
Thomas J. Wolery

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Preface

This report on the EQ3NR code is a revision of the first EQ3NR User's Guide (Wolery, 1983). It is one of a set of reports documenting version 7.0 (version 3245.1090 under the old numbering system) of the EQ3/6 software package. This set includes:


EQ3NR, the subject of the present report, is the speciation-solubility code in the EQ3/6 package. EQ6 is the reaction path code in EQ3/6. EQPT is the EQ3/6 data file preprocessor. The present report assumes that the reader is familiar with the contents of the EQ3/6 Package Overview and Installation Guide and the EQPT User's Guide.

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  
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Glossary of Symbols

\( a, a' \)
Symbols used to represent cations in the notation of Harvie, Moller, and Weare (1984); see also \( X, X' \).

\( a_i \)
Thermodynamic activity of the \( i \)-th aqueous solute species.

\( a_w \)
Thermodynamic activity of water.

\( a_{\pm MX} \)
Mean activity of neutral electrolyte \( MX; \quad \log a_{\pm MX} = \frac{v_M \log a_M + v_X \log a_X}{v_{MX}}. \)

\( a_{\alpha\psi} \)
Thermodynamic activity of the \( \alpha \)-th component of the \( \psi \)-th solid solution phase.

\( \hat{d} \)
Generalized hard core diameter or "ion size" in aqueous solution.

\( d_i \)
Hard core diameter or "size" of the \( i \)-th aqueous solute species.

\( A \)
Affinity.

\( A_j \)
Thermodynamic affinity of the \( j \)-th reaction. The forward direction is implied, which in EQ3/6 is taken to be that in which the associated species is destroyed, for example by dissolution or dissociation.

\( A_{+, j} \)
Thermodynamic affinity of the \( j \)-th reaction (forward direction).

\( A_{-, j} \)
Thermodynamic affinity of the \( j \)-th reaction (reverse direction).

\( A_h \)
Thermodynamic affinity (per electron) of a redox couple with respect to the standard hydrogen electrode; \( A_h = F E_h \).

\( A_t \)
Titration alkalinity, in units of equivalents per kilogram of solvent water or equivalents/L.

\( A_{\kappa e} \)
Debye-Hückel A parameter used in writing expressions for \( \ln \gamma_i \).

\( A_{\kappa 10} \)
Debye-Hückel A parameter used in writing expressions for \( \log_{10} \gamma_i; \quad A_{\kappa 10} = 2.303 A_{\kappa e} \).

\( A_0 \)
Debye-Hückel A parameter used in writing expressions for \( \ln a_w \).

\( A_t^* \)
Titration alkalinity, mg/L of equivalent \( CaCO_3 \); also denoted as \( T \).

\( A_{i, HCO_3}^* \)
Titration alkalinity, mg/L of equivalent \( HCO_3^- \).

\( A_{HCO_3}^* \)
Bicarbonate alkalinity, mg/L of equivalent \( CaCO_3 \).

\( A_{CO_3^2-}^* \)
Carbonate alkalinity, mg/L of equivalent \( CaCO_3 \).

\( A_{OH^-}^* \)
Hydroxide alkalinity, mg/L of equivalent \( CaCO_3 \).

\( b_{ir} \)
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.
$b_s$  Stoichiometric reaction coefficient, the number of moles of the $s$-th aqueous species appearing in the reaction for the dissolution of the $s$-th pure mineral; it is negative for reactants and positive for products.

$b_g$  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 $dB$, and appearing in Pitzer's equations with a fixed value of 1.2.

$B_y$  Debye-Hückel $B$ parameter used in writing expressions for $ln \gamma_i$ or $log_{10} \gamma_i$.

$B_{MX}(l)$  Observable second order interaction coefficient for neutral electrolyte $MX$ ($M$ = cation, $X$ = anion); a function of the ionic strength.

$B_{MX}^0(l)$  The derivative of $B_{MX}(l)$ with respect to ionic strength.

$B_{MX}^0(l)$  The compound function $B_{MX}(l) + 1B_{MX}^0(l)$.

c, c'  Symbols used to represent cations in the notation of Harvie, Moller, and Weare (1984); see also $M$, $M'$.

$C_{i, molar}$  Concentration of the $i$-th solute species in molarity (moles/L).

$C_{i, mg/L}$  Concentration of the $i$-th solute species in mg/L.

$C_{i, mg/kg}$  Concentration of the $i$-th solute species in mg/kg solution.

$C_{TS, mg/kg}$  Total dissolved solutes in mg/kg solution.

$C_{TS, mg/L}$  Total dissolved solutes in mg/L.

$C_{MX}$  Third order interaction coefficient for neutral electrolyte $MX$.

$C_{MX}$  The quantity $\frac{C_{MX}}{2\sqrt{e-M}-e_X}$.

e, e'  Subscript indexing a chemical element.

$e_T$  Total number of chemical elements in a system.

e'  The electron. In common thermodynamic formalism, this is usually a hypothetical species, not a real one.

$E_j$  Electrical potential of the $j$-th redox couple, volts.

$E_{j'}$  Standard state electrical potential of the $j$-th redox couple, volts.

$Eh$  Redox potential, volts. Theoretical equilibrium electrical potential of a redox couple; $Eh = \frac{2.303RT}{4F} (log f_{O_2} - 4pH - 2log a_w - log K_{Eh})$, where $f_{O_2}$ is understood to be the hypothetical equilibrium oxygen fugacity in aqueous solution.

$f(l)$  Debye-Hückel $f$ function.
Debye-Hückel \( f \) function; \( f(l) = df/dl \).

The quantity \( f(l)/l \).

Fugacity of the \( g \)-th gas.

Oxygen fugacity.

(1) The Faraday constant, 23062.3 cal/equiv-volt; (2) Compound electrostatic function used by Harvie, Moller, and Wcare (1984) to write Pitzer’s equations (see Chapter 3).

Subscript denoting a gas species.

Total number of gas species in a system.

A function used to describe the ionic strength dependence of the second order interaction coefficient in Pitzer’s equations.

The derivative of \( g(x) \) with respect to \( x \).

Excess Gibbs energy, as of a solution.

The factor \( \frac{m_s^s \cdot u_{r}}{b_{s}^s} \), where \( s^s \) denotes the dependent aqueous species which is associated with and destroyed by the \( r \)-th aqueous reaction.

The factor \( \frac{m_s^s \cdot z_s^s}{b_{s}^s} \) (analogous to \( H_{sr} \)).

Ionic strength.

Ion activity product; see \( Q \).

A function used to describe the higher order electrical interactions term in Pitzer’s equations.

The derivative of \( J(x) \) with respect to \( x \).

An element of the Jacobian matrix \( \frac{\partial \alpha_j}{\partial x_j} \).

The Jacobian matrix.

Thermodynamic equilibrium constant.

Thermodynamic equilibrium constant for the half-reaction \( 2H_2O \rightarrow O_{2(g)} + 4H^+ + 4e^- \).

Equilibrium constant for the reaction \( H_2O \rightarrow H^+ + OH^- \).

Molal concentration of the \( i \)-th aqueous solute species (no contributions from dependent species).

Total molal concentration of the \( i \)-th aqueous species (includes contributions from dependent species).

Symbols denoting cations (see also \( c, c' \)).

Molecular weight of the \( i \)-th substance, grams per mole; e.g. \( M_w \) is the molecular weight of water.
\( n, n' \)  
Symbols used to represent cations in the notation of Harvie, Moller, and Weare (1984); see also \( N, N' \).

\( n_i \)  
Number of moles of the \( i \)-th aqueous solute species.

\( n_s \)  
Number of moles of the \( s \)-th aqueous species.

\( n_{T,s} \)  
Total number of moles of the \( s \)-th (basis) aqueous solute species.

\( n_w \)  
Number of moles of solvent water.

\( n_{T,e} \)  
Total number of moles of the \( e \)-th chemical element.

\( N, N' \)  
Symbols denoting neutral species (see also \( n, n' \)).

\( N_w \)  
Weight fraction of water in aqueous solution.

\( N_w \)  
Site-mixing parameter for the \( w \)-th solid solution. If \( N_w = 1 \), the model is equivalent to a molecular-mixing model.

\( O_{2(g)} \)  
Oxygen gas; in aqueous solution, this refers to a hypothetical species similar to \( e^+ \); also symbolized as \( s_B \).

\( p_g \)  
Partial pressure of the \( g \)-th gas, bars.

\( p_{kq} \)  
The \( k \)-th parameter used to compute the interaction coefficients \( W_{i,j} \), which in turn are used to compute the activity coefficients of end-member components in the \( w \)-th solid solution.

\( p \)  
(1) Pressure, bars; (2) Phenolphthalein alkalinity, equivalent mg/L of \( CaCO_3 \).

\( p_e \)  
Logarithm of the hypothetical electron activity; \( p_e = \frac{E}{F} \log_e \frac{2.303}{RT} = \log (2.303) \).

\( pH \)  
The quantity \( -\log a_{H^+} \).

\( pHCl \)  
The quantity \( -\log a_{H^+} - \log a_{C^+} \).

\( Q \)  
Activity product of a reaction; \( IAP \) is used by many others (e.g., Parkhurst et al., 1980) to denote the same quantity. "Q" implies \( Q_+ \), the activity product corresponding to the reaction taken in the forward direction.

\( Q_+ \)  
Activity product of a reaction, the same as \( Q \).

\( Q_+ , H_2 \)  
Activity product of a half reaction.

\( Q_+ , H_2 \)  
Reverse activity product of a half reaction, equal to \( 1/Q_+ \).

\( r \)  
Subscript denoting an aqueous reaction.

\( r_T \)  
Total number of reactions for the dissociation/destruction of dependent aqueous species.

\( R \)  
The gas constant, 1.98726 cal/mol.°K.

\( s \)  
Subscript denoting an aqueous species (\( s = w \) implies \( H_2O(H) \)).

\( s' \)  
Subscript denoting \( s \) in the range from 1 to \( s_Q \), excluding the cases \( s = w \) and \( s = s_B \).
Subscript implying the species formally associated with the aqueous reaction designated by \( r (s^n = r + s_B). \)

Subscript denoting the hypothetical aqueous species \( O_{2(gh)} \).

The total number of aqueous master species; depending on the problem at hand, \( s_Q \) is equal to or greater than \( s_B. \)

Total number of aqueous species.

Saturation index for a mineral; \( SI = \log(Q/K) \), where \( Q \) and \( K \) are the activity product and equilibrium constant, respectively, for the dissolution reaction.

(1) Temperature, °K; (2) Titration alkalinity, mg/L of equivalent \( CaCO_3 \).

The molar volume of an ideal gas, 22,413.6 ml/mole.

Stoichiometric mass balance coefficient calculated from reaction coefficients and certain model constraints; \( u_i \) is the stoichiometric factor for computing the contribution of the \( i \)-th aqueous species to the mass balance for the \( s \)'-th basis species.

Subscript denoting water (e.g., \( a_w \), the activity of water).

Number of kilograms of solvent water.

Interaction coefficients used to compute the activity coefficients of end-member components in the \( \Psi \)-th solid solution.

Array of partial derivatives of \( \log x_w \) with respect to \( \log m_i \), where \( s' \) is a basis species. This derivative is zero for \( s' = w \) or \( s_B \).

A general algebraic variable.

Mole fraction of the \( i \)-th aqueous solute species.

Mole fraction of water in aqueous solution.

Mole fraction of the \( \sigma \)-th end member of the \( \Psi \)-th solid solution.

Symbols denoting anions (see also \( a, a' \)).

Electrical charge of the \( s \)-th aqueous species.

Subscript denoting charge balance (e.g., \( H_{cr} \)).

Vector of algebraic master variables.

Symbol for \( \ln \) and approximation of \( \ln 10. \) As an approximation, this is not sufficiently accurate for general use in calculations; this constant should be computed to full machine accuracy in a computer code in order to avoid both inaccuracy and inconsistency.

Parameters appearing in Pitzer's equations.

Newton-Raphson residual function vector.

Residual function for charge balance.
\( \alpha_s \) Residual function for mass balance of the \( s \)-th basis species.

\( \alpha_0 \) Residual function for equilibrium with a pure mineral.

\( \alpha_{\text{eq}} \) Residual function for equilibrium with the \( \sigma \)-th end member of the \( \psi \)-th solid solution.

\( \beta \) Newton-Raphson residual function vector, identical to \( \alpha \), except that mass balance residual elements are normalized by the corresponding values of total numbers of moles.

\( \beta_{\text{max}} \) The largest absolute value of any element of \( \beta \).

\( \beta_{MX}^{(0)}, \beta_{MX}^{(1)}, \beta_{MX}^{(2)} \) Observable second order interaction coefficient parameters for neutral electrolyte \( MX \).

\( \gamma_i \) Molal activity coefficient of the \( i \)-th aqueous solute species.

\( \gamma_{r,t,i} \) Stoichiometric molal activity coefficient of the \( i \)-th aqueous solute species; generally defined only for simple ions.

\( \gamma_{t,ME} \) Mean molal activity coefficient of aqueous neutral electrolyte \( MX \).

\( \gamma_{t,ME} \) Stoichiometric mean molal activity coefficient of aqueous neutral electrolyte \( MX \).

\( \delta \) Newton-Raphson correction term vector.

\( \delta_{\text{max}} \) The largest absolute value of any element of \( \delta \).

\( \delta_{\text{conv}} \) Convergence function.

\( \delta' \) Under-relaxation parameter.

\( \Delta G_{j,i} \) Gibbs energy of formation of the \( i \)-th chemical species.

\( \Delta G_{j,i}^\circ \) Standard state Gibbs energy of formation of the \( i \)-th chemical species.

\( \Delta G_r \) Gibbs energy of reaction of the \( r \)-th reaction.

\( \Delta G_r^\circ \) Standard state Gibbs energy of reaction of the \( r \)-th reaction.

\( \varepsilon \) Subscript denoting a chemical element.

\( \varepsilon_T \) Total number of chemical elements in a system.

\( \xi_{NMX} \) Observable third order interaction coefficient for neutral species \( N \), cation \( M \), and anion \( X \).

\( \theta_{M,M'}(I) \) Observable second order interaction coefficient for mixtures of neutral electrolytes \( MX \) and \( M'X \); independent of the identity of \( X \) and a function of the ionic strength.

\( \theta_{M,M'}^*(I) \) The derivative of \( \theta_{M,M'}(I) \) with respect to ionic strength.

\( \theta_{M,M'}^{E^*}(I) \) The electrostatic part of \( \theta_{M,M'}(I) \).

\( \theta_{M,M'}^{S^*} \) The short-range part of \( \theta_{M,M'}(I) \); treated as a constant.

\( \kappa \) Under-relaxation parameter in Newton-Raphson iteration.
Second-order interaction coefficient for the $i$-th and $j$-th aqueous solute species; in general, this is a function of the ionic strength.

$\lambda_{ij}(l)$

The derivative of $\lambda_{ij}(l)$ with respect to ionic strength.

$\lambda_{ij}^{(0)}, \lambda_{ij}^{(1)}, \lambda_{ij}^{(2)}$

Second order interaction coefficient parameters for cation $M$ and anion $X$.

$\lambda_{w}$

Rational (mole fraction) activity coefficient of water, $a_w = \lambda_w x_w$.

$\lambda_{o_w}$

Rational (mole fraction) activity coefficient of the $\sigma$-th end member of the $\psi$-th solid solution.

$F_{\lambda_{MM'}}(l)$

The electrostatic part of $\lambda_{MM'}(l)$.

$S_{\lambda_{MM'}}$

The short-range part of $\lambda_{MM'}(l)$, treated as a constant.

$\mu_{ijk}$

Third-order interaction coefficient for the $i$-th, $j$-th, and $k$-th aqueous solute species.

$\nu_M$

Number of cations $M$ produced by dissociation of the aqueous neutral electrolyte $MX$.

$\nu_{MX}$

Number of cations $M$ and anions $X$ produced by dissociation of the aqueous neutral electrolyte $MX$.

$\nu_X$

Number of anions $X$ produced by dissociation of the aqueous neutral electrolyte $MX$.

$\rho_{g/ml}$

Solution density, g/ml.

$\sigma, \sigma'$

Symbols denoting end-member components of a solid solution.

$\sigma_{T_r}$

Total number of end members in the $\psi$-th solid solution.

$\tau_s$

Alkalinity factor, the number of hydrogen ion neutralizing equivalents per mole of the $s$-th aqueous species.

$\phi$

(a) Subscript denoting a pure mineral; (b) the osmotic coefficient of the aqueous solution.

$\phi_{MM}(l)$

Harvie, Moller, and Weare's (1984) notation for $\theta_{MM}(l)$.

$\phi'_{MM}(l)$

Harvie, Moller, and Weare's (1984) notation for $\theta'_{MM}(l)$.

$\chi_g$

Fugacity coefficient of the $g$-th gas.

$\psi$

Subscript denoting a solid solution.

