (main program or subroutine) which writes the message, and *Message* is the message itself. The messages are designed to be as self-explanatory as possible. The messages are reproduced here using *AAAA* to stand for a character variable, *IIII* for an integer, and *RRRR* for a floating point number.

EQPT has no input file. Most of the error messages that users are likely to encounter pertain to problems regarding the **data0** data file that this code is processing. In most instances, the meaning of these messages should be immediately clear to the user. In other instances, it may be necessary to search out other information. In such cases, there are three principal actions that users should take. The first is to check the **output** file for additional diagnostic messages (*warnings* and *notes*) which may bear on the matter. You may find that certain data in the **data0** file were not entered in the correct fields, or that a line is missing or you have an extra line. User's should expect to see such errors only if they locally modify the data files supplied as part of the EQ3/6 export package or if they make up their own data files. Otherwise, the occurrence of an error is probably due to corruption of the files in the export package.

Some messages deal with programming errors. The user should see these rarely if ever. These are likely to appear somewhat more cryptic to users. Problems of this type must be dealt with by diagnosing the problem (probably with the help of a symbolic debugger) and modifying the code. Most users should probably not attempt corrective action of this sort. The code custodian should be notified of suspected programming errors and may be able to provide fixes.

Some of the messages displayed in this appendix are followed by *Comments* that may help to explain them. The list of messages given here include only those generated by EQPT modules. Users of EQPT may also encounter error messages from EQLIB modules. These messages are listed in similar format in Appendix C of the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a). The *errors* are listed first, then the *warnings* and finally the *notes*.

Message: * error - (eqpt/eqpt) Unrecognized data file key = "AAAA". Allowed values are "bdot", "hmw", and "pitzer".

Comment: In order to read the data file correctly, the code must know what kind of activity coefficient data to read. The two present data file archetypes are represented by the ***com*** *and* ***hmw*** *data files. The archetype is presently defined by the* ***ukey*** *string. The normal data file key string (****com, sup, nea, hmw,*** *or* ***pit****) is mapped in module* ***rdwttl.f*** *to* ***bdot*** *for data files of the* ***com*** *archetype, and to* ***pitzer*** *for files of the* ***hmw*** *archetype.The* ***ukey*** *value of* ***hmw*** *is not actually bused, but is equivalent to* ***pitzer****. Check the data file to see that the normal data file key string is not missing. If you have created your own such key string, you must declare it in module* ***rdwttl.f****.*

Message: * error - (eqpt/gnenb) Number of chemical elements on the data file exceeds the dimensioned limit (nctpar) of IIII.

Comment: Increase the dimensioned limit.

Message: * error - (eqpt/gnenb) End-of-file hit or other read error occurred while reading the AAAA.

Comment: Search the ***output*** *file for previous error, warning, or note messages. Check the end of the* ***data0*** *file to see that it has not been abnormally truncated. Also check the* ***data0s*** *file (the copy of* ***data0*** *that has been stripped of comments); this is what the code was actually reading.*

Message: * error - (eqpt/gnenb) Number of expanded basis species exceeds the dimensioned limit (nsqpar) of IIII.

Comment: Increase the dimensioned limit. The expanded basis set is the total basis set, including the strict and auxiliary basis sets.

Message: * error - (eqpt/intrp) Could not compute the coefficients of an interpolating polynomial in the temperature range 0-100 Celsius.

Comment: Check the data grid that was being processed.

Message: * error - (eqpt/intrp) Could not compute the coefficients of an interpolating polynomial in the temperature range 100-300 Celsius.

Comment: Check the data grid that was being processed.

Message: * error - (eqpt/pcraq) Species "AAAA" is composed of no chemical elements.

Comment: Check the elemental composition of the species specified on the data file. If it is okay, look for a missing or extra line immediately above it.

Message: * error - (eqpt/pcraq) Species "AAAA" is composed of IIII chemical elements, but there are only IIII elements on the data file.

Comment: This is most likely due to a typographical error in specifying the composition of the species. Check the specified composition. If it seems okay, check it against the chemical elements block. If that seems okay, look for a missing or extra line immediately above the composition data for the species for which the problem occurred.

Message: * error - (eqpt/pcraq) Unrecognized chemical element "AAAA" is listed in the composition of species "AAAA".

Comment: The data file may not contain a species composed of an element that has not been declared in the chemical elements block.This message is most likely to be encountered, however, because of a typographical error in the specification of the elemental composition of the species (e.g., "ci" or " cu" for "cu" when specifying a stoichiometric coefficient for copper).

Message: * error - (eqpt/pcraq) The reaction for the destruction of species "AAAA" includes IIII species, but there are only IIII basis species on the data file, so only IIII species may appear in the reaction.

Comment: This is most likely due to a typographical error in specifying the associated reaction of the species. Check the specified reaction. If it seems okay, check it against the set of basis species. If that seems okay, look for a missing or extra line immediately above the reaction for the species for which the problem occurred.

Message: * error - (eqpt/pcraq) Non-basis species "AAAA" has no species in the reaction in which it is destroyed.

Comment: This is most likely due to a typographical error in specifying the associated reaction of the species. Check the specified reaction. If it seems okay, look for a missing or extra line immediately above the reaction.

Message: * error - (eqpt/pcraq) The reaction which destroys non-basis species "AAAA" is written in terms of an unrecognized basis species "AAAA".

Comment: This is most likely due to a typographical error in specifying the associated reaction of the species (e.g., "ci++" or " cu++" for "cu++"). Check the specified reaction. If it seems okay, check it against the set of basis species. If that seems okay, look for a missing or extra line immediately above the reaction for the species for which the problem occurred.

Message: * error - (eqpt/pcrsg) Species "AAAA" is composed of no chemical elements.

Comment: Check the elemental composition of the species specified on the data file. If it is okay, look for a missing or extra line immediately above it.

Message: * error - (eqpt/pcrsg) Species "AAAA" is composed of IIII chemical elements, but there are only IIII elements on the data file.

Comment: This is most likely due to a typographical error in specifying the composition of the species. Check the specified composition. If it seems okay, check it against the chemical elements block. If that seems okay, look for a missing or extra line immediately above the composition data for the species for which the problem occurred.

Message: * error - (eqpt/pcrsg) Unrecognized chemical element "AAAA" is listed in the composition of species "AAAA".

Comment: The data file may not contain a species composed of an element that has not been declared in the chemical elements block.This message is most likely to be encountered, however, because of a typographical error in the specification of the elemental composition of the species (e.g., "ci" or " cu" for "cu" when specifying a stoichiometric coefficient for copper).

Message: * error - (eqpt/pcrsg) The reaction for the destruction of species "AAAA" includes IIII species, but there are only IIII basis species on the data file, so only IIII species may appear in the reaction.

Comment: This is most likely due to a typographical error in specifying the associated reaction of the species. Check the specified reaction. If it seems okay, check it against the set of basis species. If that seems okay, look for a missing or extra line immediately above the reaction for the species for which the problem occurred.

Message: * error - (eqpt/pcrsg) Non-basis species "AAAA" has no species in the reaction in which it is destroyed.

Comment: This is most likely due to a typographical error in specifying the associated reaction of the species. Check the specified reaction. If it seems okay, look for a missing or extra line immediately above the reaction.

Message: * error - (eqpt/pcrsg) The reaction which destroys non-basis species "AAAA" is written in terms of an unrecognized basis species "AAAA".