$\psi_T$

Total number of solid solutions in a system.

$\psi_{MMX}$

Observable third order interaction coefficient for neutral electrolytes $MX$ and $M'X$.

$\Omega$

Water constant; 1000 divided by the molecular weight of water; about 55.51.

$\kappa_{ij}$

Ionic activity combination parameter: $\kappa_{ij} = |z_j| \log a_i - |z_i| \log a_j$.

$+$

Subscript denoting a reaction proceeding in the forward sense; the convention in this report equates this with dissociation, dissolution, or destruction of the associated species.
Subscript denoting a reaction proceeding in the backward sense; the convention in this report equates this with association, precipitation, or formation of the associated species.
(Version 7.0)

Abstract
EQ3NR is an aqueous solution speciation-solubility modeling code. It is part of the EQ3/6 software package for geochemical modeling. It computes the thermodynamic state of an aqueous solution by determining the distribution of chemical species, including simple ions, ion pairs, and complexes, using standard state thermodynamic data and various equations which describe the thermodynamic activity coefficients of these species. The input to the code describes the aqueous solution in terms of analytical data, including total (analytical) concentrations of dissolved components and such other parameters as the pH, pHCl, Eh, pe, and oxygen fugacity. The input may also include a desired electrical balancing adjustment and various constraints which impose equilibrium with specified pure minerals, solid solution end-member components (of specified mole fractions), and gases (of specified fugacities). The code evaluates the degree of disequilibrium in terms of the saturation index (SI = log Q/K) and the thermodynamic affinity (A = -2.303 RT log Q/K) for various reactions, such as mineral dissolution or oxidation-reduction in the aqueous solution itself. Individual values of Eh, pe, oxygen fugacity, and A value (redox affinity) are computed for aqueous redox couples. Equilibrium fugacities are computed for gas species. The code is highly flexible in dealing with various parameters as either model inputs or outputs. The user can specify modification or substitution of equilibrium constants at run time by using options on the input file. The output consists of an output file and a pickup file, which can be used to initialize an EQ6 reaction path calculation. The chief numerical method employed is a hybrid Newton-Raphson technique. This is supported by a set of algorithms which create and optimize starting values. EQ3NR reads a secondary unformatted data file (data1) that is created from a primary formatted data file (data0) by EQPT, the EQ3/6 data file preprocessor. There is currently a set of five data (data0) files. Three of these may be used with either the Davies equation or the B-dot equation to describe the activity coefficients of the aqueous species. Their use is restricted to modeling dilute solutions. The other two of these use Pitzer’s equations and are suitable for modeling solutions to high concentrations, though with fewer chemical components. The temperature range of the thermodynamic data on the data files varies from 25°C only to 0-300°C. EQ3NR may be used by itself or to initialize a reaction path calculation by EQ6, its companion code in the EQ3/6 package. EQ3NR 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
EQ3NR is a speciation-solubility code for modeling the thermodynamic state of an aqueous solution. In essence, this involves a static calculation that is usually based on water chemistry analysis. The purpose of such a calculation is usually to find the detailed distribution of chemical species and to assess the degree of equilibrium (or disequilibrium) pertaining to various reactions, usually those involving other phases. EQ3NR can not be used to directly model the
chemical evolution of such a water. However, it can be used to initialize such a calculation, which can be made by the companion code EQ6 (Wolery and Daveler, 1992).

EQ3NR is part of the EQ3/6 software package (see Wolery, 1992). This report describes EQ3NR 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, 1992). Other codes in the package include EQPT (Daveler and Wolery, 1992), a data file preprocessor, and EQ6 (Wolery and Daveler, 1992), a reaction path code. The relationship of the EQ3NR code to EQ6, EQPT, 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. EQPT processes these 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. To run EQ3NR or EQ6, the user must provide one of these files, which is known to each code simply as data1.

The user 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 the aqueous species and contains the relevant activity coefficient data as well as standard state thermodynamic data. The activity coefficient formalisms currently built into EQ3/6 are discussed in Chapter 3. 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 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 data base and program for dealing with thermodynamic data based on the work of Helgeson and Kirkham (1974ab, 1976), Helgeson et al. (1978), Tanger and Helgeson (1989), 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 report 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
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</tbody>
</table>
the former in cases of overlap. It also includes some data found in the \textit{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 \textit{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 \textit{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 \textit{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.

The data file preprocessor EQPT (Daveler and Wolery, 1992) performs a number of functions. It checks the composition, charge, and reaction coefficient data on a \textit{data0} file for internal consistency and fits interpolating polynomials to various temperature dependent data which are organized on the \textit{data0} file on temperature grids. Such data include certain aqueous species activity coefficient parameters, such as Debye-Hückel $\Lambda^*_\nu, 10$ and $B^*_\nu$, 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 (see Chapter 3). EQPT then writes the \textit{data1} file corresponding to the input \textit{data0} file. For details of the contents and structure of \textit{data0} and \textit{data1} files, see Daveler and Wolery (1992). Run-time alteration of the values of selected equilibrium constants can subsequently be selected by the user on the EQ3NR \textit{input} file (see Chapter 6). EQPT also writes to a screen file and an \textit{output} file, both of which are generally significant only if an error condition is encountered. In addition, it writes an \textit{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 (See Chapter 5).

A speciation-solubility problem to be run with EQ3NR is described on the EQ3NR \textit{input} file. This is the subject of Chapter 6 of this report. Examples are presented in Chapter 7. The code then produces an \textit{output} file describing the results of the calculation. While the code is running, it writes to a screen file, primarily to apprise the user of what is happening. It also writes a \textit{pickup} file, which contains a compact description of the aqueous solution (see Chapter 8). This is required for a subsequent EQ6 calculation; it corresponds to the bottom part of the EQ6 \textit{input} file. It has no other real use. EQ6 in turn writes its own \textit{output} file, as well as a \textit{tab} file which contains certain data in tabular form suitable for supporting local graphics postprocessing. This code also writes to the screen file while it is running. In addition, EQ6 writes its own \textit{pickup} file, which
may be used as an input file to restart a reaction path calculation from the point at which a previous run stopped.

The input to the code consists of a chemical analysis of a water and specification of various user-defined options. The input usually consists mostly of analytical values for concentrations of dissolved components. These represent total values that do not distinguish between contributions from simple ions, ion pairs, and aqueous complexes, species which may exist in solution in mutual equilibrium. In addition, analytical data may or may not distinguish a dissolved component by oxidation state. The $pH$ is also normally an input parameter. A new alternative parameter called $pHCl$ can be input in place of $pH$ to overcome the liquid junction potential problem in measuring $pH$ in concentrated solutions (see Chapter 2). The $Eh$ (redox potential) is also a common input parameter, though its usage is somewhat problematical (see Chapter 2). One may specify the oxygen fugacity or $pe$ instead, though this is no less problematical. It is also possible to specify a redox couple to define the redox state. For example, one might specify the ferrous-ferric couple if one had two total concentration values, one for $Fe^{2+}$ and another for $Fe^{3+}$. It is best to treat as many couples as possible by this method. That way, redox equilibrium can be tested instead of merely assumed.

The basic input constraints (total concentrations, $pH$, etc.) are associated on a one-to-one basis with master or basis species. Basis species (see Chapters 2 and 5) represent the chemical components of the aqueous solution. They also function as basic elements for writing chemical reactions in a standardized format that is convenient for chemical modeling. The solvent, water, is a basis species, but is an exception in a speciation-solubility problem in that no input constraint is associated with it. The basis species used to write oxidation-reduction reactions in EQ3/6 is oxygen gas, which is treated as a fictive aqueous species. An input for it is required only if the problem has a redox aspect. The other basis species consist of simple species such as $Na^+$ and $Cl^−$ and a few more complex species such as $SO_4^{2−}$. A minimum basis set has one species representing each chemical element and its associated mass balance, plus one more representing oxidation-reduction and charge balance. The minimum basis is called the strict basis. EQ3NR also has an auxiliary basis, which consists of species which are related via associated chemical reactions to the strict basis species, but for which the user may choose to impose constraints other than equilibrium with the latter. Most auxiliary basis species represent a chemical element in a different oxidation state.

If desired, the concentration of a specified ion may be adjusted to satisfy electrical balance. An option to constrain the carbonate system by specifying the alkalinity has been deleted from the present version of EQ3NR. The reasons behind this action and suggestions for alternative measures are discussed in Chapter 2. It is also possible to constrain various species by certain equilibrium assumptions instead of analytical data. For example, the concentration of dissolved calcium may be constrained to satisfy equilibrium with calcite. It is also possible to constrain the concentration of a species to satisfy equilibrium with a solid solution end-member component of specified mole fraction. Similarly, the concentration of a species may be constrained to satisfy equilibrium with a gas species of specified fugacity.

EQ3NR computes the distribution of chemical species present in the model. Essentially, this involves partitioning the input total concentrations. The code thus determines the concentrations,
activity coefficients, and thermodynamic activities of all species present. This in turn permits
evaluation of the saturation indices \( SI = \log \frac{Q}{K} \), where \( Q \) is the activity product and \( K \) the equi­
librium constant) and thermodynamic affinities \( A = -2.303 \frac{RT}{\log Q/K} \), where \( R \) is the gas con­
stant and \( T \) the absolute temperature) of various reactions, chiefly for the dissolution of minerals. However, these functions are also evaluated for certain reactions occurring internally in the aque­
ous solution and which are normally only assumed to be in equilibrium (the input file requires additional data to do this). In the case of aqueous redox reactions, the theoretical \( E_h, \rho_e, \) oxygen fugacity, and redox affinity \( (\Delta h) \) are computed. Differences in the values of these corresponding parameters for two redox couples are measures of the degree of disequilibrium between them. The equilibrium fugacities of various gas species are also determined.

The results of these calculations depend on the supporting data read from the data file. The use of different data files may give different results. Different results may be obtained not only because of the use of different values of standard state thermodynamic data (e.g., equilibrium constants), but also by different choices in the set of equations for the activity coefficients as well as the use of different values in the choice of parameters appearing in these equations (e.g., the De­by-Hückel \( A_q \) parameter, various kinds of interaction coefficients). The equations for calculat­
ing the activity coefficients of aqueous species are discussed in Chapter 3. The equations for calculating the activity coefficients of end-member components of solid solution phases are dis­cussed in Chapter 4. In speciation-solubility calculations, these latter equations and their supporting data normally affect only the saturation indices calculated for solid solutions. However, they do affect the computed aqueous speciation model if one of the defining model constraints as­sumes equilibrium with a solid solution end-member component.

In some modes, such as when the concentration of a species is adjusted to satisfy electrical bal­ance or to satisfy an equilibrium constraint, the code actually computes part of what would nor­mally be analytical data. In this mode, for example, the code can be used to calculate recipes for custom \( pH \) buffers. An example of this is included in Chapter 7. Calculations using such con­straints can be somewhat dangerous, especially when used in combination. It is not hard to con­struct problems that have no physical solutions. In such cases, the code can of course compute no corresponding answers, but it does a generally good job of diagnosing the problems and in­forming the user of the nature of the problem.

In general, the code is highly flexible in that the roles of many parameters as inputs and outputs can be reversed. There are very few restrictions on the input combinations that may be defined by the code user. The main requirement is that the problem must have a realistic answer.

EQ3NR uses a highly efficient hybrid Newton-Raphson algorithm in which the activity coeffi­cients of the aqueous species are held constant in a Newton-Raphson step and re-adjusted be­tween such steps. The code features both user-controlled and automatic basis-switching, a procedure for rewriting reactions and redefining the set of basis species. These features are occa­sionally necessary to induce the iterative calculations to converge. The code creates its own starting estimates for Newton-Raphson iteration, and uses a first order algorithm in addition to possible automatic basis switching to optimize these before beginning Newton-Raphson iteration. The numerical methods used by the code are discussed in Chapter 9.
EQ3NR performs a number of tests on the model constraints to see if they make sense. It first checks the data and options read from the input file for inconsistent or incomplete combinations. It will write informative error messages and terminate any further action if it detects bad input. However, not all bad input can be detected at this stage. Further analysis takes place when the code chooses starting estimates for the master iteration variables. Finally, if Newton-Raphson iteration fails to converge, EQ3NR will analyze the results to generate crash diagnostics. Most of these will point to bad input, usually input that is bad in more subtle ways than those which would have been flagged earlier.

The code architecture is described in Chapter 10. 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, 1992). Appendix C contains a list of error messages generated by EQ3NR modules, along with related notes (see Appendix C of Wolery, 1992, for a similar list for EQLIB modules). Appendix D contains notes pertaining to known bugs and such.

EQ3NR 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, 1992).
activity coefficients, and thermodynamic activities of all species present. This in turn permits evaluation of the saturation indices \((SI = \log Q/K)\), where \(Q\) is the activity product and \(K\) the equilibrium constant) and thermodynamic affinities \((\Delta G = -2.303 RT \log Q/K)\), where \(R\) is the gas constant and \(T\) the absolute temperature) of various reactions, chiefly for the dissolution of minerals. However, these functions are also evaluated for certain reactions occurring internally in the aqueous solution and which are normally only assumed to be in equilibrium (the input file requires additional data to do this). In the case of aqueous redox reactions, the theoretical \(E_h, pe,\) oxygen fugacity, and redox affinity \((\Delta h)\) are computed. Differences in the values of these corresponding parameters for two redox couples are measures of the degree of disequilibrium between them. The equilibrium fugacities of various gas species are also determined.

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2. Speciation-Solubility Modeling of Aqueous Systems

2.1. Introduction

EQ3NR is a speciation-solubility code for aqueous systems. As such, given sufficient data on a specific aqueous system, it computes a model of the solution which consists of two principal parts: the distribution of species in the solution and a set of saturation indices (SI = \log \frac{Q}{K}) for various reactions of interest. The saturation indices are measures of the degree of disequilibrium of the corresponding reactions. They provide a means of searching for solubility controls on natural waters. For example, if a series of related fluids all have calcite SI values close to zero, it is probable that this mineral is present and partial equilibrium with it is maintained as the solutions evolve in composition.

EQ3NR is not a computerized geochemical model, but a code which is capable of evaluating geochemical models which are defined by the contents of a supporting data file (of which there are now five to choose from) and by other assumptions which the user sets on the EQ3NR input file. The supporting data files differ not only in terms of data values, but more importantly in terms of the identities of the components and chemical species represented and in terms of the general approaches to dealing with the problem of activity coefficients. Because of various limitations, some problems may require the use of only certain data files, while others can be treated using any of the available data files. The user must choose the best data file (or files) with which to run a particular problem. The user must also understand both the particular problem and the code capabilities and limitations well enough to construct an adequate input file.

Although speciation-solubility models are commonly used as a means of testing whether or not heterogeneous reactions are in a state of thermodynamic equilibrium, they often just assume that all reactions occurring in aqueous solution are in such a state. Such reactions most likely to be in disequilibrium are redox reactions or reactions for the formation or dissociation of large complexes that are more like small polymers, such as (UO₂)₃(OH)₇. Speciation-solubility models are better used when they are employed to test the degree of disequilibrium of these kinds of reactions than when they are forced to assume that such reactions are in equilibrium.

A speciation-solubility model can not by itself predict how aqueous solution composition will change in response to rock/water interactions. Nevertheless, this type of modeling can be a powerful tool for elucidating such interactions when it is applied to a family of related waters. Such a family might be a set of spring waters issuing from the same geologic formation, a sequence of ground water samples taken from along an underground flow path, or a sequence of water samples taken in the course of a rock/water interactions experiment in the laboratory. Jenne (1981) reviews several studies of this kind. Particularly interesting are Nordstrom and Jenne’s (1977) study of fluorite solubility equilibria in geothermal waters and Nordstrom, Jenne, and Ball’s (1979) study of controls on the concentration of iron in acid mine waters.

EQ3NR offers many options for the input file description of the composition of a given water. Consequently, the code can be used in a variety of ways. Many of the descriptive parameters of interest can be either model inputs or outputs. For example, the pH of a buffer solution can be calculated from the buffer recipe by adjusting the hydrogen ion concentration to satisfy charge balance. Alternatively, adjusting the concentration of a buffer component to satisfy the charge
balance is a means of computing the complete recipe for a buffer having a desired pH. Some of
the possible model inputs are assumptions, as of equilibrium with specified minerals. The use
of some types of model inputs also pose special problems, some of which occur in particular con­
texts. The worst of these pertain to Eh, alkalinity, and pH and will be discussed in some detail
later in this chapter.

2.2. Units of Concentration

EQ3NR uses the molal scale as the principal unit of concentration for aqueous species. The molal
concentration (molality) of a substance dissolved in water is defined as:

\[
m_i = \frac{n_i}{w_w}
\]

where \(n_i\) is the number of moles of the \(i\)-th solute species and \(w_w\) is the number of kilograms of
solvent water. Other common measures of aqueous solute concentration are the molarity (moles
of substance per liter of aqueous solution), the part-per-million or ppm by volume (mg/L, milli­
grams of substance per liter of solution), and the ppm by weight (mg/kg, milligrams of substance
per kilogram of solution). The EQ3NR code accepts concentration parameters in any of these
units (see Chapter 4), but converts non-molal concentrations to molalities before computing the
aqueous speciation model. Whether or not it does this correctly depends on circumstance and
data provided by the user.

The conversion equations in all three cases require a value for the total dissolved salts in mg/kg
solution (\(C_{TS, mg/kg}\)). The density of the aqueous solution in g/ml (\(\rho_{g/ml}\)) is also required to con­
vert molarities and mg/L concentrations to molalities. The total dissolved salts in mg/kg may be
calculated from the total dissolved salts in mg/L (\(C_{TS, mg/L}\)) and the density according to:

\[
C_{TS, mg/kg} = \frac{C_{TS, mg/L}}{\rho_{g/ml}}
\]

EQ3NR expects values of \(C_{TS, mg/kg}\) and \(\rho_{g/ml}\) on the input file if such conversions are necessary
(see Chapter 4). In place of \(C_{TS, mg/kg}\), one may enter \(C_{TS, mg/L}\) and \(\rho_{g/ml}\) and \(C_{TS, mg/kg}\) is cal­
culated from the above equation. If such values are not provided, \(C_{TS, mg/kg}\) is assigned a default
value of zero and \(\rho_{g/ml}\) is assigned a default value of unity. These values are generally adequate
for dilute solutions at temperatures near 25°C. In the case of brines, these values are not adequate,
and the user must provide actual values as part of the input in order to obtain accurate conversion.
The code provides no checks or warnings if these are not provided.

The weight fraction of solvent water is given by:

\[
N_w = \frac{1,000,000 - C_{TS, mg/kg}}{1,000,000}
\]

Letting \(C_{i, molar}\) be the molar concentration of the \(i\)-th solute species, the molality is given by
Letting $C_i, \text{mg/L}$ be the concentration in mg/L, the conversion is:

$$m_i = \frac{0.001 C_i, \text{mg/L}}{\rho_{g/ml} M_w N_w}$$

(4)

where $M_w$ is the molecular weight of the solvent, water ($M_w \approx 18.015$ g/mole). Letting $C_i, \text{mg/kg}$ be the concentration in mg/kg solution, the conversion is:

$$m_i = \frac{0.001 C_i, \text{mg/L}}{M_w N_w}$$

(5)

Some dissolved gas analyses are reported in units of ml (STP)/ml solution, where STP refers to standard temperature and pressure (0°C and 1 atm). The conversion equation is:

$$m_i = \frac{1000 C_i, \text{ml(STP)/ml}}{V_g M_w N_w}$$

(7)

where $V_g$ is the molar volume of an ideal gas at STP ($V_g = 22.413.6$ ml/mole).

The concentration of solvent water is defined as its mole fraction:

$$x_w = \frac{n_w}{n_w + \sum n_i}$$

(8)

where $n_w$ is the number of moles of water. The molality of the $i$-th solute species can also be written as:

$$m_i = \frac{\Omega n_i}{n_w}$$

(9)

where $\Omega$ is the number of moles of water comprising a mass of 1 kg ($\Omega \approx 55.51; \Omega w_w = n_w$).

Substituting this relation into the one above it gives:

$$x_w = \frac{\Omega}{\Omega + \sum m_i}$$

(10)

EQ3NR uses this relation to calculate the mole fraction of water. This is done in a self-consistent manner in the iteration process. Thus, the user is not required to input a value.
A similar self-consistent treatment could be implemented to handle both \( C_{73} \), \( \text{mg/kg} \) and the solution density. However, no such treatment exists in the current version of EQ3NR, nor any other such modeling code known to the present writers. Implementation of a self-consistent treatment of the solution density would require the addition of models for partial molar volumes to the code and incorporation of the corresponding equations in the iteration process. The theoretical and practical aspects of partial molar volumes in solutions extending to high concentration have been addressed, for example, by Millero (1977), Helgeson, Kirkham, and Flowers (1981), Kumar (1986), Connaughton, Millero, and Pitzer (1989), and Monnin (1989).

2.3. Input Constraints, Governing Equations, and Outputs

2.3.1. Overview

Aqueous speciation models can be constructed to satisfy a wide variety of combinations of possible input constraints and governing equations. The input constraints may include total (analytical) concentrations, an electrical balance requirement, free concentrations, activities, \( pH \), \( Eh \), \( pe \), oxygen fugacity, phase equilibrium requirements, homogeneous equilibria, and run-specific values for equilibrium constants. The governing equations are the corresponding mathematical expressions, such as the mass balance equation and the charge balance equation.

The choice of governing equations in large part depends on which parameters are to be inputs to the model and which are to be outputs. This, in turn, is a function of what data on a given water are available, what form they are in, and what assumptions the modeler would like to use.

Chemical analysis provides mainly a set of values for the so-called total concentrations of dissolved components. The analytical value for an ion such as calcium is an example. It does not discriminate between the various calcium species in solution, but rather estimates the dissolved calcium contributed by all of them. This leads to a mass balance equation of the form:

\[
m_{T, Ca^{2+}} = m_{Ca^{2+}} + m_{CaOH_{(aq)}} + m_{CaCO_{3(aq)}} + m_{CaHCO_{3(aq)}} + \ldots
\]

where \( m_{T, Ca^{2+}} \) is the total or analytical concentration (on the molal scale) and \( m_i \) is the molality of any individual chemical species contributing to the mass balance. The summations must be weighted by the appropriate stoichiometric equivalences; e.g., in the case of \( F^- \), one has:

\[
m_{T, F^-} = m_{F^-} + m_{HF_{(aq)}} + 2m_{H_2F_2(aq)} + 2m_{HF_2} + 3m_{AlF_3(aq)} + \ldots
\]

The total concentration is the most common type of input parameter to an aqueous speciation model. The mass balance constraint, which corresponds to it, is therefore the most common governing equation. As we shall see, there are situations in which a total concentration is replaced by another type of input. In these cases, the mass balance constraint is replaced by a different governing equation, and the total concentration becomes something to be calculated (an output parameter).

From a purely mathematical point of view, there is no reason to discriminate among ion pairs (and ion-triplets, etc.) and complexes. For some investigators, the term "ion pair" implies a spe-
cies in which an anion is separated from a cation by an unbroken hydration sheath about the latter, whereas the term “complex” implies direct contact and perhaps some degree of covalent bonding. Other investigators use these terms interchangeably. It is a general assumption in cases of geochemical interest that the concentrations of ion-pairs and complexes are governed by thermodynamic equilibrium.

Each case of this equilibrium can be represented by a mass-action equation for the dissociation of the ion-pair or complex. An example will illustrate this. The calcium sulfate ion-pair dissociates according to the reaction:

$$CaSO_4(aq) = Ca^{2+} + SO_4^{2-}$$  \hspace{1cm} (13)

where “=” is used as the sign for a reversible chemical reaction. The corresponding mass action equation is:

$$K_{CaSO_4(aq)} = \frac{a_{Ca^{2+}} a_{SO_4^{2-}}}{a_{CaSO_4(aq)}}$$  \hspace{1cm} (14)

where $K$ is the equilibrium constant and $a_i$ represents the thermodynamic activity of each species. This may also be written in logarithmic form:

$$log K_{CaSO_4(aq)} = log a_{Ca^{2+}} + log a_{SO_4^{2-}} - log a_{CaSO_4(aq)}$$  \hspace{1cm} (15)

The thermodynamic activity is related to the molal concentration by the relation:

$$a_i = m_i \gamma_i$$  \hspace{1cm} (16)

where $\gamma_i$ is the activity coefficient, a function of the composition of the aqueous solution. As the solution approaches infinite dilution, the value of $\gamma_i$ for each species approaches unity. The set of equations for computing the activity coefficients of aqueous species is chosen by the user on the EQ3NR input file (by means of the iopgl option switch). The requisite supporting data are on the EQ3/6 data file. The various formulations presently treated by EQ3/6 are discussed in Chapter 3.

The following subsections discuss the formulation of aqueous speciation problems in general terms. The rigorous mathematical development is presented in Chapter 9. How to implement these models in EQ3NR is the subject of Chapter 6, and examples are presented in Chapter 7.

2.3.2. Reference Formulation of the Aqueous Speciation Problem

In general terms, setting up an aqueous speciation model involves choosing $n$ unknowns and $n$ governing equations. The EQ3NR code offers a very wide range of options in this regard. In order to make sense of the different ways of setting up a model, we define a reference formulation for the aqueous speciation problem. This reference formulation serves as a springboard for discussing what goes into speciation models, what comes out, and what the options are. It is also used to compare how the aqueous speciation problem is formulated in EQ3NR (and other speciation-solubility codes in general) with how it is formulated in a reaction-path code like EQ6.
In the reference formulation, we assume that the activity coefficients are known parameters (the numerical treatment of these is discussed in Chapter 9). Note that the molal concentration of the solvent is fixed as the number of moles of water in a one kilogram mass of the pure substance.

We assume that there are \( \varepsilon_T \) chemical elements in the model. In order to further simplify the reference formulation, we assume that each element is present in only one oxidation state. Suppose that chemical analysis has given us \( \varepsilon_T - 2 \) total concentration values, each for a chemical species, each of which corresponds to a chemical element other than oxygen and hydrogen (e.g., \( Na^+ \) for \( Na \), \( SO_4^{2-} \) for \( S \)). That gives \( \varepsilon_T - 2 \) mass balance equations as governing equations.

The charge balance equation plays the role that might have been played by a mass balance equation for hydrogen. The charge balance equation may be written in the general form:

\[
\sum_{s=1}^{s_T} z_s m_s = 0
\]

where the summation is over all aqueous species, \( z_s \) is the electrical charge of a species, and \( m_s \) is its molal concentration. The hydrogen mass balance equation cannot be used as a governing equation to calculate the \( pH \) from the corresponding analytical data. This is due to the impracticability if not impossibility of ever measuring the total concentration of hydrogen with sufficient accuracy when nearly all of it is contributed by the solvent. As a practical matter, even the charge balance equation can be used for this purpose only in limited circumstances.

One may associate the solvent, water, with a mass balance for oxygen. However, the mass of water in a speciation-solubility calculation is fixed at 1 kg, and the concentration of water is entirely determined by the concentrations of the other components in the solution. Therefore, no such mass balance is required.

To sum up, the reference formulation consists of \( \varepsilon_T - 2 \) mass balance equations/total concentrations (one pair for every element except oxygen and hydrogen) and the charge balance equation (to calculate \( pH \)). Each element is present in only one oxidation state. Activity coefficients are treated as known parameters.

Before proceeding, we contrast this framework (common to speciation-solubility codes in general) with that employed in the EQ6 code. In the corresponding problem in that code, we would be given \( \varepsilon_T \) masses, in moles, and the same number of mass balance equations, this time written in terms of masses instead of concentrations. There we have a mass balance equation for oxygen, and we must calculate the mass of the solvent, water. In the case where each element appears in only one oxidation state, as we have temporarily assumed here, the charge balance equation is a linear combination of the mass balance equations, and the governing equation associated with \( H^+ \) can be either a hydrogen mass balance equation or the charge balance equation. The speciation-solubility problem has one fewer unknown, hence one less governing equation, than the corresponding EQ6 problem.
In either the EQ3NR or EQ6 type formulation of the problem, we may formally associate one aqueous species with each balance equation; e.g., \( Na^+ \) with sodium balance, \( Al^{3+} \) with aluminum balance, and \( H^+ \) with charge balance. Suppose our model must consider \( n \) balance equations and \( k \) aqueous complexes (using the term to include ion-pairs). That gives \( k \) mass action relationships which are also governing equations. We now have \( n + k \) equations in \( n + k \) unknowns (the masses/concentrations/activities of the \( n + k \) aqueous species).

The number of aqueous complexes is usually much greater than the number of balance equations. This is especially true when the number of balance equations becomes very large. A useful approach is to reduce the number of equations and unknowns by substituting the aqueous mass action equations into the balance equations (see Chapter 9). This leaves us with \( n \) equations (modified balance equations) in \( n \) unknowns (the concentrations or activities of the aqueous species that were chosen to formally correspond to the balance relationships).

This approach leads us to the concept of dealing with a set of master aqueous species. These may also be termed basis species. However, the concept does not arise purely from an attempt to reduce the number of iteration variables. The \( k \) aqueous complexes give us \( k \) linearly independent dissociation reactions and \( k \) linearly independent logarithmic mass action equations. An efficient way to write these reactions and equations is in terms of the associated complex (the species that dissociates) and such a set of master aqueous species. The dissociation reactions are then written as overall dissociation reactions but never as stepwise reactions; e.g., one has:

\[
HgCl_3 = Hg^{2+} + 3Cl^-
\]

not:

\[
HgCl_3 = HgCl_2^0 + Cl^-
\]

We will also use this format to write dissolution reactions for minerals and gases and their associated heterogeneous mass action equations.

### 2.3.3. Alternative Constraints

The reference formulation of the aqueous speciation problem consists of:

1. 2 mass balance equations/total concentrations.
2. The charge balance equation (to calculate \( pH \)).

We now discuss alternative constraints to the balance equations in the reference formulation. We discuss how to put oxidation-reduction problems into the formulation in the following subsection.

The alternative constraints are:

- Specifying log activity for a species (recall \( pH = -\log a_{H^+} \)).
• Log activity combination functions (e.g., $pHCl$; Section 2.3.4).

• Log mean activity of an ion and one of opposite charge (Section 2.3.4).

• Applying the charge balance constraint to a master species other than $H^+$. 

• Phase equilibrium with a pure mineral.

• Phase equilibrium with an end member of a solid solution (the composition of the solid solution must be specified).

• Phase equilibrium with a gas (the fugacity of the gas must be specified).

• Equilibrium with other aqueous species, without falling under a mass balance constraint.

• Specifying the individual concentration of an aqueous basis species.

When a mass balance constraint is replaced by one of the above, we continue to reduce the number of unknowns to a master set as discussed above. The corresponding total concentrations become parameters to be calculated. We can calculate, for example, the total mass/concentration of hydrogen. This can be done with sufficient relative accuracy to permit the EQ6 code to use it as a constraint to solve for $pH$.

The log activity constraint. The first substitution that we discuss is most often applied to the hydrogen ion. In the course of chemical analysis, the $pH$ of an aqueous solution is usually determined by means of a specific-ion electrode. This gives us the activity of the hydrogen ion from the relation:

$$pH = -\log a_{H^+}.$$  \hspace{1cm} (20)

The activities of many other species, including $Na^+$, $Ca^{2+}$, $S^{2-}$, $F^-$, and $Cl^-$, to name but a few, may also be measured by specific-ion electrodes.

EQ3NR will accept as an input the logarithm of the activity of a species. Note that this means that the code expects to see $-pH$, not $pH$, on the input file when this option is invoked. The new governing equation is just:

$$m_i = \frac{a_i}{\gamma_i}.$$  \hspace{1cm} (21)

The charge balance constraint. This can be applied to one of the major ions if a charge-balanced speciation model is desired. If EQ3NR does not use the charge balance equation as a constraint, it will calculate the charge imbalance. Otherwise, it will notify the user of the change in total concentration or $pH$ that was required to generate a charge-balanced model.

We recommend routinely calculating $pH$ from electrical balance only in cases of synthetic solutions for which the ionic totals are exact with respect to charge balance. Such solutions are most likely to be $pH$ buffer solutions. In other circumstances, this practice is potentially dangerous be-
cause the result is affected by the error in every analytical value that is put in the model and also by every analytical value that should have been put in the model but was not. In general, apart from the case of pH buffer solutions, it is only safe to calculate pH this way if the pH is low (high concentrations of $H^+$) or high (high concentrations of $OH^-$).

**Equilibrium constraint involving a non-aqueous species.** A mass balance constraint may also be replaced by an equilibrium constraint involving a specified pure mineral, solid solution component species, or gas species. Suppose we wanted to know what concentration of dissolved calcium would be required for a water to be in equilibrium with calcite (the stable polymorph of $CaCO_3(c)$ at 25°C). The dissolution reaction may be written as:

\[
\text{Calcite} + H^+ = Ca^{2+} + HCO_3^-
\]  

(22)

and the corresponding governing equation is then:

\[
K_{\text{Calcite}} = \frac{a_{Ca^{2+}} a_{HCO_3^-}}{a_{Calcite} a_{H^+}}
\]  

(23)

Because calcite is a pure phase, its activity is fixed at unity.