Comment: This is most likely due to a typographical error in specifying the associated reaction of the species (e.g., "ci++" or " cu++" for "cu++"). Check the specified reaction. If it seems okay, check it against the set of basis species. If that seems okay, look for a missing or extra line immediately above the reaction for the species for which the problem occurred.

Message: * error - (eqpt/pcrss) Solid solution "AAAA" is composed of IIII end-members, which exceeds the maximum dimension (iktpar) of IIII.

Comment: Increase the dimensioned limit.

Message: * error - (eqpt/pdpz2) The number of single salt entries exceeds the dimension limit (npxpar) of IIII.

Comment: Increase the dimensioned limit. A "single salt entry" refers to a block of Pitzer coefficient data for a pure aqueous neutral electrolyte or a pair of aqueous neutral species.

Message: * error - (eqpt/pdpz2) End-of-file hit or other read error occurred while reading single salt parameters.

Comment: The "single salt parameters" refer to the superblock of Pitzer coefficient data for pure aqueous neutral electrolytes or pairs of aqueous neutral species. Search the output file for previous error, warning, or note messages. Check the end of the data0 file to see that it has not been abnormally truncated. Also check the data0s file (the copy of data0 that has been stripped of comments); this is what the code was actually reading.

Message: * error - (eqpt/rdbdot) The number of bdot lines on the data file exceeds the dimensioned limit (nstpar) of IIII.

Comment: Increase the dimensioned limit. The "bdot lines" are the lines in the block of activity coefficient data for data files of the com archetype. They contain the hard core diameters and neutral species treatment flags for the aqueous species on the data file.

Message: * error - (eqpt/rdbdot) End-of-file hit or other read error occurred while reading bdot parameters.

Comment: The "bdot lines" are the lines in the block of activity coefficient data for data files of the com archetype. They contain the hard core diameters and neutral species treatment flags for the aqueous species on the data file. Search the output file for previous error, warning, or note messages. Check the end of the data0 file to see that it has not been abnormally truncated. Also check the data0s file (the copy of data0 that has been stripped of comments); this is what the code was actually reading.

Message: * error - (eqpt/rdpar) End-of-file hit or other read error occurred while reading data0 parameters.

Comment: The "data0 parameters" refers to the blocks containing the temperatures on the standard grid, the pressure grid, the grids for the Debye-Hückel and related parameters, and the grid for the log equilibrium constant for the "Eh reaction.". Search the output file for previous error, warning, or note messages. Check the end of the data0 file to see that it has not been abnormally truncated. Also check the data0s file (the copy of data0 that has been stripped of comments); this is what the code was actually reading.

Message: * error - (eqpt/rdpz3) The species triplet of "AAAA", AAAA", and "AAAA" representing two electrolytes with a common ion has one species appearing twice.

Comment: This refers to an error in one of the blocks of Pitzer coefficient data for mixtures of two aqueous neutral electrolytes. The species triplet for one of these mixtures is improperly specified.

Message: * error - (eqpt/rdpz3) Psi array index overflow. The dimensioning parameter npxpar is too small.

Comment: Increase the dimensioned limit.

Message: * error - (eqpt/rdpz3) Theta array index overflow. The dimensioning parameter npxpar is too small.

Comment: Increase the dimensioned limit.

Message: * error - (eqpt/rdpz3) Have ixs array index overflow. The dimensioning parameter ixspar is too small.

Comment: Increase the dimensioned limit.

Message: * error - (eqpt/rdpz3) End-of-file hit or other read error occurred while reading mixture term parameters.

Comment: The "mixture term parameters" refer to the superblock of Pitzer coefficient data for mixtures of two aqueous neutral electrolytes. Search the output file for previous error, warning, or note messages. Check the end of the data0 file to see that it has not been abnormally truncated. Also check the data0s file (the copy of data0 that has been stripped of comments); this is what the code was actually reading.

Message: * error - (eqpt/rdwele) End-of-file hit or other read error occurred while reading chemical elements block.

Comment: Search the output file for previous error, warning, or note messages. Check the end of the data0 file to see that it has not been abnormally truncated. Also check the data0s file (the copy of data0 that has been stripped of comments); this is what the code was actually reading.

Message: * error - (eqpt/rdwttl) Have read invalid data0 file header: AAAA

Comment: Check the header. It must begin with "data0".

Message: * error - (eqpt/rdwttl) End-of-file hit or other read error occurred while the data0 file title.

Comment: Search the output file for previous error, warning, or note messages. Check the end of the data0 file to see that it has not been abnormally truncated. Also check the data0s file (the copy of data0 that has been stripped of comments); this is what the code was actually reading.

Message: * error - (eqpt/rxnchk) The following reaction has a computed electrical imbalance of RRRR-

Comment: Check the reaction. If it seems okay, check the electrical charges specified for the species which appear in the reaction.

Message: * error - (eqpt/rxnchk) The following reaction has a computed mass imbalance for "AAAA" of RRRR-

Comment: Check the reaction. If it seems okay, check the elemental compositions specified for the species which appear in the reaction.

Message: * error - (eqpt/wrpz3) Can not find the species pair "AAAA" and "AAAA" in the parallel species name arrays umsp and uxsp. Unable to process psi data.

Comment: This is probably due to the specification of Pitzer coefficient data for a mixture of two aqueous neutral electrolytes, but without specification of the corresponding data for one or both electrolytes. If these data seem to be present, look for a typographical error in a species name (e.g., "na++" or " na+" for "na+").

Message: * note - (eqpt/pcrsg) The pure liquids block has not been written on the data1 and data1f files, because the EQ3NR and EQ6 codes presently do not treat non-aqueous liquids.

Comment: In the future, EQ3/6 may be expanded to handle non-aqueous liquids. In the meantime, EQ3NR and EQ6 have no way to deal with thermodynamic data for such species/phases.

Message: * note - (wrpz3) alphas=99. since lambda1=lambda2=zero

Comment: This message is only written to the dpt1 file. It is written as part of the header for the Pitzer theta coefficient block. It is intended merely to note that the lambda coefficients obtained from the theta coefficients have no ionic strength dependence.This message is largely vestigial.

Appendix D. Known Bugs and Such

This appendix presents notes on known bugs and other known unusual phenomena.

1. EQPT does not currently provide for treating all types of observable interaction coefficients belonging to Pitzer's equations involving interactions with electrically neutral species. See Chapter 3 of the EQ3NR Theoretical Manual and User's Guide (Wolery, 1992b) for a discussion of the various types of observable interaction coefficients belonging to Pitzer's equations.

For a complete list of known bugs and such for EQ3/6, see Appendix D of the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Appendix F. The slist Files for the com and hmw Data Files

This appendix presents the **slist** ("species list") files for the **data0.com.R10** and **data0.hmw.R10** data files.

The slist file for the data0.com.R10 data file:

```
EQPT Species List File:

          no. of elements on the data file =     78
             the dimensioned limit =   100
          no. of aqueous species in the master set =   147
             the dimensioned limit =   500


data0.com.R10
THERMODYNAMIC DATABASE
generated by gembochs/INGRES  15-apr-91
+-------------------------------------------------------------------


element = o          , atwt =   15.99940
element = ag         , atwt =  107.86820
element = al         , atwt =   26.98154
element = am         , atwt =  243.00000
element = ar         , atwt =   39.94800
element = au         , atwt =  196.96654
element = b          , atwt =   10.81100
element = ba         , atwt =  137.32700
element = be         , atwt =    9.01218
element = br         , atwt =   79.90400
element = ca         , atwt =   40.07800
element = cd         , atwt =  112.41100
element = ce         , atwt =  140.11500
element = cl         , atwt =   35.45270
element = co         , atwt =   58.93320
element = cr         , atwt =   51.99610
element = cs         , atwt =  132.90543
element = cu         , atwt =   63.54600
element = dy         , atwt =  162.50000
element = er         , atwt =  167.26000
element = eu         , atwt =  151.96500
element = f          , atwt =   18.99840
element = fe         , atwt =   55.84700
element = ga         , atwt =   69.72300
element = gd         , atwt =  157.25000
element = h          , atwt =    1.00794
element = as         , atwt =   74.92159
element = c          , atwt =   12.01100
element = he         , atwt =    4.00206
element = hg         , atwt =  200.59000
element = ho         , atwt =  164.93032
element = p          , atwt =   30.97362
element = i          , atwt =  126.90447
element = in         , atwt =  114.82000
element = k          , atwt =   39.09830
element = kr         , atwt =   83.80000
element = la         , atwt =  138.90550
element = li         , atwt =    6.94100
element = lu         , atwt =  174.96700
element = mg         , atwt =   24.30500
element = mn         , atwt =   54.93085
element = mo         , atwt =   95.94000
element = na         , atwt =   22.98977
element = nd         , atwt =  144.24000
element = ne         , atwt =   20.17970
element = ni         , atwt =   58.69000
element = n          , atwt =   14.00674
element = np         , atwt =  237.04800
element = pb         , atwt =  207.20000
element = pd         , atwt =  106.42000
element = pr         , atwt =  140.90765
element = pu         , atwt =  244.00000
element = ra         , atwt =  226.02500
element = rb         , atwt =   85.46780
element = re         , atwt =  186.20700
element = rn         , atwt =  222.00000
element = ru         , atwt =  101.07000
element = sc         , atwt =   44.95591
element = se         , atwt =   78.96000
element = si         , atwt =   28.08550
element = sm         , atwt =  150.36000
element = sn         , atwt =  118.71000
element = s          , atwt =   32.06600
```

```
element = sr       , atwt =   87.62000
element = tb       , atwt =  158.92534
element = tc       , atwt =   98.00000
element = th       , atwt =  232.03810
element = ti       , atwt =   47.88000
element = tl       , atwt =  204.38330
element = tm       , atwt =  168.93421
element = u        , atwt =  238.02890
element = v        , atwt =   50.94150
element = w        , atwt =  183.85000
element = xe       , atwt =  131.29000
element = y        , atwt =   88.90585
element = yb       , atwt =  173.04000
element = zn       , atwt =   65.39000
element = zr       , atwt =   91.22400


aqueous

    1  h2o                          ag+
    3  al+++                        am+++
    5  ar(aq)                       au+
    7  b(oh)3(aq)                   ba++
    9  be++                         br-
   11  ca++                         cd++
   13  ce+++                        cl-
   15  co++                         cro4--
   17  cs+                          cu++
   19  dy+++                        er+++
   21  eu+++                        f-
   23  fe++                         ga+++
   25  gd+++                        h+
   27  h2aso4-                      hco3-
   29  he(aq)                       hg++
   31  ho+++                        hpo4--
   33  i-                           in+++
   35  k+                           kr(aq)
   37  la+++                        li+
   39  lu+++                        mg++
   41  mn++                         moo4--
   43  na+                          nd+++
   45  ne(aq)                       ni++
   47  no3-                         np++++
   49  pb++                         pd++
   51  pr+++                        pu++++
   53  ra++                         rb+
   55  reo4-                        rn(aq)
   57  ruo4--                       sc+++
   59  seo3--                       sio2(aq)
   61  sm+++                        sn++
   63  so4--                        sr++
   65  tb+++                        tco4-
   67  th++++                       ti(oh)4(aq)
   69  tl+                          tm+++
   71  uo2++                        vo++
   73  wo4--                        xe(aq)
   75  y+++                         yb+++
   77  zn++                         zr(oh)2++
   79  o2(g)                        (o-phth)--
   81  acetic acid(aq)              acetone(aq)
   83  ag++                         am++++
   85  amo2+                        amo2++
   87  au+++                        benzene(aq)
   89  clo4-                        co+++
   91  co2(aq)                      co3--
   93  cr++                         cr+++
   95  cro4---                      cu+
   97  ethane(aq)                   eu++
   99  fe+++                        glycine(aq)
  101  h2(aq)                       h2aso3-
  103  h2po4-                       hg2++
  105  hs-                          io3-
  107  methanamine(aq)              methane(aq)
  109  methanol(aq)                 mn+++
  111  mno4--                       n2(aq)
  113  n3-                          nh4+
  115  no2-                         np+++
  117  npo2+                        npo2++
  119  o2(aq)                       oh-
  121  pb++++                       po4---
  123  pu+++                        puo2+
  125  puo2++                       ru(oh)2++
  127  ru++                         ru+++
  129  ruo4(aq)                     ruo4-
  131  se--                         seo4--
  133  sm++                         sn++++
  135  so3--                        tc+++
  137  tco++                        tco4--
  139  tco4---                      u+++
  141  u++++                        uo2+
  143  v+++                         vo2+
```

```
145  vo4---                         yb++
147  zr++++                         (npo2)2(oh)2++
149  (npo2)3(oh)5+                  (puo2)2(oh)2++
151  (puo2)3(oh)5+                  (tco(oh)2)2(aq)
153  (uo2)11(co3)6(oh)12--          (uo2)2(oh)2++
155  (uo2)2co3(oh)3-                (uo2)2oh+++
157  (uo2)3(co3)6(6-)               (uo2)3(oh)4++
159  (uo2)3(oh)5+                   (uo2)3(oh)5co2+
161  (uo2)3(oh)7-                   (uo2)4(oh)7+
163  (vo)2(oh)2++                   1-butanamine(aq)
165  1-butanol(aq)                  1-butene(aq)
167  1-butyne(aq)                   1-heptanamine(aq)
169  1-heptanol(aq)                 1-heptene(aq)
171  1-heptyne(aq)                  1-hexanamine(aq)
173  1-hexanol(aq)                  1-hexene(aq)
175  1-hexyne(aq)                   1-octanamine(aq)
177  1-octanol(aq)                  1-octene(aq)
179  1-octyne(aq)                   1-pentanamine(aq)
181  1-pentanol(aq)                 1-pentene(aq)
183  1-pentyne(aq)                  1-propanamine(aq)
185  1-propanol(aq)                 1-propene(aq)
187  1-propyne(aq)                  2-butanone(aq)
189  2-heptanone(aq)                2-hexanone(aq)
191  2-octanone(aq)                 2-pentanone(aq)
193  a-aminobutyric(aq)             acetate
195  ag(co3)2---                    agcl(aq)
197  agcl2-                         agcl3--
199  agcl4---                       agco3-
201  agf(aq)                        agno3(aq)
203  al(o-phth)+                    al(oh)2+
205  al(oh)3(aq)                    al(oh)4-
207  al(so4)2-                      al13o4(oh)24(7+)
209  al2(oh)2++++                   al3(oh)4(5+)
211  alanine(aq)                    alch3coo++
213  alf++                          alf2+
215  alf3(aq)                       alf4-
217  alh2po4++                      alhpo4+
219  aloh++                         also4+
221  am(co3)2-                      am(co3)3---
223  am(h2po4)2+                    am(h2po4)3(aq)
225  am(h2po4)4-                    am(no3)2+
227  am(oh)2+                       am(oh)3(aq)
229  am(so4)2-                      amcl++
231  amcl2+                         amco3+
233  amf++                          amf2+
235  amf3(aq)                       amh2po4++
237  amno3++                        amo2hco3(aq)