If the required equilibrium involves an end-member component of a solid solution, the governing equation is slightly modified. Suppose we choose equilibrium with a calcite end-member of a high-magnesium calcite ($Ca.Mg)CO_3(c)$. The governing equation has the same form as above, but the activity of the calcite end-member is no longer unity. Instead, one has:

\[
a_{Calcite} = \lambda_{Calcite} x_{Calcite}
\]  

(24)

where $\lambda_{Calcite}$ is the activity coefficient and $x_{Calcite}$ is the mole fraction of the calcite component. The mole fraction of the $\sigma$-th component of the $\psi$-th solid solution is given by:

\[
x_{\sigma\psi} = \frac{n_{\sigma\psi}}{\sigma_{\psi}} \frac{1}{\sum_{\sigma'} n_{\sigma'\psi}}
\]  

(25)

where $n_{\sigma\psi}$ is the number of moles of the $\sigma$-th component and $\sigma_{\psi}$ is the number of such components. The current version of EQ3NR deals only with solid solutions that are composed of end-member components. The activity coefficients ($\lambda_{\sigma\psi}$) may be computed from a variety of equations. The activity coefficient model for a given solid solution is specified on the EQ3/6 data file, which also contains the requisite supporting parameters. The formulations presently treated in EQ3/6 are discussed in Chapter 4.

Suppose we would like to know how much dissolved carbonate would be in solution if it were in equilibrium with $CO_2(g)$. The $CO_2(g)$ dissolution reaction may be written as:
\[ CO_2(g) + H_2O(l) = H^+ + HCO^3_3 \]  

(26)

The corresponding governing equation is:

\[ K_{CO_2} = \frac{a_{H^+} a_{HCO^3_3}}{f_{CO_2} a_w} \]  

(27)

Here \( f_{CO_2} \) is the fugacity of \( CO_2 \). In order to use this option, the user must provide an input value for it to the speciation model.

Fugacity is a thermodynamic variable for gases that is akin to partial pressure in the same way the thermodynamic activity of an aqueous species is akin to the molal concentration. The formal relationship is given by:

\[ f_g = \chi_g p_g \]  

(28)

where \( p_g \) is the partial pressure and \( \chi_g \) is the fugacity coefficient of the \( g \)-th gas. The fugacity coefficient is analogous to the activity coefficient. At low pressures, it approaches unity and hence the fugacity approaches the partial pressure.

Specifying heterogeneous equilibria as inputs to an aqueous speciation model can be a bit dangerous. First, the user must choose which phases, stable or metastable, are controlling solubility equilibria. If a choice is an extremely poor one, the equilibrium concentration of a species so constrained may be very large. Furthermore, the expressions for the logarithm of the ion activity products for all such relations must be a linearly independent set in the corresponding aqueous species. (A corollary to this is that one may not constrain more than one species by the same heterogeneous equilibrium.) Such linear dependence violates the “apparent” or “mineralologic” phase rule (Wolery, 1979). This is slightly more restrictive than the phase rule of thermodynamics. Sets of equilibria that satisfy the phase rule, but only because the temperature and pressure happen to fall on a univariant curve, do not satisfy the apparent phase rule.

Equilibrium constraint involving an aqueous species. It is possible to specify equilibrium with other species in a manner in which the species so constrained does not fall under any mass balance constraints. As an example, one might treat dissolved sulfide (represented by \( HS^- \)) in this manner, computing it on the basis of equilibrium with sulfate and oxygen gas. The reaction relating sulfide to sulfate is:

\[ HS^- + 2O_2(g) = H^+ + SO_4^{2-} \]  

(29)

The governing equation is the corresponding mass action equation:

\[ K_{HS^-} = \frac{a_{H^+} a_{SO_4^{2-}}}{a_{HS^-} f_{O_2}} \]  

(30)
The sulfide component ($HS^-$ and related species such as $H_2S_{(aq)}$) does not count in the mass balance defined for sulfate. This option is similar to those involving specifying various heterogenous equilibria.

**Direct specification of individual molality.** EQ3NR allows input of the individual concentrations of master species. The governing equation in this case is just the identity:

$$m_i = \text{constant}$$ (31)

It is largely appropriate only for master species that form no complexes, such as $O_2(aq)$ and other dissolved gases.

2.3.4. pH in Brines: pHCl and Related Functions as Alternative Constraints

Using standard methods (e.g., Bates, 1964), the $pH$ is measured using an ion-specific electrode for the hydrogen ion in combination with a standard reference electrode (usually silver-silver chloride). The electrode pair (commonly marketed as a combination electrode) is calibrated when used by immersion in at least two standard solutions whose $pH$ values bracket the expected sample values. This method is appropriate in dilute solutions, but not in brines. The problem is the presence of a liquid junction potential in the reference electrode at the interface between the standard or sample solution and an internal solution composed of concentrated potassium chloride. The idea behind the standard measurement is that for sufficiently dilute sample or standard solutions, the liquid junction potential will remain at an essentially constant value (which can be factored out in the calibration process). As proposed by Bates (1964), the method should be restricted to solutions of ionic strength no greater than 0.1 molal. However, it is routinely applied to more concentrated solutions, such as seawater (for which the ionic strength is nearly 0.7 molal).

The standard method fails when applied to brines because the liquid junction potential obtained with the sample is significantly changed from that obtained with the relatively dilute calibration buffers. The theory describing liquid junction potentials has been reviewed by Baes and Mesmer (1976). In general, the dependence of the liquid junction potential on the sample solution composition is complex and cannot be solely related to the ionic strength. Thus, one cannot simply make $pH$ measurements in the usual way using concentrated calibration standards whose ionic strengths match those of the samples. Furthermore, the theory consists of an ideal and a non-ideal part. Taking only the ideal part and making some approximations leads to the Henderson equation. This has occasionally been put forth as a means of correcting $pH$ values in concentrated solutions obtained by going through the mechanics of the standard method. This approach is highly dubious.

Recently Knauss, Wolery, and Jackson (1990, 1991) have proposed a method to quantify $pH$ in concentrated solutions which avoids the liquid junction potential problem by eliminating the standard reference electrode. In this method, this electrode is replaced by another specific ion electrode. If this is a chloride electrode, what one measures is $pHCl$, which is the sum of $pH$ and $pCl$. As an input to a speciation-solubility code, this is just as adequate as the $pH$ as long as there is a separate measurement of dissolved chloride to also input. This maintains a system of $n$ equations in $n$ unknowns. The code is able to separate $pH$ from $pCl$ using an activity coefficient model.
for the dissolved species and a chosen pH scale. The subject of aqueous species activity coefficients and pH scales is addressed in Chapter 3.

Knauss, Wolery, and Jackson (1990) used EQ3NR to compute the pHCl and related functions corresponding to different combinations of specific-ion electrodes of various test solutions, such as 0.01 molal HCl with varying concentrations of NaCl. Pitzer's equations were used to compute the activity coefficients in these solutions, using mostly the model of Harvie, Möller, and Weare (1984) and sometimes an alternative data set given by Pitzer (1979). They then measured the corresponding electrical potentials and plotted them against the computed pHCl or other function. In most cases, excellent Nernstian responses were obtained, in essence identical to those one would obtain examining the standard pH method. This indicated that such solutions could be defined as calibration buffers. Of critical importance to constraining the pH in concentrated solutions was the fact that no interference due to sodium was found in the case of the hydrogen ion electrode, even in solutions with very low hydrogen ion concentration and very high sodium ion concentration.

The only observed failures of the method involved cases in which a specific-ion electrode responded to an ion other than the one to which it was supposed to respond. The chloride electrode was found to respond to bromide, for example. In solutions containing both bromide and chloride, however, pHBr could be measured without interference by using a bromide electrode. Interferences of this type were no surprise and are in fact well known from the use of the specific ion electrodes in dilute solutions, where they are paired with a standard reference electrode.

The method appears to work, but should receive more study. There are no official recommendations or standards concerning this method, such as those which the National Institute of Standards and Technology (formerly the National Bureau of Standards) has promulgated in the case of the standard pH measurement technique. One must currently make up one's own calibration buffers, which ideally should closely resemble the samples. The method has been criticized by Mesmer (1991), who prefers not to obtain pH by a method which requires the use of a model for the activity coefficients in the solution. He proposes alternative approaches which involve measuring the concentration of the hydrogen ion. These in turn are criticized by Knauss, Wolery, and Jackson (1991).

Values of pHCl and related functions such as pHBr and pH/Na (= pH - pNa) can now be input to EQ3NR as alternative constraints. In the case of pHCl, the governing equation takes the form:

\[ \log m_{H^+} = -pHCl - \log \gamma_{H^+} - \log m_{Cl^-} - \log \gamma_{Cl^-} \]  

EQ3NR expects to receive input of this type in one of two general forms. The first is the activity combination parameter defined by:

\[ \xi_{ij} = \frac{|z_i z_j|}{|z_j|} \log a_i - \frac{|z_i z_j|}{|z_j|} \log a_j \]
This is valid for \( i \) and \( j \) of any charge combination. Note that \( \mathbf{H}^{+}, \mathbf{Cl^{-}} = -\text{pHCl} \), so it is actually 
\(-\text{pHCl}\) that is input to the code, not \( \text{pHCl} \) (analogous to the input of 
\(-\text{pH}\) instead of \( \text{pH} \)). The more general form of the governing equation is then:

\[
\log m_i = -\frac{\mathbf{H}^{+}}{z_i} \log \gamma_i + \frac{z_i}{z_j} \log m_j + \frac{z_i}{z_j} \log \gamma_j
\]  
(34)

The second general form is to input the mean log activity of the electrolyte composed of ions \( i \) and \( j \):

\[
\log a_{i,j} = \frac{|z_i| \log a_i + |z_j| \log a_j}{|z_i| + |z_j|}
\]  
(35)

This is not quite as general, because the two ions must have opposite signs of electrical charge. Note that \( \log a_{+, \text{HCl}} = -1/2 \text{pHCl} \). The corresponding governing equation is:

\[
\log m_i = \frac{|z_i| + |z_j|}{|z_j|} \log a_{i,j} - \log \gamma_i - \frac{z_i}{z_j} \log m_j - \frac{z_i}{z_j} \log \gamma_j
\]  
(36)

2.3.5. The Carbonate System: Dealing with Alkalinity

To model the carbonate system, EQ3NR expects as normal input an analytical value for total dissolved bicarbonate \((\text{CO}_2^{(aq)} + \text{HCO}_3^- + \text{CO}_3^{2-})\), where these are taken in the sense of components, including any ion pairs or complexes of the corresponding species). The appropriate measurement can be made using ion chromatography or infrared detection of carbon dioxide released from an acidified sample. The results might be expressed on a data sheet as total dissolved CO\(_2\) in mg/L. This must be converted to the equivalent concentration of \(\text{HCO}_3^-\) for input to EQ3NR, as it is defined on the supporting data files as the basis species corresponding to carbonate mass balance. This can be done by multiplying this quantity by the ratio of the molecular weight of \(\text{HCO}_3^-\) (61.016 g/mole) to that of \(\text{CO}_2^{(aq)}\) (44.009 g/mole) (the value of this ratio being 1.3864).

A data sheet might also list a value for “total free \(\text{CO}_2\)” This represents only the \(\text{CO}_2^{(aq)}\) component. If this is the only available measure of dissolved bicarbonate, the total dissolved bicarbonate can be computed from this and the \(\text{pH}\) by inverting the relevant equations given later in this section.

Carbonate (in the form of \(\text{CO}_3^{2-}\) and \(\text{HCO}_3^-\), including any ion pairs of these species) makes up nearly all of the alkalinity of many aqueous solutions. Strictly speaking, the alkalinity is a measure of the acid neutralizing capability of an aqueous solution. However, it is also commonly used as a measure of the carbonate system. In fact, alkalinity is only an indirect measure of this system, and its usage as such a measure entails a number of assumptions which are not always valid. In this context, it is also frequently misunderstood and misused. The worst consequence of this usage of alkalinity is that it leads people to think that a direct measurement of total dissolved bicarbonate (in the sense discussed in the above paragraph) is unnecessary. Indeed, it is common to find analytical data sheets on groundwater chemistry which lack such direct measurements.
The purpose of this section is to discuss these problems, and to suggest means by which the total dissolved bicarbonate (in the desired sense) can be estimated, in the case in which direct measurements are lacking. These means are not always entirely satisfactory, and are here suggested mainly for the benefit of those who must work with historical data.

EQ3NR formerly allowed titration alkalinity \( A_t \) to be input for bicarbonate instead of total concentration. This capability essentially matched that used in the PHREEQE code (Plummer, Parkhurst, and Thorstenson, 1980). The approach is to define an alkalinity balance equation, which is very similar to a mass balance equation. It may be written in the general form:

\[
A_t = \sum_{s=1}^{S_T} \tau_s m_s
\]  

where \( \tau_s \) is the alkalinity factor of the \( s \)-th species. This is the number of moles of hydrogen ion neutralized by one mole of species in the process of titrating the solution with an acid solution (usually of dilute sulfuric acid) to some end-point, usually in the range of \( \text{pH} \) 4.0 to 4.5 (See Standard Methods, 1976, p. 278-293; see also Plummer, Parkhurst, and Thorstenson, 1980, p. 17-18). Titration alkalinity defined in this manner is in units of equivalents per kilogram of solvent water, where “equivalent” means hydrogen ion neutralizing equivalent.

Titration alkalinity is usually not reported in these units, however. Standard Methods calls for reporting the titration alkalinity in terms of the stoichiometric equivalent of mg/L of \( \text{CaCO}_3 \). We will mark alkalinitities in such units with an asterisk (*). Thus, the form of titration alkalinity usually reported must be converted according to:

\[
A_t = \frac{A_t^*}{50,000 \rho_{g/ml}}
\]

The “50,000” in the above equation is actually the product of 1000 mg/g and the molecular weight of calcium carbonate (taken as 100 g/mole following Standard Methods), divided by the alkalinity factor of \( \text{CaCO}_3 \) (2.0 equivalents/mole). The molecular weight of \( \text{CaCO}_3 \) is more accurately 100.088 g/mole, but the 100 g/mole value is used by Standard Methods in the formula for calculating \( A_t^* \) from the titration data, so retaining it as above is actually more consistent with the titration measurement.

The titration alkalinity \( (A_t^*) \) is referred to in Standard Methods as \( T \). This quantity may appear on analytical data sheets as “T” or “titration alkalinity” and in units marked “mg/L” or “mg/L \( \text{CaCO}_3 \).” In this context, “mg/L” means “mg/L \( \text{CaCO}_3 \).” Users of geochemical modeling codes sometimes mistakenly interpret “mg/L” to mean that the titration alkalinity is given in units of mg/L \( \text{HCO}_3^- \) \( (A_t, \text{HCO}_3^-) \). It is not unknown for analysts to report the titration alkalinity in such units as well, though this is not a standard practice. It can be obtained by multiplying \( A_t^* \) by the
The molecular weight of $HCO_3^-$ (61.016 g/mole) and the alkalinity factor of $CaCO_3$ (2.0 equivalents/mole) and dividing the result by the product of the molecular weight of $CaCO_3$ and the alkalinity factor of $HCO_3^-$ (1.0 equivalents/mole). In simpler terms, one has:

$$A_{t,HCO_3} = 1.2192 \cdot A_t$$ (39)

It is very important to note that the titration alkalinity expressed in mg/L $HCO_3^-$ is not equal to the total dissolved bicarbonate (in the sense required for input to EQ3NR) expressed in the same units. Recall that $CO_2(aq)$ does not contribute to the titration alkalinity, while it does contribute to the desired total dissolved bicarbonate. Furthermore, $CO_3^{2-}$ contributes differently to the titration alkalinity (by a factor of 2) than it does to the desired total dissolved bicarbonate.

In the determination of alkalinity, Standard Methods calls for two end points to be determined in the titration. One of these gives $T$, the titration alkalinity, the other $P$, the phenolphthalein alkalinity. The latter corresponds to an end point of pH 8.3. If the pH of the sample solution is already less than or equal to this, then $P = 0$. The phenolphthalein alkalinity may also appear on an analytical data sheet. Standard Methods calls for using $P$ to partition the titration alkalinity into components due to bicarbonate, carbonate, and hydroxide; thus, one may write:

$$A_t^* = A_{HCO_3}^* + A_{CO_3}^* + A_{OH}^*$$ (40)

This scheme implicitly assumes that no other components are present which contribute to the alkalinity. It also ignores ion pairing and complexing as it pertains to these species. Note that each of these component alkalinities is reported in units of equivalent mg/L $CaCO_3$.

These three components, bicarbonate alkalinity, carbonate alkalinity, and hydroxide alkalinity, are determined from $T$ and $P$ according to the partitioning formula given in Standard Methods (1976, Table 403:1, p. 281). At least one of these three always has a value of zero. Sometimes two are zero. They are supposed to be reported in units of mg/L $CaCO_3$. They are commonly found on analytical data sheets. Since they in essence determine the titration alkalinity, this quantity is sometimes omitted, and if it is desired, it must be computed from then using the above equation.

It is not unknown for analysts to report the bicarbonate alkalinity in units of mg/L $HCO_3^-$. Users have been known to confuse the bicarbonate alkalinity expressed in such units with the total dissolved bicarbonate (the desired input to EQ3NR), which may be expressed in the same units.