239  amoh++                         amso4+
241  as(oh)3(aq)                    ash3(aq)
243  aso2-                          aso2oh--
245  aso3f--                        aso4---
247  asparagine(aq)                 aspartic acid(aq)
249  ass2-                          b2o(oh)5-
251  b3o3(oh)4-                     b4o5(oh)4--
253  ba(o-phth)(aq)                 bab(oh)4+
255  bach3coo+                      bacl+
257  baco3(aq)                      baf+
259  bano3+                         baoh+
261  beo2--                         bf2(oh)2-
263  bf3oh-                         bf4-
265  bh4-                           bo2-
267  br3-                           bro-
269  bro3-                          bro4-
271  butanoate                      butanoic acid(aq)
273  ca(h3sio4)2(aq)                ca(o-phth)(aq)
275  cab(oh)4+                      cach3coo+
277  cacl+                          cacl2(aq)
279  caco3(aq)                      caf+
281  cah2po4+                       cah2sio4(aq)
283  cah3sio4+                      cahco3+
285  cahp2o7-                       cahpo4(aq)
287  cano3+                         caoh+
289  cap2o7--                       capo4-
291  caso4(aq)                      cdseo4(aq)
293  clo-                           clo2-
295  clo3-                          cn-
297  co(hs)2(aq)                    co(oh)2(aq)
299  co(oh)4--                      co2(oh)3+
301  co4(oh)4++++                   cobr2(aq)
303  cocl+                          cohs+
305  coi2(aq)                       cono3+
307  cos2o3(aq)                     coseo4(aq)
309  coso4(aq)                      cr(oh)2+
311  cr(oh)3(aq)                    cr(oh)4-
313  cr2(oh)2++++                   cr2o7--
315  cr3(oh)4(5+)                   crbr++
317  crcl++                         crcl2+
319  cro3cl-                        croh++
321  csbr(aq)                       cscl(aq)
323  csi(aq)                        cu(co3)2--
325  cu(nh3)2+                      cu(nh3)2++
327  cu(nh3)3++                     cu(no2)2(aq)
329  cucl+                          cucl2(aq)
```

```
331  cucl2-                     cucl3--
333  cucl4--                    cuco3(aq)
335  cuco3(oh)2--               cuf+
337  cuh2po4+                   cuhpo4(aq)
339  cunh3+                     cunh3++
341  cuno2+                     cuo2--
343  cuoh+                      cupo4-
345  ethanamine(aq)             ethanol(aq)
347  ethylbenzene(aq)           ethylene(aq)
349  ethyne(aq)                 eu(co3)2-
351  eu(co3)3---                eu(hco3)++
353  eu(oh)(co3)2--             eu(oh)2+
355  eu(oh)2co3-                eu(oh)3(aq)
357  eu(oh)4-                   eu(oh)co3(aq)
359  eu(so4)2-                  eu2(oh)2++++
361  eubr++                     eubr2+
363  eubro3++                   eucl++
365  eucl2+                     euco3+
367  euf++                      euf2+
369  euio3++                    euno3++
371  euoh++                     euso4+
373  fe(ch3coo)2(aq)            fe(ch3coo)2+
375  fe(ch3coo)3(aq)            fe(oh)2(aq)
377  fe(oh)2+                   fe(oh)3(aq)
379  fe(oh)3-                   fe(oh)4-
381  fe(so4)2-                  fe2(oh)2++++
383  fe3(oh)4(5+)               fech3coo+
385  fech3coo++                 fecl+
387  fecl++                     fecl2(aq)
389  fecl2+                     fecl4-
391  fecl4--                    feco3(aq)
393  feco3+                     fef+
395  fef++                      fef2+
397  feh2po4+                   feh2po4++
399  fehco3+                    fehpo4(aq)
401  fehpo4+                    fehseo3++
403  fehso4++                   feno2++
405  feno3++                    feoh++
407  fepo4-                     feso4(aq)
409  feso4+                     formate
411  formic acid(aq)            glutamic acid(aq)
413  glutamine(aq)              h(o-phth)-
415  h2(o-phth)(aq)             h2cro4(aq)
417  h2f2(aq)                   h2p2o7--
419  h2po3f(aq)                 h2s(aq)
421  h2se(aq)                   h2seo3(aq)
423  h2sio4--                   h2so3(aq)
425  h2so4(aq)                  h2vo4-
427  h3aso3(aq)                 h3aso4(aq)
429  h3p2o7-                    h3po4(aq)
431  h4(h2sio4)4----            h4p2o7(aq)
433  h6(h2sio4)4--              haso2(aq)
435  haso3f-                    haso4--
437  hass2(aq)                  hbro(aq)
439  hcl(aq)                    hclo(aq)
441  hclo2(aq)                  hcoo2-
443  hcro4-                     heptanoate
445  heptanoic acid(aq)         hexanoate
447  hexanoic acid(aq)          hf(aq)
449  hf2-                       hio3(aq)
451  hn3(aq)                    hno2(aq)
453  hno3(aq)                   ho2-
455  hp2o7---                   hpo3f-
457  hruo5-                     hs2o3-
459  hse-                       hseo3-
461  hseo4-                     hsio3-
463  hso3-                      hso4-
465  hso5-                      hvo4--
467  i3-                        io-
469  io4-                       isoleucine(aq)
471  kbr(aq)                    kcl(aq)
473  khpo4-                     khso4(aq)
475  ki(aq)                     koh(aq)
477  kp2o7---                   kso4-
479  leucine(aq)                licl(aq)
481  lioh(aq)                   liso4-
483  methionine(aq)             mg(h3sio4)2(aq)
485  mg4(oh)4++++               mgb(oh)4+
487  mgch3coo+                  mgcl+
489  mgco3(aq)                  mgf+
491  mgh2po4+                   mgh2sio4(aq)
493  mgh3sio4+                  mghco3+
495  mghp2o7-                   mghpo4(aq)
497  mgp2o7--                   mgpo4-
499  mgso4(aq)                  mn(no3)2(aq)
501  mn(oh)2(aq)                mn(oh)3-
503  mn(oh)4--                  mn2(oh)3+
505  mn2oh+++                   mncl+
507  mncl3-                     mnco3(aq)
509  mnf+                       mnh2po4+
511  mnhco3+                    mnhpo4(aq)
513  mnno3+                     mno4-
515  mnoh+                      mnpo4-
```

```
517  mnseo4(aq)                  mnso4(aq)
519  n-butane(aq)                n-butylbenzene(aq)
521  n-heptane(aq)               n-heptylbenzene(aq)
523  n-hexane(aq)                n-hexylbenzene(aq)
525  n-octane(aq)                n-octylbenzene(aq)
527  n-pentane(aq)               n-pentylbenzene(aq)
529  n-propylbenzene(aq)         na(o-phth)-
531  na2p2o7--                   nab(oh)4(aq)
533  nabr(aq)                    nach3coo(aq)
535  nacl(aq)                    naco3-
537  naf(aq)                     nah3sio4(aq)
539  nahco3(aq)                  nahp2o7--
541  nahpo4-                     nahsio3(aq)
543  nai(aq)                     naoh(aq)
545  nap2o7---                   naso4-
547  nh3(aq)                     nh4so4-
549  ni(nh3)2++                  ni(nh3)6++
551  ni(no3)2(aq)                ni(oh)2(aq)
553  ni(oh)3-                    ni2oh+++
555  ni4(oh)4++++                nibr+
557  nicl+                       nihp2o7-
559  nino3+                      nip2o7--
561  niseo4(aq)                  niso4(aq)
563  np(co3)5(6-)                np(h2po4)2+
565  np(h2po4)3(aq)              np(hpo4)2(aq)
567  np(hpo4)3--                 np(hpo4)4----
569  np(hpo4)5(6-)               np(oh)2++
571  np(oh)3+                    np(oh)4(aq)
573  np(oh)5-                    np(so4)2(aq)
575  npcl+++                     npcl2++
577  npf+++                      npf2++
579  nph2po4++                   nphpo4++
581  npo2(co3)2--                npo2(co3)2---
583  npo2(co3)3(5-)              npo2(co3)3----
585  npo2cl(aq)                  npo2cl+
587  npo2co3-                    npo2f(aq)
589  npo2f+                      npo2f2(aq)
591  npo2h2po4(aq)               npo2h2po4+
593  npo2hpo4(aq)                npo2hpo4-
595  npo2oh(aq)                  npo2oh+
597  npo2so4(aq)                 npo2so4-
599  npoh++                      npoh+++
601  npso4++                     octanoate
603  octanoic acid(aq)           p2o7----
605  pb(ch3coo)2(aq)             pbch3coo+
607  pbcl+                       pbcl2(aq)
609  pbcl3-                      pbcl4--
611  pbf+                        pbf2(aq)
613  pbh2po4+                    pbhpo4(aq)
615  pentanoate                  pentanoic acid(aq)
617  ph4+                        phenol(aq)
619  phenylalanine(aq)           po3f--
621  propane(aq)                 propanoate
623  propanoic acid(aq)          pu(hpo4)2(aq)
625  pu(hpo4)3--                 pu(hpo4)4----
627  pu(oh)2++                   pu(oh)3+
629  pu(oh)4(aq)                 pu(oh)5-
631  pu(so4)2(aq)                pu(so4)2-
633  pucl++                      pucl+++
635  puf+++                      puf2++
637  puf3+                       puf4(aq)
639  puh2po4++                   puhpo4++
641  puo2(co3)2--                puo2cl+
643  puo2f+                      puo2f2(aq)
645  puo2f3-                     puo2f4--
647  puo2h2po4+                  puo2oh(aq)
649  puo2oh+                     puo2so4(aq)
651  puoh++                      puoh+++