The concentration of the bicarbonate component can be computed from the bicarbonate alkalinity:

$$C_{HCO_3^-, mg/L} = 1.2192 \cdot A_{HCO_3}^*$$ (41)

The numerical factor on the right hand side is the same as that appearing in eq (39). The molality of the bicarbonate component can be computed directly from the bicarbonate alkalinity:
The denominator on the right hand side is the product of 1000 mg/g, the molecular weight of $CaCO_3$, and the alkalinity factor of $HCO_3^-$, divided by the alkalinity factor of $CaCO_3$. The molecular weight of $HCO_3^-$ is factored out in the derivation of this equation.

The concentration of the carbonate component can be similarly computed from the carbonate alkalinity:

$$C_{CO_3^{2-}, mg/L} = 0.5996 A_{CO_3^{2-}}^*$$

The numerical factor on the right hand side is the product of the molecular weight of $CO_3^{2-}$ (60.008 g/mole) and the alkalinity factor of $CaCO_3$, divided by the product of the molecular weight of $CaCO_3$ and the alkalinity factor of $CO_3^{2-}$ (also 2.0 equivalent/mole, so the alkalinity factors cancel out). The molality of the carbonate component can be computed directly from the carbonate alkalinity:

$$m_{CO_3^2} = \frac{A_{CO_3^2}^*}{100,088}$$

It is not unknown for analysts to report the total concentration of bicarbonate as:

$$C_{total} = \frac{AC_{HCO_3^2}}{50,044} = C_{HCO_3^2, mg/L} + 1.0168 C_{CO_3^{2-}, mg/L}$$

where the concentrations on the right hand side are obtained from alkalinities as above and the factor 1.0168 is the ratio of the molecular weight of $HCO_3^-$ to that of $CO_3^{2-}$ and is used to convert the units of carbonate concentration from mg/L $CO_3^{2-}$ to the equivalent mg/L $HCO_3^-$. In terms of molalities, this is equivalent to taking:

$$m_{total} = m_{HCO_3^2} + m_{CO_3^2}$$

This measure of total bicarbonate, whether reported in mg/L or molality, is not the measure of total bicarbonate which is to be input to EQ3NR, because it does not include the contribution from the component $CO_2(aq)$.

Above pH 8.3, the contribution of $CO_2(aq)$ to total bicarbonate is negligible (1% or less), and estimates based on the above formulations may be input to EQ3NR with negligible error. At lower pH values, the concentration of $CC_{2(aq)}$ can be estimated from the bicarbonate alkalinity and the pH. Standard Methods (1976, Figure 407-4, p. 297) gives a nomograph for this purpose. The nomograph also takes into account the dependency on the temperature and the ionic strength, using
the quantity "total filterable residue" as a proxy for the latter. If this procedure is followed, the total dissolved bicarbonate to be input to EQ3NR can be estimated as:

\[ C_{T, \text{mg/L, } HCO_3^-} = 1.3864 C_{\text{mg/L, } CO_2(aq)} + C_{\text{mg/L, } HCO_3^-} + 1.0168 C_{\text{mg/L, } CO_3^{2-}} \]  

(47)

where the factor 1.3864 is the ratio of the molecular weight of \textit{HCO}_3^- to that of \textit{CO}_2(aq) (44.009 g/mole). In terms of molalities, this is equivalent to:

\[ m_{T, \text{HCO}_3^-} = m_{\text{CO}_2(aq)} + m_{\text{HCO}_3^-} + m_{\text{CO}_3^{2-}} \]  

(48)

As an alternative to the nomograph of Standard Methods, we note that the molality of \textit{CO}_2(aq) may be estimated from the molality of \textit{HCO}_3^- and the pH by considering equilibrium for the reaction:

\[ \text{CO}_2(aq) + H_2O(l) = H^+ + \text{HCO}_3^- \]  

(49)

Assuming that the activity of water differs negligibly from a value of unity, the following equation is obtained:

\[ m_{\text{CO}_2(aq)} = 10^{\left(-\log K_{\text{CO}_2} + \log \gamma_{\text{HCO}_3^-} - \log \gamma_{\text{CO}_2} - \text{pH}\right)} m_{\text{HCO}_3^-} \]  

(50)

The \textit{log K} for reaction (49) has values of -6.5804, -6.3447, and -6.2684 at 0, 25, and 60°C (data taken from the \texttt{data0.sup.R10} data file). At 25°C, this reduces to:

\[ m_{\text{CO}_2(aq)} = 10^{6.32 - \text{pH}} m_{\text{HCO}_3^-} \]  

(51)

for a dilute solution of ionic strength 0.0024 molal (using the B-dot equation to calculate the activity coefficients; see Chapter 3). From this, one can see that at pH 4.33, the molality \textit{CO}_2(aq) is 100 times that of \textit{HCO}_3^-.

For seawater (ionic strength of 0.662 molal), the equation becomes:

\[ m_{\text{CO}_2(aq)} = 10^{6.14 - \text{pH}} m_{\text{HCO}_3^-} \]  

(52)

One of the points that may be deduced from these equations is that alkalinity is a poor way to measure the carbonate system in waters of relatively low pH, in which \textit{CO}_2(aq) dominates the total dissolved bicarbonate (defined in the sense desired for input to EQ3NR). The propagated uncertainty in such calculations can become large owing to a contribution from the uncertainty in pH measurement in addition to one from the uncertainty in the measurement in the titration alkalinity (which is interpreted as entirely bicarbonate alkalinity at such low pH). The propagated error is also affected to some degree by uncertainty in the values of the activity coefficients, though this is not likely to be of much significance in very dilute solutions. It is probably affected much more by contributions due to uncertainties regarding the contribution to the measured al-
kalinity of non-carbonate species. This is a potential major problem regarding the use of alkalinity in solutions of any pH value.

We have shown above how the total dissolved bicarbonate (in the sense of including aqueous carbon dioxide and carbonate) may be estimated from alkalinity measurements. These methods assume that only bicarbonate, carbonate, and hydroxide contribute to the measured alkalinity. Alkalinity can also be contributed by dissolved organic species such as acetate, by components such as borate, phosphate, silicate, and sulfide, and by some dissolved metals, such as iron and aluminum, in the form of hydroxy complexes. Of course, if one knows the concentrations of the relevant species, corrections may be attempted. Such corrections could take the form of subtracting the estimated contributions from the measured titration alkalinity. Alternatively, one can make the corrections in a speciation-solubility calculation, using an alkalinity balance equation. It requires assigning alkalinity factors to all the relevant species. Such an approach is available in the PHREEQE code (Plummer, Parkhurst, and Thorstenson, 1980) and previous versions of EQ3NR (Wolery, 1983). Either form of correction carries various uncertainties, however, and major problems arise when the corrections are large. In using previous versions of the EQ3NR code in this way, the code has occasionally terminated unsuccessfully because the magnitude of the corrections would have exceeded the value of the reported titration alkalinity.

Many waters of interest to geochemists have substantial amounts of alkalinity due to non-carbonate species. In oil field waters, the titration alkalinity is often heavily dominated (50-100%) by short chain aliphatic anions, chiefly acetate, propionate, butyrate, and valerate, in order of decreasing importance (Willey et al., 1975; Carothers and Kharaka, 1978). Organic anions are also present in significant concentrations in the water in and around many landfills and other geologic waste disposal sites. These may be both products of the decomposition of organic wastes and original components of the disposed waste. Waters at disposal sites may also be rich in other components which contribute to alkalinity, such as sulfide, ammonia, phosphate, silicate, and metal hydroxy complexes. Many natural waters of interest are also high in sulfate, and a few are high in borate.

The titration alkalinity input option was removed from EQ3NR for the following reasons:

- To avoid undue propagation of errors inherent in the method, which can be severe in certain cases.
- To avoid possible errors by both analysts and code users concerning the nature, interpretation, and usage of analytical data.
- To avoid the problem of having to assign alkalinity factors to new species added to the supporting data files.
- To encourage the practice of obtaining direct analytical measures of total dissolved bicarbonate.

For cases in which the code user must deal with historical data which include alkalinity measurements but no direct measures of the carbonate system, the following procedure is recommended:
• Using the reported alkalinity and pH values, estimate the total dissolved bicarbonate (total dissolved carbon dioxide expressed as bicarbonate) using the methods presented above; make rough corrections if possible for contributions of organics, sulfide, etc.

• Compute a model of the solution.

• Feed the model of the solution to the EQ6 code; simulate the titration process as described by Standard Methods (1976) and compute the corresponding value of the titration alkalinity (an example of this use of EQ6 is given in the EQ6 Theoretical Manual and User’s Guide, Wolery and Daveler, 1992).

• Compare the computed value of the titration alkalinity with the reported value; if they match, stop; if not, adjust the estimate of the total dissolved bicarbonate accordingly and repeat the process until a reasonable match is obtained.

This procedure may not always work. For example, if the contribution of bicarbonate/carbonate to the alkalinity is very small compared to that of organics, sulfide, etc., then the available data really offer no constraint on the bicarbonate/carbonate system. In such cases, the user would be wise to recognize the futility of the situation.

23.6. Redox Constraints

23.6.1. There is No “System” Eh in Most Real Systems

The high degree of emphasis on trying to understand the geochemistry of natural waters in terms of pure equilibrium thermodynamics has misled many people into believing that the redox state of real aqueous systems can be characterized by a single parameter, usually the Eh (a redox potential, given in volts). The related parameter pe, the negative of the logarithm of the hypothetical electron, is similarly incapable of describing the overall redox state of a real aqueous system.

The concept of there being such a thing as a “system” Eh or a “system” pe is based on the assumption that all redox reactions in an aqueous system are in a state of thermodynamic equilibrium. This assumption is a poor one for most real systems (Morris and Stumm, 1967; Jenne, 1981; Thorstenson, 1983; Hostetler, 1984; Lindberg and Runnells, 1984). In the rush to interpret geochemical data by means of Eh-pH and pe-activity diagrams, this point is often forgotten or simply ignored. This has had the unfortunate consequence of legitimizing these variables as all-encompassing redox descriptors in the minds of many students.

This misconception has no doubt been reinforced by the use of Eh (and sometimes pe) as inputs to speciation-solubility codes. Some of these codes require the assumption of a system Eh. Most of the better known codes, EQ3NR, WATEQ2 (Ball, Jenne, and Nordstrom, 1979), and PHREEQE (Parkhurst, Plummer, and Thorstenson, 1980) permit the use of such an input but do not require it. With sufficient analytical data, the degree of disequilibrium among various redox couples may be calculated, and the existence of a system Eh thus tested. Often, however, the available analytical data are insufficient to do this, and one is forced to assume a system Eh.

Redox disequilibrium in natural aqueous systems is created by solar irradiation, radioactive decay, fluid mixing, and transfer of redox components from one phase to another. It is maintained
primarily by the strength of covalent bonds, a major factor in the redox disequilibrium of the light elements such as carbon, hydrogen, oxygen, nitrogen, and sulfur. Biological activity literally feeds on redox disequilibrium (e.g., photosynthesis, if one counts the initial disequilibrium due to solar radiation, and chemosynthesis) and catalyzes an overall approach toward redox equilibrium.

Several well-known examples of redox disequilibrium in natural aqueous systems can be cited. One is the coexistence of dissolved oxygen and organic carbon in nearly all natural waters, implying disequilibrium between the $O_2(aq)/H_2O(l)$ couple and organic/HCO$_3^-$ couples. Another is the disequilibrium between $CH_4(aq)/HCO_3^-$ and HS$^-$/SO$_4^{2-}$ in many marine sediments (Thorstenson, 1970). A third example is the disequilibrium of $N_2(aq)/NO_3^-$ with $O_2(aq)/H_2O(l)$ in marine surface waters (Berner, 1971, p. 119).

As shown below, each such couple can be treated as having its own redox state. This can be expressed in a variety of ways, including a couple-specific $E_h$ or $p_e$. These can be calculated using the Nernst equation in conjunction with chemical analyses that are specific with respect to the two oxidation states represented in any redox couple. In the following section, we will discuss the details of this concept.

### 2.3.6.2. Background: Redox Couples and Half-Reactions

Oxidation-reduction in aqueous systems is commonly treated in terms of redox couples and their associated half-reactions. Common couples in aqueous solution include $O_2(aq)/H_2O(l)$, $H_2(aq)/H_2O(l)$, $Fe^{2+}/Fe^{3+}$, $HS^2-/SO_4^{2-}$, $SO_3^{2-}/SO_4^{2-}$, $S_2O_3^{2-}/SO_4^{2-}$, $NH_4^+/NO_3^-$, $N_2(aq)/NO_3^-$, $CH_4(aq)/HCO_3^-$, and a host of organic/HCO$_3^-$ couples. The half-reaction is illustrated in the case of the very important couple $O_2(aq)/H_2O(l)$:

$$2H_2O(l) = O_2(aq) + 4H^+ + 4e^- \quad (53)$$

Another very important half-reaction corresponds to the so-called hydrogen electrode:

$$H_2(g) = 2H^+ + 2e^- \quad (54)$$

Multiplying this half-reaction by two and subtracting it from the first yields the following complete redox reaction (which has no electrons among the reactants or products):

$$2H_2O(l) = O_2(aq) + 2H_2(g) \quad (55)$$

The thermodynamic convention used to describe the state of electrical potentials of half-reactions in terms of $E_h$ values is to take the electrical potential of the standard hydrogen electrode as zero at all temperatures and pressures. This is consistent with the following additional thermodynamic conventions, where $\Delta G_{f,i}^0$ is the standard state Gibbs energy of the $i$-th species:

- $\Delta G_{f,H_2(g)}^0 = 0$ at all temperatures and pressures (the standard state fugacity is 1 bar)
\( \Delta G^0_{f, H^+} = 0 \) at all temperatures and pressures

\( \Delta G^0_{f, e^-} = \Delta G^0_{f, e^+} = 0 \) at all temperatures and pressures

The Gibbs energy (\( \Delta G \)) is related to the electrical potential (\( \mathcal{E} \)) by the Nernst equation (cf. Garrels and Christ, 1965):

\[
\Delta G = +nFE
\]

where \( n \) is the number of electrons in the half-reaction and \( F \) is the Faraday constant.

An alternative treatment almost equivalent to that above is to write the half-reactions as reduction reactions, so that the electron appears on the left hand side. One then reverses the sign of the right hand side of the Nernst equation as written above. This development is equivalent to the one above, except that the signs of the Gibbs energies and corresponding equilibrium constants and activity products are reversed (Stumm and Morgan, 1981, Chapter 8).

The standard thermodynamic relation describing the Gibbs energy of reaction (\( \Delta G_r \)), of the \( r \)-th reaction is:

\[
\Delta G_r = \Delta G^0_r + 2.303RT\log Q_r
\]  

where \( \Delta G^0_r \) is the corresponding standard state Gibbs energy of reaction and \( Q_r \) is the corresponding activity product. Applying this to half-reactions and using the positive convention version of the Nernst equation, one obtains:

\[
E = E^0 + \frac{2.303RT}{nF}\log Q^+, \frac{1}{2}
\]

where \( E^0 \) is the standard state electrical potential, and \( Q^+, \frac{1}{2} \) is the activity product of the half-reaction. If one uses the negative convention version of the Nernst equation, one obtains instead:

\[
E = E^0 - \frac{2.303RT}{nF}\log Q^-, \frac{1}{2}
\]

where \( Q^-, \frac{1}{2} \) is the activity product of the reverse half-reaction. These relations are equivalent because \( \log Q^-, \frac{1}{2} = -\log Q^+, \frac{1}{2} \). Because the Gibbs energy of the hypothetical electron is always zero, whether it is in the standard state or not, its thermodynamic activity is fixed at unity and it need not explicitly appear in the activity product expressions for half-reactions.

2.3.6.3. Background: \( Eh, pe, Ah, \) and Equilibrium Oxygen Fugacity

One can write a modified Nernst equation for any redox couple. In the case of the ferrous-ferric couple, the corresponding half-reaction is:

\[
Fe^{2+} = Fe^{3+} + e^-
\]

The corresponding form of the Nernst equation is:
Under the thermodynamic conventions adopted above, the potential $E$ on the left hand side of each of the above equations can be taken as the $Eh$ for this specific couple. This may or may not equate to the results of an “$Eh$” measurement.

If the two redox couples are in equilibrium with each other, they must have the same $Eh$. Conversely, if they have the same $Eh$, they must be in equilibrium. Any difference in couple-specific $Eh$ values is a measure (in volts) of the degree of disequilibrium. This can be shown by relating the Gibbs energy of a combined, complete reaction to the differences in potentials. If the first half-reaction has $Eh_1$ and $n_1$ electrons appear in it, and the second half-reaction has $Eh_2$ and $n_2$ electrons, one can construct a complete reaction by multiplying the second half-reaction by $-n_1/n_2$ and adding the result to the first half-reaction. Then $n_1$ electrons are transferred in the complete reaction. The Gibbs energy of this reaction is then given by:

$$\Delta G_r = n_1 F (Eh_1 - Eh_2)$$

(62)

The condition of zero Gibbs energy of reaction (thermodynamic equilibrium) is met if and only if $Eh_1 = Eh_2$.