653  puso4+                      puso4++
655  rbbr(aq)                    rbcl(aq)
657  rbf(aq)                     rbi(aq)
659  ru(cl)2+                    ru(cl)3(aq)
661  ru(oh)2+                    ru(oh)2cl+
663  ru(oh)2cl2(aq)              ru(oh)2cl3-
665  ru(oh)2cl4--                ru(oh)2so4(aq)
667  ru(oh)4(aq)                 ru(so4)2-
669  ru4(oh)12++++               rucl+
671  rucl++                      rucl4-
673  rucl5--                     rucl6---
675  ruoh++                      ruso4(aq)
677  ruso4+                      s--
679  s2--                        s2o3--
681  s2o4--                      s2o5--
683  s2o6--                      s2o8--
685  s3--                        s3o6--
687  s4--                        s4o6--
689  s5--                        s5o6--
691  scn-                        serine(aq)
693  sif6--                      sn(oh)2(aq)
695  sn(oh)2++                   sn(oh)3+
697  sn(oh)3-                    sn(oh)4(aq)
699  sn(so4)2(aq)                sncl+
701  sncl2(aq)                   sncl3-
```

```
703  snf+                       snf2(aq)
705  snf3-                      snoh+
707  snoh+++                    snso4++
709  so2(aq)                    srch3coo+
711  srcl+                      srco3(aq)
713  srf+                       srh2po4+
715  srhpo4(aq)                 srno3+
717  sroh+                      srp2o7--
719  srpo4-                     srso4(aq)
721  tc++                       tco(oh)2(aq)
723  tcooh+                     th(h2po4)2++
725  th(hpo4)2(aq)              th(hpo4)3--
727  th(oh)2++                  th(oh)4(aq)
729  th(so4)2(aq)               th(so4)3--
731  th(so4)4----               th2(oh)2(6+)
733  th4(oh)8(8+)               th6(oh)15(9+)
735  thcl+++                    thcl2++
737  thcl3+                     thcl4(aq)
739  thf+++                     thf2++
741  thf3+                      thf4(aq)
743  thh2po4+++                 thh3po4++++
745  thoh+++                    threonine(aq)
747  thso4++                    tl+++
749  toluene(aq)                tryptophan(aq)
751  tyrosine(aq)               u(co3)4----
753  u(co3)5(6-)                u(no3)2++
755  u(oh)4(aq)                 u(scn)2++
757  u(so4)2(aq)                ubr+++
759  ucl+++                     uf+++
761  uf2++                      uf3+
763  uf4(aq)                    uf5-
765  uf6--                      ui+++
767  uno3+++                    uo2(co3)2--
769  uo2(co3)3(5-)              uo2(co3)3----
771  uo2(h2po4)2(aq)            uo2(h2po4)h3po4+
773  uo2(io3)2(aq)              uo2(n3)2(aq)
775  uo2(n3)3-                  uo2(n3)4--
777  uo2(oh)2(aq)               uo2(oh)3-
779  uo2(oh)4--                 uo2(scn)2(aq)
781  uo2(scn)3-                 uo2(so3)2--
783  uo2(so4)2--                uo2br+
785  uo2bro3+                   uo2cl+
787  uo2cl2(aq)                 uo2clo3+
789  uo2co3(aq)                 uo2f+
791  uo2f2(aq)                  uo2f3-
793  uo2f4--                    uo2h2po4+
795  uo2h3po4++                 uo2hpo4(aq)
797  uo2io3+                    uo2n3+
799  uo2no3+                    uo2oh+
801  uo2po4-                    uo2s2o3(aq)
803  uo2scn+                    uo2so3(aq)
805  uo2so4(aq)                 uoh+++
807  uscn+++                    uso4++
809  v(oh)2+                    v2(oh)2++++
811  valine(aq)                 vo(oh)3(aq)
813  vo2(hpo4)2---              vo2(oh)2-
815  vo2f(aq)                   vo2f2-
817  vo2h2po4(aq)               vo2hpo4-
819  vo2so4-                    vo3oh--
821  vof+                       vof2(aq)
823  voh++                      vooh+
825  voso4(aq)                  [illegible]+
827  zn(ch3coo)2(aq)            zn(ch3coo)3-
829  znch3coo+                  zncl+
831  zncl2(aq)                  zncl3-
833  zncl4--                    znf+
835  znh2po4+                   znhco3+
837  znhpo4(aq)                 znoh+
839  znpo4-                     znseo4(aq)
841  zr(oh)3+                   zr(oh)4(aq)
843  zr(so4)2(aq)               zr(so4)3--
845  zrf+++                     zrf2++
847  zrf3+                      zrf4(aq)
849  zrf5-                      zrf6--
851  zroh+++                    zrso4++


minerals

  1  (pb(oh)2)3.pbcl2           (uo2)2as2o7
  3  (uo2)2cl3                  (uo2)2p2o7
  5  (uo2)3(aso4)2              (uo2)3(po4)2
  7  (uo2)3(po4)2:4h2o          (vo)3(po4)2
  9  acanthite                  afwillite
 11  silver                     ag3po4
 13  ahlfeldite                 akermanite
 15  al                         al2(so4)3
 17  al2(so4)3:6h2o             alabandite
 19  alamosite                  albite
 21  albite high                albite low
 23  alf3                       alstonite
 25  alum-k                     alunite
 27  am                         am(oh)3
```

```
 29  am(oh)3(am)                  amesite-14a
 31  amohco3                      analcime
 33  analcime-dehy                andalusite
 35  andradite                    anglesite
 37  anhydrite                    annite
 39  anorthite                    antarcticite
 41  anthophyllite                antigorite
 43  antlerite                    aphthitalite
 45  aragonite                    arcanite
 47  arsenolite                   arsenopyrite
 49  artinite                     as
 51  as2o5                        as4o6(mono)
 53  as4o6(octa)                  atacamite
 55  gold                         azurite
 57  b                            b2o3
 59  ba                           ba(oh)2:8h2o
 61  ba2si3o8                     ba2sio4
 63  babr2                        babr2:2h2o
 65  bacl2                        bacl2:2h2o
 67  bacl2:h2o                    bacro4
 69  baddeleyite                  bahpo4
 71  bai2                         bamno4
 73  bao                          barite
 75  barytocalcite                bas
 77  baseo3                       baseo4
 79  basif6                       bassanite
 81  bassetite                    bauo4
 83  bazro3                       be
 85  bel3u                        beidellite-ca
 87  beidellite-cs                beidellite-h
 89  beidellite-k                 beidellite-mg
 91  beidellite-na                berlinite
 93  berndtite                    bieberite
 95  birnessite                   bischofite
 97  bixbyite                     bloedite
 99  boehmite                     boltwoodite
101  boltwoodite-na               borax
103  boric acid                   bornite
105  brezinaite                   brochantite
107  brucite                      brushite
109  bunsenite                    burkeite
111  graphite                     ca
113  ca-al pyroxene               ca2al2o5:8h2o
115  ca2cl2(oh)2:h2o              ca2v2o7
117  ca3(aso4)2                   ca3al2o6
119  ca3v2o8                      ca4al2fe2o10
121  ca4al2o7:13h2o               ca4al2o7:19h2o
123  ca4cl2(oh)6:13h2o            caal2o4
125  caal2o4:10h2o                caal4o7
127  cadmoselite                  calcite
129  calomel                      carnallite
131  carnotite                    caseo3:2h2o
133  caseo4                       caso4:0.5h2o(beta)
135  cassiterite                  cattierite
137  cauo4                        cav2o6
139  cazro3                       cd
141  cdcr2o4                      cdseo3
143  cdseo4                       cdso4:8/3h2o
145  ce                           celadonite
147  celestite                    cerussite
149  chalcanthite                 chalcedony
151  chalcocite                   chalcocyanite
153  chalcopyrite                 chamosite-7a
155  chlorargyrite                chloromagnesite
157  chromite                     chrysocolla
159  chrysotile                   cinnabar
161  claudetite                   clausthalite
163  clinochalcomenite            clinochlore-14a
165  clinochlore-7a               clinoptilolite
167  clinoptilolite-ca            clinoptilolite-cs
169  clinoptilolite-dehy          clinoptilolite-dehy-ca
171  clinoptilolite-dehy-cs       clinoptilolite-dehy-k
173  clinoptilolite-dehy-na       clinoptilolite-dehy-nh4
175  clinoptilolite-dehy-sr       clinoptilolite-k
177  clinoptilolite-na            clinoptilolite-nh4
179  clinoptilolite-sr            clinozoisite
181  co                           co(no3)2
183  co(oh)2                      co2sio4
185  co3(aso4)2                   co3(po4)2
187  cocl2                        cocl2:2h2o
189  cocl2:6h2o                   coesite
191  cof2                         cof3
193  cofe2o4                      coffinite
195  cohpo4                       colemanite
197  coo                          cordierite anhyd
199  cordierite hydr              corkite
201  corundum                     cos
203  coseo3                       coso4
205  coso4.3co(oh)2               coso4:6h2o
207  coso4:h2o                    cotunnite
209  covellite                    cowo4
211  cr                           crcl3
213  crf3                         crf4
```

215	cri3	cristobalite
217	cristobalite-a	cristobalite-b
219	cro2	cro3
221	crocoite	cronstedtite-7a
223	crs	cs
225	cs2u2o7	cs2u4o12
227	copper	cu3(po4)2
229	cu3(po4)2:3h2o	cucl2
231	cucr2o4	cuf
233	cuf3	cuf2:2h2o
235	cuprite	cuseo3
237	daphnite-14a	daphnite-7a
239	dawsonite	delafossite
241	diaspore	dicalcium silicate
243	diopside	dioptase
245	dolomite	dolomite-dis
247	dolomite-ord	downeyite
249	dy	enstatite
251	epidote	epidote-ord
253	epsomite	er
255	erythrite	eskolaite
257	ettringite	eu
259	eu(io3)3:2h2o	eu(no3)3:6h2o
261	eu(oh)2.5cl.5	eu(oh)2cl
263	eu(oh)3	eu2(co3)3:3h2o
265	eu2(so4)3:8h2o	eu2o3(cubic)
267	eu2o3(monoclinic)	eu3o4
269	eubr3	eucl2
271	eucl3	eucl3:6h2o
273	eucryptite	euf3:0.5h2o
275	euo	euocl
277	eus	euso4
279	fayalite	iron
281	fe(oh)2	fe(oh)3
283	fe2(so4)3	feaso4
285	fef2	fef3
287	*feo*	*ferrite-ca*
289	ferrite-cu	ferrite-dicalcium
291	ferrite-mg	ferrite-zn
293	ferroselite	ferrosilite
295	feso4	fev2o4
297	fluorapatite	fluorite
299	forsterite	foshagite
301	frankdicksonite	freboldite
303	ga	galena
305	gaylussite	gd
307	gehlenite	gibbsite
309	gismondine	glauberite
311	goethite	greenalite
313	grossular	gypsum
315	gyrolite	h-autunite
317	haiweeite	halite
319	hatrurite	hausmannite
321	*heazlewoodite*	*hedenbergite*
323	hematite	hercynite
325	herzenbergite	heulandite
327	hexahydrite	hg2seo3
329	hg2so4	hgseo3
331	hillebrandite	hinsdalite
333	ho	hopeite
335	htco4	huntite
337	hydroboracite	hydrocerussite
339	hydromagnesite	hydrophilite
341	hydroxylapatite	i2
343	ice	illite
345	ilmenite	in
347	jadeite	jarosite
349	jarosite-na	k
351	k-feldspar	k2co3:3/2h2o
353	k2o	k2se
355	*k2uo4*	*k3h(so4)2*
357	k8h4(co3)6:3h2o	kainite
359	kal(so4)2	kalicinite
361	kalsilite	kaolinite
363	karelianite	kasolite
365	katoite	kbr
367	kieserite	klockmannite
369	kmgcl3	kmgcl3:2h2o
371	knaco3:6h2o	krutaite
373	ktco4	kuo2aso4
375	kyanite	la
377	lammerite	lanarkite
379	lansfordite	larnite
381	laumontite	laurite
383	lawrencite	lawsonite
385	leonite	li
387	li2se	li2uo4
389	lime	linnaeite
391	litharge	liuo2aso4
393	lopezite	lu
395	magnesiochromite	magnesite
397	magnetite	malachite
399	manganite	manganosite