The redox parameter $pe$, popularized by Truesdell (1968) and Stumm and Morgan (1981), is defined to be analogous to $pH$:

$$pe = -\log a_e$$

(63)

where $e^*$ is the hypothetical aqueous electron. It should not be confused with real aqueous electrons, which are extremely scarce in nature. Their thermodynamic properties are not the same. In fact, the hypothetical electron used to define $pe$ is not the same as the one used to define $Eh$. The $Eh$ conventions require the activity of the hypothetical electron to always be unity. That convention would fix $pe$ at a value of zero.

The relation between $pe$ and $Eh$ is:

$$pe = \left(\frac{F}{2.303RT}\right)Eh$$

(64)

(Thorstenson, 1970; Stumm and Morgan, 1981). One may derive that this requires the thermodynamic convention

$$\Delta G_{f. e^*} = \frac{1}{2} \Delta G_{H_2(\epsilon)} - \Delta G_{H^*}$$

at all temperatures and pressures

This in turn requires that

$$\Delta G_{f. e^*} = 0$$

at all temperatures and pressures

whereas the $Eh$ convention for the hypothetical electron was
\( \Delta G_f^{\circ} = \Delta G_f^{\circ} = 0 \) at all temperatures and pressures

It should be clear that \( \text{pe} \) is not a perfect analog to \( \text{pH} \), because \( \text{pH} \) is defined with respect to \( H^+ \), a real aqueous species, whereas \( \text{pe} \) is defined with respect to a hypothetical species. Each redox couple can have its own \( \text{pe} \), just as it can have its own \( \text{Eh} \), the two being related by the equation given above. It follows from the previous development that thermodynamic equilibrium between two redox couples is synonymous with each having the same value of \( \text{pe} \).

The state of an aqueous redox couple can also be expressed in terms of chemical affinity by the redox affinity, \( \text{Ah} \) (Wolery, 1983). This is a special case of the thermodynamic affinity function (its application to half-reactions). It is related to \( \text{Eh} \) by the relation

\[
\text{Ah} = F\text{Eh} \tag{65}
\]

The driving force for any kind of complete chemical reaction (meaning to exclude half-reactions) can be expressed by the thermodynamic affinity \( (A_r) \), which is related to the equilibrium constant \( K_r \) and the activity product \( Q_r \) by the equation:

\[
A_r = -2.303RT\log\left(\frac{Q_r}{K_r}\right) \tag{66}
\]

If \( n_1 \) electrons appear in one half-reaction and \( n_2 \) in another, the two half-reactions can be combined into a complete redox reaction in the manner discussed previously. The thermodynamic affinity of the complete reaction, in which \( n_1 \) electrons are transferred, is then related to the \( \text{Ah} \) values \( (\text{Ah}_1 \) and \( \text{Ah}_2 \), respectively) of the two half reactions by the equation:

\[
A_r = n_1 (\text{Ah}_1 - \text{Ah}_2) \tag{67}
\]

Thermodynamic equilibrium \( (A = 0) \) among two redox couples is the case if and only if both couples have the same value of \( \text{Ah} \).

Alternatively, the state of a redox couple may be expressed in terms of an equilibrium oxygen fugacity (a couple-specific oxygen fugacity). Fugacities are properties of gas species. Gas species do not exist in aqueous solution because, by definition, all species in aqueous solution are aqueous species. Therefore, we can only talk about oxygen fugacities in aqueous solution by reference to hypothetical equilibria with a gas phase. Putting it another way, \( O_2(g) \) makes a perfectly good hypothetical aqueous species, much like the hypothetical aqueous electron.

Consider the half-reaction:

\[
2H_2O (l) = O_2(g) + 4H^+ + 4e^- \tag{68}
\]

where we now take \( O_2(g) \) to be a hypothetical aqueous species with the thermodynamic properties of the real gas species. We can calculate an equilibrium oxygen fugacity for any half-reaction by coupling it with this one to form a complete redox reaction.
Let $K_{Eh}$ be the equilibrium constant for the $O_{2(g)}/H_2O_{(l)}$ half-reaction given above. $Eh$ and oxygen fugacity are then related by the equation:

$$
\log f_{O_2} = \left( \frac{4F}{2.303RT} \right) Eh - 4\log a_{H^+} + 2\log a_w + \log K_{Eh}
$$

This equation can be used to relate the equilibrium oxygen fugacity of any redox couple with its own $Eh$. Two redox couples are in thermodynamic equilibrium with each other if and only if they have the same equilibrium oxygen fugacity.

### 2.3.6.4. Redox Options: Testing versus Assuming Equilibrium

A commonly used approach in aqueous speciation modeling is to input a total concentration for a dissolved element that occurs in more than one oxidation state and partition it according to a given $Eh$, $p_e$, or oxygen fugacity. This, however, requires us to assume that all redox couples in the system are in a state of thermodynamic equilibrium. The EQ3NR code offers this option.

If we constrain the thermodynamic activities of all the aqueous species appearing in a couple's half-reaction without resorting to an input $Eh$, $a_h$, $p_e$, or oxygen fugacity, the equations presented above give us a means to calculate its individual redox state expressed as any of the following:

- $Eh$ (in terms of an electrical potential).
- $a_h$ (in terms of a chemical potential).
- $p_e$.
- Oxygen fugacity.

Analytical techniques do not generally discriminate between a simple species and its ion-pairs and complexes. However, there are techniques in many cases to discriminate between different oxidation states. To calculate the $Eh$ of the ferrous-ferric couple, for example, we must have analytical data for both $Fe^{2+}$ and $Fe^{3+}$ (see for example Nordstrom, Jenne, and Ball, 1979). If these data are both total concentrations (e.g., total $Fe^{2+}$, total $Fe^{3+}$), we simply have two mass balance equations for iron in the aqueous speciation model instead of one.

This is the preferred approach for treating oxidation-reduction in aqueous speciation modeling (see Nordstrom et al., 1979). One may then test whether or not various redox couples are in equilibrium with each other. EQ3NR can treat any redox couple in this fashion. Alternative constraints discussed in the previous subsection could substitute for one or both total concentrations/mass balances in the usual way. The code will use a redox default to partition an element that appears in more than one oxidation state if insufficient data are input to calculate a couple-specific parameter. The redox default may be an input $Eh$, $p_e$, or log oxygen fugacity. Alternatively, it may be defined by a redox couple for which sufficient data are input to calculate couple-specific parameters. By constraining one or more of the species in the corresponding half-reaction by a heterogeneous equilibrium constraint, it is possible to constrain the default redox state by a heterogeneous equilibrium.
2.3.7. Measures of Mineral Saturation.

EQ3NR employs two measures of the saturation state of an aqueous solution with respect to minerals. The first is the saturation index defined as:

\[ SI = \log \frac{Q}{K} \]  

(70)

where it is understood that \( Q \) is the activity product and \( K \) the equilibrium constant for a dissolution reaction. In the case of the dissolution of calcite, for example, if the reaction is written as:

\[ \text{Calcite} + H^+ = Ca^{2+} + HCO_3^- \]  

(71)

the ion activity product is then defined as:

\[ Q_{\text{Calcite}} = \frac{a_{Ca^{2+}}a_{HCO_3^-}}{a_{\text{Calcite}}a_{H^+}} \]  

(72)

The second measure of the saturation state is the thermodynamic affinity of the precipitation reaction. The affinity of a reaction (no matter how it is written) is related to its activity product and equilibrium constant by:

\[ A = -2.303RT \log K - 2.303RT \log \frac{Q}{K} \]  

(73)

Because \( \log Q/K \) reverses sign when the reaction is reversed, the affinity to precipitate is related to the saturation index by:

\[ A_\sigma = 2.303RT SI \]  

(74)

Following these conventions, both \( SI \) and \( A_\sigma \) are positive for supersaturated minerals, zero for saturated ones, and negative for undersaturated minerals.

In the case of solid solution minerals with end-member components, the saturation index of the \( \sigma \)-th end member is related to that of the corresponding pure phase \( \phi \) by:

\[ SI_{\sigma\psi} = SI_{\phi} - \log a_{\sigma\psi} = SI_{\phi} - \log x_{\sigma\psi} - \log \lambda_{\sigma\psi} \]  

(75)

where \( a_{\sigma\psi} \) is the thermodynamic activity of the end-member, \( x_{\sigma\psi} \) is its mole fraction, and \( \lambda_{\sigma\psi} \) is its mole fraction activity coefficient. Consideration of an overall dissolution reaction of a solid solution of given composition suggests that the saturation index of the \( \psi \)-th solid solution should be defined by:

\[ SI_{\psi} = \sum_{\sigma = 1}^{\sigma_{r,\psi}} x_{\sigma\psi} SI_{\sigma\psi} \]  

(76)
Affinity functions can be defined analogously.

The problem of defining the saturation state of a solid solution for which no composition is given is not so straightforward, because the result is composition-dependent. One way to approach this would be to find the compositions that maximize the $SI$. This is the method presently employed in EQ3/6 (see Bourcier, 1985, 1989).

2.4. Use and Misuse of Speciation-Solubility Codes

There is significant potential to misuse any speciation-solubility code. No such code should be used as a "black box". As Jenne (1981, p. 36) puts it, "... each application should be viewed as a partial validation." The geochemical model of each new scenario (e.g., a set of waters in a compositional range not previously studied) may have a different set of important aqueous species, and hence provide a test of some thermodynamic data that have not previously been exercised. Also, reactions controlled by equilibrium in one situation may be in disequilibrium in another, and vice versa, especially heterogeneous and aqueous redox reactions.

Geochemical modeling with aqueous speciation-solubility codes must actively address three questions. First, are all the significant species in the model? Second, are all the important thermodynamic data sufficiently correct? Do they make sense when compared with the model outputs when working with a set of water samples? Do they make sense in comparison with other knowledge about an aqueous system such as data on the identities of minerals with which the water is in contact? Third, would disequilibrium constraints be more appropriate than equilibrium constraints for some reactions (especially aqueous redox reactions)? Users should keep in mind the admonition of Nordstrom et al. (1979) that "... no model is better than the assumptions on which it is based."

If no thermodynamic data are available for species known or suspected to be important in a given application, then such data should be estimated by empirical or semi-empirical methods. EQ3NR has an input file option which permits the user to temporarily modify equilibrium constants at run time (see Chapter 6). This makes it convenient to conduct sensitivity studies of the uncertainty in such estimated values. Langmuir (1979) summarizes approaches for estimating thermodynamic properties of aqueous species and reactions. Tardy and Garrels (1974), Wolery (1978), and Helgeson et al. (1978) discuss methods for estimating the thermodynamic properties of minerals.

A common problem faced by novices at speciation-solubility modeling is that their models come out grossly supersaturated with nearly every aluminum and ferric iron bearing mineral in the data base. This often occurs because analysis is made of inadequately filtered samples, which commonly contain colloidal particles of these two components. These particles then "inflate" the corresponding chemical analyses. Busenberg (1978) showed that large quantities of a colloidal aluminum phase occurred in the size range 0.1-0.45 μm during a set of feldspar dissolution experiments. Laxen and Chandler (1982) did more detailed studies of iron particulate size distribution in fresh waters. Their work shows that a filter finer than 0.1 μm is necessary to effectively remove these particulates from the chemical analysis.

The modeler should be aware that many solubility-controlling phases, especially at low temperature, are metastable (e.g., amorphous $Fe(OH)_3$ may control the level of dissolved iron, not the
more stable hematite, $Fe_2O_3$). In addition, the stability of some controlling phases may be somewhat variable due to such factors as crystallinity (i.e., crystal size), order/disorder, ionic substitution, or, in the case of fresh precipitates, aging. Helgeson et al. (1978) discuss many of these effects.

One approach that may be helpful to users is to estimate the amount of aluminum or iron that would be in solution under the assumption of appropriate solubility equilibria. For example, one might constrain dissolved aluminum to satisfy equilibrium with gibbsite ($Al(OH)_3$) or constrain iron to satisfy equilibrium with amorphous $Fe(OH)_3$ or a nontronite (ferric-rich smectite) clay. However, this is not a substitute for analysis of carefully filtered samples.

The state of available analytical data on water compositions is often a limiting factor in the usage of EQ3NR or any other speciation-solubility code. In general, the data must be both accurate and sufficiently complete. Inaccurate data often result when methods suitable for analyzing drinking water are applied to waters very dissimilar to this medium. This can take the form of both positive and negative interferences. Some analytical parameters (e.g., $pH$, alkalinity, dissolved sulfide) must be measured immediately upon sampling to avoid changes due to mineral precipitation, ingassing, or outgassing. Water samples should be inspected after transportation and storage for the formation of precipitates. Quite often, analytical data are incomplete for geochemical modeling purposes. This may have the effect of completely inhibiting modeling work, or it may result in modeling with assumptions that could have been avoided if the right hard data had been available. In general, analytical work is most useful to modeling if there is interplay between the modeler and the analyst.

Internal consistency can provide useful tests of the quality of aqueous speciation models (see Merino, 1979). One such test is to compare the calculated electrical imbalance with the cation/anion subtotals for charge equivalents. EQ3NR makes these calculations, which are a meaningful test if electrical balance is not used as an input constraint. Merino (1979) also recommends the technique of comparing measured and independently calculated values of titration alkalinity. In essence, his recommendation corresponds to the currently recommended procedure for dealing with alkalinity described earlier in this chapter.
3. Activity Coefficients of Aqueous Species

3.1. Introduction

The thermodynamic activities \(a_i\) of aqueous solute species are usually defined on the basis of molalities. Thus, they can be described by the product of their molal concentrations \(m_i\) and their molal activity coefficients \(\gamma_i\):

\[
a_i = m_i \gamma_i
\]

(77)

The thermodynamic activity of the water \(a_w\) is always defined on a mole fraction basis. Thus, it can be described analogously by product of the mole fraction of water \(x_w\) and its mole fraction activity coefficient \(\lambda_w\):

\[
a_w = x_w \lambda_w
\]

(78)

It is also possible to describe the thermodynamic activities of aqueous solutes on a mole fraction basis. However, such mole fraction-based activities \(a_i^{(x)}\) are not the same as the more familiar molality-based activities \(a_i^{(m)}\), as they are defined with respect to different choices of standard states. Molality based activities and activity coefficients \(\gamma_i\), are occasionally applied to aqueous nonelectrolyte species, such as ethanol in water. In geochemistry, the aqueous solutions of interest almost always contain electrolytes, so mole-fraction based activities and activity coefficients of solute species are little more than theoretical curiosities. In EQ3/6, only molality-based activities and activity coefficients are used for such species, so \(a_i\) always implies \(a_i^{(m)}\). Because of the nature of molality, it is not possible to define the activity and activity coefficient of water on a molal basis; thus, \(a_w\) always means \(a_w^{(x)}\).

Solution thermodynamics is a construct designed to approximate reality in terms of deviations from some defined ideal behavior. The complex dependency of the activities on solution composition is thus dealt with by shifting the problem to one of describing the activity coefficients. The usual treatment of aqueous solutions is one which simultaneously employs quantities derived from, and therefore belonging to, two distinct models of ideality (Wolery, 1990). All solute activity coefficients are based on molality and have unit value in the corresponding model of ideality, called molality-based ideality. The activity and activity coefficient of water are not constant in an ideal solution of this type, though they do approach unit value at infinite dilution. These solvent properties are derived from mole fraction-based ideality, in which the mole fraction activity coefficients of all species components in solution have unit value. In an ideal solution of this type, the molal activity coefficients of the solutes are not unity, though they approach it at infinite dilution (see Wolery, 1990).

Any geochemical modeling code which treats aqueous solutions must provide one or more models by which to compute the activity coefficients of the solute species and the solvent. In many codes, what is computed is the set of \(\gamma_i\) plus \(a_w\). As many of the older such codes were constructed to deal only with dilute solutions in which the activity of water is no less than about 0.98, some of these just take the activity of water to be unity. With the advent of activity coefficient models
of practical usage in concentrated solutions (mostly based on Pitzer's 1973, 1975 equations),
there has been a movement away from this particular and severe approximation. Nevertheless, it
is generally the activity of water, rather than the activity coefficient of water, which is evaluated
from the model equations. This is what was previously done in EQ3/6. However, EQ3/6 now
evaluates the set of \( \gamma_i \) plus \( \lambda_w \). This is done to avoid possible computational singularities that may
arise, for example if heterogeneous equilibria happen to fix the activity of water (e.g., when a
solution is saturated with both gypsum and anhydrite).

Good models for activity coefficients must be accurate. A prerequisite for general accuracy is
thermodynamic consistency. The activity coefficient of each aqueous species is not independent
of that of any of the others. Each is related to a corresponding partial derivative of the excess
Gibbs energy of the solution (\( G^{EX} \)). The excess Gibbs energy is the difference between the
complete Gibbs energy and the ideal Gibbs energy. Because there are two models of ideality, hence
two models for the ideal Gibbs energy, there are two forms of the excess Gibbs energy, \( G^{EXm} \)
(molality-based) and \( G^{EXr} \) (mole fraction-based). The consequences of this are discussed by
Wolery (1990). In version 7.0 of EQ3/6, all activity coefficient models are based on ideality de­
defined in terms of molality. Thus, the excess Gibbs energy of concern is \( G^{EXm} \). The activity of wa­
ter, which is based on mole-fraction ideality, is imported into this structure as discussed by
Wolery (1990). The relevant differential equations are:

\[
\ln \gamma_i = \frac{1}{RT} \frac{\partial G^{EXm}}{\partial n_i} \quad (79)
\]

\[
\ln a_w = -\frac{\Sigma m}{\Omega} + \frac{1}{RT} \frac{\partial G^{EXm}}{\partial n_w} \quad (80)
\]

where \( R \) is the gas constant, \( T \) the absolute temperature, \( \Omega \) the number of moles of solvent water
comprising a mass of 1 kg (\( \Omega \approx 55.51 \)), and:

\[
\Sigma m = \sum_{i} m_i \quad (81)
\]

the sum of molalities of all solute species. Given an expression for the excess Gibbs energy, such
equations give a guaranteed route to thermodynamically consistent results (Pitzer, 1984; Wolery,
1990). Equations that are derived by other routes may be tested for consistency using other rela­tions, such as the following forms of the cross-differentiation rule (Wolery, 1990):

\[
\frac{\partial \ln \gamma_j}{\partial m_i} = \frac{\partial \ln \gamma_i}{\partial m_j} \quad (82)
\]

\[
\frac{\partial \ln a_w}{\partial n_i} = \frac{\partial \ln \gamma_i}{\partial n_w} - \frac{1}{n_w} \quad (83)
\]
In general, such equations are most easily used to prove that a set of model equations is not thermodynamically consistent. The issue of sufficiency in proving consistency using these and related equations (Gibbs-Duhem equations and sum rules) is addressed by Wolery (1990).

The activity coefficients in reality are complex functions of the composition of the aqueous solution. In electrolyte solutions, the activity coefficients are influenced mainly by electrical interactions. Much of their behavior can be correlated in terms of the ionic strength, defined by:

\[ I = \frac{1}{2} \sum_i m_i z_i^2 \]  

where the summation is over all aqueous solute species and \( z_i \) is the electrical charge. However, the use of the ionic strength as a means of correlating and predicting activity coefficients has been taken to unrealistic extremes (e.g., in the mean salt method of Garrels and Christ, 1965, p. 58-60). In general, model equations which express the dependence of activity coefficients on solution composition only in terms of the ionic strength are restricted in applicability to dilute solutions.

The three basic options for computing the activity coefficients of aqueous species in EQ3/6 are models based respectively on the Davies (1962) equation, the “B-dot” equation of Helgeson (1969), and Pitzer’s (1973, 1975, 1979, 1987) equations. The first two models, owing to limitations on accuracy, are only useful in dilute solutions (up to ionic strengths of 1 molal at most). The third basic model is useful in highly concentrated as well as dilute solutions, but is limited in terms of the components that can be treated.

With regard to temperature and pressure dependence, all of the following models are parameterized along the 1 atm/steam saturation curve. This corresponds to the way in which the temperature and pressure dependence of standard state thermodynamic data are also presently treated in the software. The pressure is thus a function of the temperature rather than an independent variable, being fixed at 1.013 bar from 0-100°C and the pressure for steam/liquid water equilibrium from 100-300°C. However, some of the data files have more limited temperature ranges.

3.2. The Davies Equation

The first activity coefficient model in EQ3/6 is based on the Davies (1962) equation:

\[ \log \gamma_i = -A_y 10 z_i^2 \left( \sqrt{I} + 0.2I \right) \]  

(the constant 0.2 is sometimes also taken as 0.3). This is a simple extended Debye-Hückel model (it reduces to a simple Debye-Hückel model if the “0.2I” part is removed). The Davies equation is frequently used in geochemical modeling (e.g., Parkhurst, Plummer, and Thorstenson, 1980; Stumm and Morgan, 1981). Note that it expresses all dependence on the solution composition through the ionic strength. Also, the activity coefficient is given in terms of the base ten logarithm, instead of the natural logarithm. The Debye-Hückel \( A_y \) parameter bears the additional label “10” to ensure consistency with this. The Davies equation is normally only used for temperatures close to 25°C. It is only accurate up to ionic strengths of a few tenths molal in most
solutions. In some solutions, inaccuracy, defined as the condition of model results differing from experimental measurements by more than the experimental error, is apparent at even lower concentrations.

In EQ3/6, the Davies equation option is selected by setting the option flag \( \text{iopgl} = -1 \). A supporting data file consistent with the use of a simple extended Debye-Hückel model must also be supplied (e.g., data1 = data1.com, data1.sup, or data1.nea). If \( \text{iopgl} = -1 \) and the supporting data file is not of the appropriate type, the software terminates with an error message.

The Davies equation has one great strength: the only species-specific parameter required is the electrical charge. This equation may therefore readily be applied to a wide spectrum of species, both those whose existence is well-established and those whose existence is only hypothetical.

The Davies equation predicts a unit activity coefficient for all neutral solute species. This is known to be inaccurate. In general, the activity coefficients of neutral species that are non-polar (such as \( O_2(aq) \), \( H_2(aq) \), and \( N_2(aq) \)) increase with increasing ionic strength (the "salting out effect," so named in reference to the corresponding decreasing solubilities of such species as the salt concentration is increased; cf. Garrels and Christ, 1965, p. 67-70). In addition, Reardon and Langmuir (1976) have shown that the activity coefficients of two polar neutral species (the ion pairs \( CaSO_4(aq) \) and \( MgSO_4(aq) \)) decrease with increasing ionic strength, presumably as a consequence of dipole-ion interactions.

The Davies equation is thermodynamically consistent. It is easy to show, for example, that it satisfies the solute-solute form of the cross-differentiation equation.

Most computer codes using the Davies equation set the activity of water to one of the following: unity, the mole fraction of water, or a limiting expression for the mole fraction of water. Usage of any of these violates thermodynamic consistency, but this is probably not of great significance as the inconsistency is numerically not significant at the relatively low concentrations at which the Davies equation itself is accurate. For usage in EQ3/6, we have used standard thermodynamic relations to derive the following expression:

\[
\log a_w = \frac{1}{\Omega} \left( -\frac{\sum m}{2.303} + \frac{2}{3} A \gamma 10^2 \sigma (\sqrt{I}) - 2 (0.2) A \gamma 10 I^2 \right) \quad (86)
\]

where "2.303" is a symbol for and approximation of \( \ln 10 \) (warning: this is not in general a sufficiently accurate approximation) and:

\[
\sigma (x) = \frac{3}{x^3} \left( 1 + x - \frac{1}{1 + x} - 2 \ln (1 + x) \right) \quad (87)
\]

This result is thermodynamically consistent with the Davies equation.

### 3.3. The B-dot Equation

The second model for activity coefficients available in EQ3/6 is based on the B-dot equation of Helgeson (1969) for electrically charged species:
Here $d_i$ is the hard core diameter of the species, $B_γ$ is the Debye-Hückel $B$ parameter, and $\dot{B}$ is the characteristic B-dot parameter. Like the Davies equation, this is a simple extended Debye-Hückel model, the extension being the "$\dot{B}I$" term. The Debye-Hückel part of this equation is equivalent to that of the Davies equation if the product "$d_iB_γ$" has a value of unity. In the extended part, these equations differ in that the Davies equation has a coefficient in place of $\dot{B}$ which depends on the electrical charge of the species in question.

In EQ3/6, the B-dot equation option is selected by setting the option flag $\text{iopgl} = 0$. A supporting data file consistent with the use of a simple extended Debye-Hückel model must also be supplied (e.g., $\text{data1 = data1.com, data1.sup, or data1.nea}$). Note that these data files support the use of the Davies equation as well (the $\dot{I}$ data on these files is simply ignored in that case). If $\text{iopgl} = 0$ and the supporting data file is not of the appropriate type, the software terminates with an error message.

The B-dot equation has about the same level of accuracy as the Davies equation, and almost as much universality (one needs to know $d_i$ in addition to $z_i$). However, it fails to satisfy the solute-solute form of the cross-differentiation rule. The first term is consistent with this rule only if all hard core diameters have the same value. The second is consistent only if all ions share the same value of the square of the electrical charge. However, the numerical significance of the inconsistency is small in the range of low concentrations in which this equation can be applied with useful accuracy. On the positive side, the B-dot equation has been developed (Helgeson, 1969) to span a wide range of temperature (up to 300°C).

For electrically neutral solute species, the B-dot equation reduces to:

$$\log \gamma_i = \dot{B}I$$

As $\dot{B}$ has positive values at all temperatures in the range of application, the equation predicts a salting out effect. However, by tradition (Helgeson et al., 1970), the B-dot equation itself is not used in the case of neutral solute species. The practice, as suggested by Garrels and Thompson (1962) and reiterated by Helgeson (1969), is to assign the value of the activity coefficient of aqueous $CO_2$ in otherwise pure sodium chloride solutions of the same ionic strength. This function was represented in previous versions of EQ3/6 by a power series in the ionic strength:

$$\log \gamma_i = k_1I + k_2I^2 + k_3I^3 + k_4I^4$$

The first term on the right hand side dominates the others. The first coefficient is positive, so the activity coefficient of $CO_2$ increases with increasing ionic strength (consistent with the "salting out" effect). As it was applied in EQ3/6, the coefficients for the power series themselves were represented as similar power series in temperature, and this model was fit to data taken from Ta-
ble 2 of Helgeson (1969). These data (including extrapolations made by Helgeson) covered the range 25-300°C and 0-3 molal NaCl.

The high order power series in eq (90) was unfortunately very unstable when extrapolated outside the range of the data to which it was fit. EQ3NR and EQ6 would occasionally run into an unrecoverable problem attempting to evaluate this model for high ionic strength values generated in the process of attempting to find a numerical solution (not necessarily because the solutions in question really had high ionic strength). To eliminate this problem, the high order power series has been replaced by a new expression after Drummond (1981, p. 19):

\[
\ln \gamma_i = \left( C + FT + \frac{G}{I} \right) I - \left( E + HT \right) \left( \frac{I}{I+1} \right)
\]  

(91)

where \( T \) is the absolute temperature and \( C = -1.0312, F = 0.0012806, G = 255.9, E = 0.4445, \) and \( H = -0.001606 \). Note that this is presented in terms of the natural logarithm. Conversion is accomplished by using the relation:

\[
\log x = \frac{\ln x}{2.303}
\]  

(92)

This expression is both much simpler (considering the dependencies on both temperature and ionic strength) and is more stable. However, in deriving it, the ionic strength was taken to be equivalent to the sodium chloride molality. In the original model (based on Helgeson, 1969), the ionic strength was based on correcting the sodium chloride molality for ion pairing. This correction is numerically insignificant at low temperature. It does become significant at high temperature. However, neither this expression nor the power series formulation it replaced is thermodynamically consistent with the B-dot equation itself, as can be shown by applying the solute-solute cross-differentiation rule.

The more recent previous versions of EQ3/6 only applied the "CO₂" approximation to species that are essentially nonpolar (e.g., \( O_{2(aq)}, H_{2(aq)}, N_{2(aq)} \), for which salting-out would be expected. In the case of polar neutral aqueous species, the activity coefficients were set to unity (following the recommendation of Garrels and Christ, 1965, p. 70); i.e., one has:

\[
\log \gamma_i = 0
\]  

(93)

This practice is still followed in the present version of the code.

EQ3/6 formerly complemented the B-dot equation with an approximation for the activity of water that was based on assigning values in pure sodium chloride solutions of the same "stoichiometric" ionic strength (Helgeson et al., 1970). This approximation was fairly complex and was, of course, not thermodynamically consistent with the B-dot equation itself. In order to simplify the data requirements, as well as avoid the need to employ a second ionic strength function, this formulation has been replaced by a new one which depends on the \( \tilde{B} \) parameter and is quasi-consistent with the B-dot equation:
The solute hard core diameter ($\hat{a}$) is assigned a fixed value of 4.0Å (a reasonable value). This equation is consistent with the B-dot equation if all solute species are ions, have the same fixed value of the hard core diameter, and have the same value of the square of the electrical charge.

3.4. Scaling of Individual Ionic Activity Coefficients: pH Scales

Before proceeding to a discussion of Pitzer's (1973, 1975) equations, we will address the problem of scaling associated with the activity coefficients of individual ions. It is not possible to observe (measure) any of the thermodynamic functions of such species, because any real solution must be electrically balanced. Thus, the activity coefficients of aqueous ions can only be measured in electrically neutral combinations. These are usually expressed as the mean activity coefficients of neutral electrolytes. The mean activity coefficient of neutral electrolyte $MX$ ($M$ denoting the cation, $X$ the anion) is given by:

$$\log \gamma_{\pm, MX} = \frac{v_M \log \gamma_M + v_X \log \gamma_X}{v_{MX}}$$

(95)

where $v_M$ is the number of moles of cation produced by dissociation of one mole of the electrolyte, $v_X$ is the number of moles of anion produced, and:

$$v_{MX} = v_M + v_X$$

(96)

Electrical neutrality requires that:

$$z_M \gamma_M = -z_X \gamma_X$$

(97)

Although the activity coefficients of ions can not be individually observed, the corresponding molal concentrations can be. The corresponding products, the thermodynamic activities of the ions, are not individually observable, precisely because of the problem with the activity coefficients. Thus, the problem of obtaining individual activity coefficients of the ions and the problem of obtaining individual activities of the same species is really the same problem.

Individual ionic activity coefficients can be defined on a conventional basis by introducing some arbitrary choice. This is can be made by adopting some expression for the activity coefficient of a single ion. The activity coefficients of all other ions then follow via electroneutrality relations. The activities for all the ions are then also determined (cf. Bates and Alfenaar, 1969). Because this applies to the hydrogen ion, such an arbitrary choice then determines the $pH$. Such conventions are usually made precisely for this purpose, and they are generally known as $pH$ scales. The NBS $pH$ scale, which is the basis of nearly all modern conventional $pH$ measurement, is based on the Bates-Guggenheim equation (Bates, 1964):
This scale is significant not only to the measurement of \( \text{pH} \), but of corresponding quantities (e.g., \( pCl, pBr, pNa \)) obtained using other specific-ion electrodes (cf. Bates and Alfenaar, 1969; Bates, 1973; Bates and Robinson, 1974).

The Bates-Guggenheim equation, like the Davies equation and the B-dot equation, is an extended Debye-Hückel formula. However, if one applies the Davies equation or the B-dot equation to the chloride ion, the result is not precisely identical. The difference approaches zero as the ionic strength approaches zero, and is not very significant quantitatively in the low range of ionic strength in which either the Davies equation or the B-dot equation has useful accuracy. Nevertheless, the use of either of these equations in uncorrected form introduces an inconsistency with measured \( \text{pH} \) values, as use of the Davies equation for example would interpret the \( \text{pH} \) as being on an implied "Davies" scale.

Activity coefficients (and activities) of ions can be moved from one scale to another. The general relation for converting from scale (1) to scale (2) is (Knauß, Wolery, and Jackson, 1991):

\[
\log \gamma_i^{(2)} = \log \gamma_i^{(1)} = \frac{z_i}{z_j} (\log \gamma_j^{(2)} - \log \gamma_j^{(1)} )
\]

For example, if we evaluate the Davies equation for all ions, we may take the results as being on scale (1). To convert these to the NBS scale (here scale (2)), we take the \( j \)-th ion to be the chloride ion and evaluate the Bates-Guggenheim equation. We then apply the scale conversion equation to every other ion \( i \).

In EQ3/6, activity coefficients are first calculated from the "raw" single-ion equations. They are then immediately rescaled, unless no rescaling is to be done. Thus, rescaling occurs during the iteration process; it is not deferred until convergence has been achieved. The user has control over rescaling via the option switch \textit{iopg2}. If \textit{iopg2} = 0, all single-ion activity coefficients and activities are put on the NBS scale. If \textit{iopg2} = -1, no rescaling is performed. If \textit{iopg2} = 1, all single-ion activity coefficients and activities are put on a scale which is defined by the relation:

\[
\log \gamma_{H^+} = 0
\]

This has the effect of making the activity and the molality of the hydrogen ion numerically equal. This may have some advantages in comparing with experimental measurements of the hydrogen ion molality. Such measurement techniques have recently been discussed by Mesmer (1991).