401	margarite	massicot
403	*matlockite*	*maximum microcline*
405	mayenite	melanterite
407	mercallite	merwinite
409	mesolite	metacinnabar
411	mg	mg1.25so4(oh)0.5:0.5h2o
413	mg1.5so4(oh)	mg2v2o7
415	mg3(aso4)2	mgbr2
417	mgbr2:6h2o	mgcl2:2h2o
419	mgcl2:4h2o	mgcl2:h2o
421	mgohcl	mgseo3
423	mgseo3:6h2o	mgso4
425	mguo4	mgv2o6
427	millerite	minium
429	minnesotaite	mirabilite
431	misenite	mn
433	mn(oh)2(am)	mn(oh)3
435	mn3(aso4)2	mn3(po4)2
437	mncl2:2h2o	mncl2:4h2o
439	mncl2:h2o	mnhpo4
441	mno2(gamma)	mnse
443	mnseo3	mnseo3:2h2o
445	mnso4	mnv2o6
447	mo	*modderite*
449	molysite	monohydrocalcite
451	monteponite	monticellite
453	montmor-ca	montmor-cs
455	montmor-k	montmor-mg
457	montmor-na	montroydite
459	mordenite	mordenite-dehy
461	morenosite	mose2
463	muscovite	na
465	na2co3	na2co3:7h2o
467	na2cr2o7	na2cro4
469	na2o	na2se
471	na2se2	na2sio3
473	na2u2o7	na2uo4(alpha)
475	na3h(so4)2	na3uo4
477	na4ca(so4)3:2h2o	na4sio4
479	na4uo2(co3)3	na6si2o7
481	nabr	nabr:2h2o
483	nafeo2	nahcolite
485	nanpo2co3:3.5h2o	nantokite
487	natco4	natrolite
489	natron	natrosilite
491	naumannite	nauo3
493	nd	nepheline
495	nesquehonite	nh4hse
497	ni	ni(oh)2
499	ni2p2o7	ni2sio4
501	ni3(po4)2	nickelbischofite
503	nicl2	nicl2:2h2o
505	nicl2:4h2o	nico3
507	nif2	nif2:4h2o
509	ningyoite	niso4
511	niso4:6h2o(alpha)	niter
513	nitrobarite	nontronite-ca
515	nontronite-cs	nontronite-h
517	nontronite-k	nontronite-mg
519	nontronite-na	np
521	np(hpo4)2	np(oh)4
523	np2o5	npo2
525	npo2(oh)2	npo2oh(am)
527	o-phthalic acid	okenite
529	orpiment	otavite
531	ottemannite	oxychloride-mg
533	p	paragonite
535	paralaurionite	pargasite
537	parsonsite	pb
539	pb(h2po4)2	pb2sio4
541	pb3(po4)2	pb3so6
543	pb4o(po4)2	pb4so7
545	pbco3.pbo	pbf2
547	pbhpo4	pbseo4
549	pbso4.2nh3	pd
551	penroseite	pentahydrite
553	periclase	petalite
555	phlogopite	phosgenite
557	picromerite	pirssonite
559	plattnerite	plumbogummite
561	polydymite	polyhalite
563	portlandite	pr
565	prehnite	przhevalskite
567	pseudowollastonite	pu
569	pu(hpo4)2	pu(oh)3
571	pu(oh)4	pu2o3(beta)
573	puf3	puf4
575	*puo2*	*puo2(oh)2*
577	puo2hpo4	puo2oh(am)
579	pyrite	pyrolusite
581	pyromorphite	pyromorphite-oh
583	pyrophyllite	pyrrhotite
585	quartz	ra

```
587  ra(no3)2                    racl2:2h2o
589  rankinite                   raso4
591  rb                          rb2uo4
593  re                          realgar
595  rhodochrosite               rhodonite
597  ripidolite-14a              ripidolite-7a
599  romarchite                  ru
601  ru(oh)3:h2o(am)             rubr3
603  rucl3                       rui3
605  ruo2                        ruo2:2h2o(am)
607  ruo4                        rutherfordine
609  rutile                      sulfur
611  safflorite                  saleeite
613  sanbornite                  sanidine high
615  saponite-ca                 saponite-cs
617  saponite-h                  saponite-k
619  saponite-mg                 saponite-na
621  sc                          scacchite
623  schoepite                   schoepite-dehy(.393)
625  schoepite-dehy(.648)        schoepite-dehy(.85)
627  schoepite-dehy(.9)          schoepite-dehy(1.0)
629  scolecite                   se
631  se2o5                       secl4
633  sellaite                    seo3
635  sepiolite                   shcherbinaite
637  si                          siderite
639  sillimanite                 sio2(am)
641  sklodowskite                sm
643  smectite-high-fe-mg         smectite-low-fe-mg
645  smithsonite                 tin
647  sn(oh)2                     sn(so4)2
649  sn3s4                       snbr2
651  snbr4                       sncl2
653  snse                        snse2
655  snso4                       soddyite
657  sphaerocobaltite            sphalerite
659  spinel                      spinel-co
661  spodumene                   sr
663  sr(no3)2                    sr(no3)2:4h2o
665  sr(oh)2                     sr2sio4
667  sr3(aso4)2                  srbr2
669  srbr2:6h2o                  srbr2:h2o
671  srcl2                       srcl2:2h2o
673  srcl2:6h2o                  srcl2:h2o
675  srcro4                      srf2
677  srhpo4                      sri2
679  sro                         srs
681  srseo4                      srsio3
683  sruo4(alpha)                srzro3
685  starkeyite                  stilbite
687  stilleite                   strengite
689  strontianite                sylvite
691  syngenite                   tachyhydrite
693  talc                        tarapacaite
695  tb                          tc
697  tc(oh)2                     tc(oh)3
699  tc2s7                       tc3o4
701  tc4o7                       tco2:2h2o(am)
703  tco3                        tcoh
705  tcs2                        tcs3
707  tenorite                    tephroite
709  th                          th(no3)4:5h2o
711  th(oh)4                     th(so4)2
713  th2s3                       th2se3
715  th7s12                      thbr4
717  thcl4                       thenardite
719  thermonatrite               thf4
721  thf4:2.5h2o                 thi4
723  thorianite                  ths2
725  ti                          tiemannite
727  titanite                    tl
729  tm                          tobermorite-11a
731  tobermorite-14a             tobermorite-9a
733  todorokite                  torbernite
735  tremolite                   trevorite
737  tridymite                   troilite
739  trona-k                     tsumebite
741  tyuyamunite                 u
743  u(co3)2                     u(hpo4)2:4h2o
745  u(oh)2so4                   u(so3)2
747  u(so4)2                     u(so4)2:4h2o
749  u(so4)2:8h2o                u2c3
751  u2f9                        u2o2cl5
753  u2o3f6                      u2s3
755  u2se3                       u3as4
757  u3o5f8                      u3p4
759  u3s5                        u3se4
761  u3se5                       u4f17
763  u5o12cl                     uas
765  uas2                        ubr2cl
767  ubr2cl2                     ubr3
769  ubr3cl                      ubr4
771  ubr5                        ubrcl2
```

```
 773  ubrcl3                    uc
 775  ucl.94(alpha)             ucl2f2
 777  ucl2i2                    ucl3
 779  ucl3f                     ucl3i
 781  ucl4                      ucl5
 783  ucl6                      uclf3
 785  ucli3                     uf3
 787  uf4                       uf4:2.5h2o
 789  uf5(alpha)                uf5(beta)
 791  uf6                       uh3(beta)
 793  ui3                       ui4
 795  umangite                  uo2(am)
 797  uo2(aso3)2                uo2(io3)2
 799  uo2(no3)2                 uo2(no3)2:2h2o
 801  uo2(no3)2:3h2o            uo2(no3)2:6h2o
 803  uo2(no3)2:h2o             uo2(oh)2(beta)
 805  uo2(po3)2                 uo2.25
 807  uo2.3333(beta)            uo2.6667
 809  uo2br2                    uo2br2:3h2o
 811  uo2br2:h2o                uo2broh:2h2o
 813  uo2cl                     uo2cl2
 815  uo2cl2:3h2o               uo2cl2:h2o
 817  uo2cloh:2h2o              uo2f2
 819  uo2f2:3h2o                uo2foh
 821  uo2foh:2h2o               uo2foh:h2o
 823  uo2hpo4                   uo2hpo4:4h2o
 825  uo2so3                    uo2so4
 827  uo2so4:2.5h2o             uo2so4:3.5h2o
 829  uo2so4:3h2o               uo2so4:h2o
 831  uo3(alpha)                uo3(beta)
 833  uo3(gamma)                uobr2
 835  uobr3                     uocl
 837  uocl2                     uocl3
 839  uof2                      uof2:h2o
 841  uof4                      uofoh
 843  uofoh:.5h2o               up
 845  up2                       up2o7
 847  up2o7:20h2o               upo5
 849  uraninite                 uranocircite
 851  uranophane                us
 853  us1.9                     us2
 855  us3                       use
 857  use2(alpha)               use2(beta)
 859  use3                      v
 861  v2o4                      v3o5
 863  v4o7                      vaesite
 865  vivianite                 w
 867  wairakite                 weeksite
 869  whitlockite               wilkmanite
 871  witherite                 wollastonite
 873  wurtzite                  wustite
 875  xonotlite                 y
 877  yb                        zincite
 879  zircon                    zn
 881  zn3(aso4)2                zncr2o4
 883  znf2                      znseo3:h2o
 885  zoisite                   zr


liquids

   1  br2                       quicksilver

* note - (eqpt/pcrsg) The pure liquids block has
      not been written on the data1 and data1f files,
      because the EQ3NR and EQ6 codes presently do not
      treat non-aqeuous liquids.


gases

   1  ag(g)                     al(g)
   3  ar(g)                     b(g)
   5  bf3(g)                    br2(g)
   7  c(g)                      ca(g)
   9  cd(g)                     ch4(g)
  11  cl2(g)                    co(g)
  13  co2(g)                    cs(g)
  15  cu(g)                     f2(g)
  17  h2(g)                     h2o(g)
  19  h2s(g)                    hbr(g)
  21  hcl(g)                    he(g)
  23  hf(g)                     hg(g)
  25  hi(g)                     i2(g)
  27  k(g)                      kr(g)
  29  li(g)                     mg(g)
  31  n2(g)                     na(g)
  33  no(g)                     nh3(g)
  35  o2(g)                     pb(g)
  37  rb(g)                     rn(g)
  39  s2(g)                     si(g)
  41  sif4(g)                   sn(g)
  43  so2(g)                    tc2o7(g)
```

```
    45  th(g)                          ti(g)
    47  ticl4(g)                       u(g)
    49  u2cl10(g)                      u2cl8(g)
    51  u2f10(g)                       ubr(g)
    53  ubr2(g)                        ubr3(g)
    55  ubr4(g)                        ucl(g)
    57  ucl2(g)                        ucl3(g)
    59  ucl4(g)                        ucl5(g)
    61  ucl6(g)                        uf(g)
    63  uf2(g)                         uf3(g)
    65  uf4(g)                         uf5(g)
    67  uf6(g)                         ui(g)
    69  ui2(g)                         ui3(g)
    71  ui4(g)                         uo2cl2(g)
    73  uo2f2(g)                       uof4(g)
    75  xe(g)                          zn(g)

solid solutions

     1  biotite
           annite                      phlogopite
     2  carbonate-calcite
           calcite                     magnesite
           rhodochrosite               siderite
           smithsonite                 strontianite
     3  chlorite-ss
           clinochlore-14a             daphnite-14a
     4  clinoptilolite-ss
           clinoptilolite-ca           clinoptilolite-cs
           clinoptilolite-k            clinoptilolite-na
           clinoptilolite-nh4          clinoptilolite-sr
     5  epidote-ss
           clinozoisite                epidote
     6  garnet-ss
           andradite                   grossular
     7  olivine
           fayalite                    forsterite
     8  orthopyroxene
           enstatite                   ferrosilite
     9  plagioclase
           albite high                 anorthite
           sanidine high
    10  sanidine-ss
           albite high                 sanidine high
           anorthite
    11  saponite-tri
           saponite-ca                 saponite-h
           saponite-k                  saponite-mg
           saponite-na
    12  smectite-di
           beidellite-ca               beidellite-k
           beidellite-mg               beidellite-na
           montmor-ca                  montmor-k
           montmor-mg                  montmor-na
           nontronite-ca               nontronite-k
           nontronite-mg               nontronite-na
```

The slist file for the data0.hmw.R10 data file:

```
EQPT Species List File:


          no. of elements on the data file =      9
              the dimensioned limit =   100
          no. of aqueous species in the master set =     13
              the dimensioned limit =   500


data0.hmw.R10
THERMODYNAMIC DATABASE
generated by gembochs/INGRES  16-apr-91
+-----------------------------------------------------------------------


element = o          , atwt =   15.99940
element = ca         , atwt =   40.07800
element = cl         , atwt =   35.45270
element = h          , atwt =    1.00794
element = c          , atwt =   12.01100
element = k          , atwt =   39.09830
element = mg         , atwt =   24.30500
element = na         , atwt =   22.98977
element = s          , atwt =   32.06600
```

```
aqueous

     1  h2o                           ca++
     3  cl-                           h+
     5  hco3-                         k+
     7  mg++                          na+
     9  so4--                         o2(g)
    11  co2(aq)                       co3--
    13  oh-                           caco3(aq)
    15  hso4-                         mgco3(aq)
    17  mgoh+

minerals

     1  anhydrite                     antarcticite
     3  aphthitalite                  aragonite
     5  arcanite                      bischofite
     7  bloedite                      brucite
     9  burkeite                      ca2cl2(oh)2:h2o
    11  ca4cl2(oh)6:13h2o             cacl2:4h2o
    13  calcite                       carnallite
    15  dolomite                      epsomite
    17  gaylussite                    glauberite
    19  gypsum                        halite
    21  hexahydrite                   k2co3:3/2h2o
    23  k3h(so4)2                     k8h4(co3)6:3h2o
    25  kainite                       kalicinite
    27  kieserite                     knaco3:6h2o
    29  leonite                       magnesite
    31  mercallite                    mirabilite
    33  misenite                      na2co3:7h2o
    35  na3h(so4)2                    na4ca(so4)3:2h2o
    37  nahcolite                     natron
    39  nesquehonite                  oxychloride-mg
    41  picromerite                   pirssonite
    43  polyhalite                    portlandite
    45  sylvite                       syngenite
    47  tachyhydrite                  thenardite
    49  thermonatrite                 trona
    51  trona-k

liquids

     0  none

* note - (eqpt/pcrsg) The pure liquids block has
      not been written on the data1 and data1f files,
      because the EQ3NR and EQ6 codes presently do not
      treat non-aqeuous liquids.


gases

     1  co2(g)                        h2(g)
     3  o2(g)

solid solutions

     0  none
```

End Date
3/8/93