The problem of scaling the activity coefficients of ions is more acute in concentrated solutions, and the need to discriminate among different scales in geochemical modeling codes has only been addressed as such codes have been written or modified to treat such solutions (e.g., Harvie, Møller, and Weare, 1984; Plummer et al., 1988).
3.5. Pitzer’s Equations

3.5.1. Introduction

Pitzer (1973, 1975) proposed a set of semi-empirical equations to describe activity coefficients in aqueous electrolytes. These equations have proven to be highly successful as a means of dealing with the thermodynamics of concentrated solutions (e.g., Pitzer and Kim, 1974). Models based on these equations have been developed to describe not only solution properties, but also equilibrium between such solutions and salt minerals (e.g., Harvie and Weare, 1980; Harvie, Möller, and Weare, 1984). The utility of these models in geochemical studies has been well established. For example, such models have been shown to account for the mineral sequences produced by evaporation of seawater (Harvie et al., 1980), the process of trona deposition in Lake Magadi, Kenya (Monnin and Schott, 1984), and the formation of the borate-rich evaporite deposits at Searles Lake, California (Felmy and Weare, 1986).

Pitzer’s equations are based on a semi-theoretical (see Pitzer, 1973) interpretation of ionic interactions, and are written in terms of interaction coefficients (and parameters from which such coefficients are calculated). There are two main categories of such coefficients, “primitive” ones which appear in the original theoretical equations, but most of which are only observable in certain combinations, and others which are “observable” by virtue of corresponding to observable combinations of the primitive coefficients or by virtue of certain arbitrary conventions. Only the observable coefficients are reported in the literature.

There is a very extensive literature dealing with Pitzer’s equations and their application in both interpretation of experimental data and calculational modeling. A complete review is beyond the scope of the present manual. Discussion here will be limited to the equations themselves, how to use them in EQ3/6, and certain salient points that are necessary in order to use them in an informed manner. Readers who wish to pursue the subject further are referred to reviews given by Pitzer (1979, 1987, 1992). Jackson (1988) has addressed the verification of the addition of Pitzer’s equations to EQ3/6.

In EQ3/6, the Pitzer’s equations option is selected by setting the option flag $iopgl = 1$. A supporting data file consistent with this option must also be supplied (e.g., datal = datal.hmww or datal.pit). If $iopgl = 1$ and the supporting data file is not of the appropriate type, the software terminates with an error message.

Pitzer’s equations are based on the following virial expansion for the excess Gibbs energy:

\[
G^\text{EXm} = RT\left(\frac{1}{w_w}f(I) + \sum_{i,j}^n \lambda_{ij}(I)n_in_j + \sum_{i,j,k}^n \mu_{ijk}n_in_jn_k\right)
\]

(191)

where $w_w$ is the number of kilograms of solvent water, $f(I)$ is a Debye-Hückel function describing the long-range electrical interactions to first order, the subscripts $i, j,$ and $k$ denote aqueous solute species, and $n_i$ is the number of moles of the $i$-th solute species. The equation also contains two kinds of interaction or virial coefficients: the $\lambda_{ij}$ are second order interaction coefficients, and the $\mu_{ijk}$ are third order interaction coefficients. A key element in the success of Pitzer’s equations is...
the treatment of the second order interaction coefficients as functions of ionic strength. As will be discussed later in more detail, the $\lambda_{ij}$ consist of both theoretically defined and empirical parts, while the $\mu_{ijk}$ are completely empirical. As the term is used here, "empirical" means that at least some of the parameter values required to evaluate a quantity must be obtained by fitting experimental data.

The sums in the interaction coefficient terms are actually double and triple sums. As the number of components in a system increases, the number of interaction coefficients of the type shown above becomes very large. It turns out there are many more of the $\lambda_{ij}$ and $\mu_{ijk}$ than can actually be observed, other than in combination. For example, in the equation for the excess Gibbs energy, it is quickly obvious that $\lambda_{12}$ and $\lambda_{21}$ can only be seen in the combination $(\lambda_{12} + \lambda_{21})$, and a similar situation holds in the case of the $\mu_{ijk}$. This leads to the first simplification in dealing with these coefficients, which is that those with the same subscripts (regardless of order or permutation) are required to be equal (Pitzer, 1973). This is not the end of the story, as other constraints (mostly related to electrical neutrality) force even more simplifications (which will be addressed later).

A set of thermodynamically consistent equations for the activity coefficients follows by application of the partial differential equations given previously. In the case of solute species, this leads to:

$$
\ln \gamma_i = \left(\frac{q_i^2}{2}\right)f'(I) + 2 \sum_j \lambda_{ij}(I)m_j + \sum_{jk} \left(\frac{q_i^2}{2}\right)\lambda_{jk}^\prime(I) + 3 \mu_{ijk}m_jm_k
$$

(102)

where $f'(I)$ is the derivative $df/I$ and $\lambda_{ij}(I)$ is similarly $d\lambda_{ij}/I$. For water, the corresponding result is:

$$
\ln a_w = -\frac{\Sigma m}{\Omega} - \frac{1}{\Omega} (If'(I) - f(I)) + \frac{1}{\Omega} \left(\sum_{ij} (\lambda_{ij}(I) + \lambda_{ij}^\prime(I))m_im_j + 2\sum_{ijk} \mu_{ijk}m_im_jm_k\right)
$$

(103)

The activity of water is closely related to the osmotic coefficient ($\phi$):

$$
\ln a_w = -\frac{\Sigma m}{\Omega} \phi
$$

(104)

The thermodynamic properties of water are often discussed in the physical chemistry literature in terms of the osmotic coefficient instead of the activity of water (or the mole fraction activity coefficient of water).

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 relevant equations are:
The Debye-Hückel parameter $A_\phi$ is related to the more familiar $A_{\gamma,10}$ by:

$$A_\phi = \frac{2.3034 A_{\gamma,10}}{3}$$

The parameter $b$ is assigned a constant value of 1.2 (Pitzer, 1973). Theoretically, this is the product $d_B$, thus the hard core diameter at 25°C is effectively fixed at a value of about 3.65 Å (and somewhat different values at other temperatures). Differences in the hard core diameters of various ions in solution are not explicitly accounted for (this is the case also in the Davies equation). However, the interaction coefficient terms of the equation effectively compensate for this. A very important feature of the Debye-Hückel-osmotic model is that it, like the Debye-Hückel-charging model, is consistent with the Debye-Hückel limiting law:

$$\log \gamma_i \to -A_{\gamma,10} z_i^2 \sqrt{I} \quad \text{as} \quad I \to 0$$

### 3.5.2. Solutions of Electrolytes

In a pure solution of aqueous neutral electrolyte $MX$, the following combinations of interaction coefficients are observable:

$$B_{MX} (I) = \lambda_{MX} (I) + \left| \frac{z_M}{2z_M} \right| \lambda_{MM} (I) + \left| \frac{z_M}{2z_X} \right| \lambda_{XX} (I)$$

$$C_{MX}^\phi = 3 \left( \left| \frac{z_M}{z_M} \right|^2 \mu_{MMX} + \left| \frac{z_M}{z_X} \right|^2 \mu_{MXX} \right)$$

For example, the osmotic coefficient for such a solution can be written in the form (Pitzer, 1973):

$$\phi - 1 = \frac{|z_M z_X|}{2} (I f'(I) - f(I))$$

$$+ \left( \frac{2 \gamma_M \gamma_X}{\gamma_{MX}} \right) B_{MX}^\phi (I) m_{MX} + \left( \frac{2 (\gamma_M \gamma_X)^{3/2}}{\gamma_{MX}} \right) C_{MX}^\phi m_M^2$$

Appearing in this equation is $B_{MX}^\phi$, which is given by:
Here $B'_{MX}(I)$ is the derivative of $B_{MX}(I)$ with respect to the ionic strength. The ionic strength dependence of $B^\phi_{MX}$ was defined by Pitzer (1973) to take the following form:

$$B^\phi_{MX}(I) = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} e^{-\alpha \sqrt{I}}$$

(113)

where $\alpha$ was assigned a constant value of 2.0. $\beta_{MX}^{(0)}$ and $\beta_{MX}^{(1)}$, along with $C^\phi_{MX}$, are parameters whose values are determined by fitting experimental data, such as for the osmotic coefficient. Corresponding to the above equation is:

$$B_{MX}(I) = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} g(\alpha \sqrt{I})$$

(114)

where:

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

(115)

Pitzer and Mayorga (1974) proposed a description for $B^\phi_{MX}$ in the case of 2:2 electrolytes that is based on an additional fitting parameter:

$$B^\phi_{MX}(I) = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} e^{-\alpha_1 \sqrt{I}} + \beta_{MX}^{(2)} e^{-\alpha_2 \sqrt{I}}$$

(116)

Here $\alpha_1$ is assigned a value of 1.4 and $\alpha_2$ one of 12.0 and $\beta_{MX}^{(2)}$ is the additional fitting parameter. Corresponding to this is:

$$B_{MX}(I) = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} g(\alpha_1 \sqrt{I}) + \beta_{MX}^{(2)} g(\alpha_2 \sqrt{I})$$

(117)

We consider first the exponential function in eqs (113) and (117). This is shown in Figure 2 for the three commonly used values of $\alpha$. At zero ionic strength, this function has a value of unity. Thus, $B^\phi_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)}$ or $B^\phi_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} + \beta_{MX}^{(2)}$. The magnitude of each term containing $\beta_{MX}^{(1)}$ or $\beta_{MX}^{(2)}$ decreases exponentially as the ionic strength increases, approaching zero as the ionic strength approaches infinity (a limit which is not of physical interest). Most of the decay takes place in the very low ionic strength range. Thus, the terms in $\beta_{MX}^{(1)}$ and $\beta_{MX}^{(2)}$ are important parts of the model, even in dilute solutions.
The function $g(x)$ is shown in Figure 3 for the three commonly used $\alpha$ values. It resembles the above exponential function, though it does not decay quite so rapidly. This function may be expanded as follows:

$$g(x) = 1 - 2 \left( \frac{2x}{3!} - \frac{3x}{4!} + \frac{4x^2}{5!} - \frac{5x^3}{6!} + \ldots \right)$$  

This shows that $g(x) = 1$ at $x = 0$ ($I = 0$). Thus, at zero ionic strength, $B_{MX}^{(0)} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)}$ or $B_{MX}^{(1)} = \beta_{MX}^{(0)} + \beta_{MX}^{(0)} + \beta_{MX}^{(2)}$. It can be shown that $g(x)$ approaches zero as $x$ (and $I$) approach infinity.

The development thus far shows that there are two major categories of interaction coefficients. The $\lambda_{ij}$ and the $\mu_{ijk}$ in terms of which the theoretical equations were originally derived are what we will call the primitive interaction coefficients. The observable combinations of these, such as $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, $\beta_{MX}^{(2)}$, and $C_{MX}^{(0)}$, are what we will call the observable interaction coefficients. This latter kind of interaction coefficient represents the model data that are reported for the various systems for which Pitzer’s equations have been fit to experimental data.
It is possible to rewrite the equations for $\ln \gamma_i$ and $\ln a_{iw}$ in complex mixtures in terms of the observable interaction coefficients. An example of such equations was suggested by Pitzer (1979) and adopted with changes in notation by Harvie, Møller, and Weare (1984). These equations are much more complex than the original form written in terms of the primitive interaction coefficients. They have been incorporated into computer codes, such as that of Harvie, Møller, and Weare (1984), PHRQPITZ (Plummer et al., 1988), and SOLMINEQ.88 (Perkins et al., 1990). As noted in the previous section, there is no unique way to construct equations for single-ion activity coefficients. Furthermore, direct usage of such equations constitutes implicit adoption of a corresponding pH scale. In the case of the single-ion activity coefficient equation suggested by Pitzer, this could be termed the "Pitzer" scale.

The equations for $\ln \gamma_i$ and $\ln a_{iw}$ which are evaluated in EQ3/6 are those written in terms of the primitive interaction coefficients. The set of these which is used is not the generalized theoretical set, which is not obtainable for the reasons discussed previously, but a practical set that is obtained by mapping the set of reported observable interaction coefficients using a set of equations that contain arbitrary conventions. These mapping equations imply a $pH$ scale. We will show that the conventions chosen here match those suggested by Pitzer (1979), so this implied $pH$ scale is identical to his.

The basic guides to choosing such mapping conventions are pleasing symmetries and the desirability of minimizing the number of conventional primitive interaction coefficients with non-zero values. In the case of the second order coefficients, both of these considerations suggest the following definitions:
\[ \lambda_{MM}(I) = 0 \quad (119) \]
\[ \lambda_{XX}(I) = 0 \quad (120) \]
\[ \lambda_{MX}(I) = B_{MX}(I) \quad (121) \]

Analogous to the formulas used to describe \( B_{MX} \), one may write:

\[ \lambda_{MX}(I) = \lambda_{MX}^{(0)} + \lambda_{MX}^{(1)}(\alpha_1 \sqrt{I}) \quad (122) \]

or:

\[ \lambda_{MX}(I) = \lambda_{MX}^{(0)} + \lambda_{MX}^{(1)}(\alpha_1 \sqrt{I}) + \lambda_{MX}^{(2)}(\alpha_2 \sqrt{I}) \quad (123) \]

From the principle of corresponding terms, it follows that the corresponding mapping equations are:

\[ \lambda_{MM}^{(n)} = 0 \quad \text{for } n = 0, 2 \quad (124) \]
\[ \lambda_{XX}^{(n)} = 0 \quad \text{for } n = 0, 2 \quad (125) \]
\[ \lambda_{MX}^{(n)} = \beta_{MX}^{(n)} \quad \text{for } n = 0, 2 \quad (126) \]

Evaluation of the equations for \( \ln y \) and \( \ln a_v \) also requires the ionic strength derivatives of the \( \lambda_{ij} \) coefficients. These are given by:

\[ \lambda'_{MX}(I) = \lambda_{MX}^{(1)}g'(x)\left(\frac{\alpha}{2\sqrt{I}}\right) \quad (127) \]

or:

\[ \lambda'_{MX}(I) = \lambda_{MX}^{(1)}g'(x)\left(\frac{\alpha_1}{2\sqrt{I}}\right) + \lambda_{MX}^{(2)}g'(x)\left(\frac{\alpha_2}{2\sqrt{I}}\right) \quad (128) \]

where \( g'(x) \) is the derivative of \( g(x) \) (with respect to \( x \), not \( I \)), given by

\[ g'(x) = -\left(\frac{4}{x^3}\right)(1 - e^{-x}(1 + x + \frac{x^2}{2})) \quad (129) \]

The principle of pleasing symmetry suggests the following mapping equations for dealing with the \( C_{MX}^\phi \) parameter:
The two \( \mu \) coefficients are then related by:

\[
\frac{\mu_{MMX}}{z_M} = \frac{\mu_{MXX}}{|z_X|} \quad \text{(132)}
\]

These are in fact the mapping equations used in EQ3/6. However, the principle of minimizing the number of conventional primitive interaction coefficients would suggest instead mapping relations such as:

\[
\mu_{MMX} = \frac{1}{3} \frac{z_M}{|z_X|} C_{MX}^\phi \quad \text{(133)}
\]

\[
\mu_{MXX} = 0 \quad \text{(134)}
\]

Note that with this set of mapping relations, a different pH scale would be implied.

In mixtures of aqueous electrolytes with a common ion, two additional observable combinations of interaction coefficients appear (Pitzer, 1973; Pitzer and Kim, 1974):

\[
\theta_{MM'}(I) = \lambda_{MM'}(I) - \left(\frac{z_{M'}}{2z_M}\right) \lambda_{MM}(I) - \left(\frac{z_M}{2z_{M'}}\right) \lambda_{M'M'}(I) \quad \text{(135)}
\]

and:

\[
\psi_{MM'X} = 6 \mu_{MM'X} - \left(\frac{3z_{M'}}{z_M}\right) \mu_{MMX} - \left(\frac{3z_M}{z_{M'}}\right) \mu_{M'M'X} \quad \text{(136)}
\]

Here \( M \) and \( M' \) are two cations and \( X \) is the anion, or \( M \) and \( M' \) are two anions and \( X \) is the cation. From previously adopted mapping conventions, it immediately follows that the corresponding mappings are given by:

\[
\lambda_{MM'}(I) = \theta_{MM'}(I) \quad \text{(137)}
\]

\[
\mu_{MM'X} = \frac{1}{6} \left(\psi_{MM'X} + \left(\frac{3z_{M'}}{z_M}\right) \mu_{MMX} + \left(\frac{3z_M}{z_{M'}}\right) \mu_{M'M'X}\right) \quad \text{(138)}
\]
In the original formulation of Pitzer's equations (Pitzer, 1973), the $\theta_{MM'}$ coefficient is treated as a constant. It was later modified by Pitzer (1975) to take the following form:

$$\theta_{MM'}(I) = S\theta_{MM'} + E\theta_{MM'}(I)$$  \hspace{1cm} (139)$$

$\theta_{MM'}(I)$ corresponds to the $\Phi_{ij}$ of Harvie, Møller, and Weare (1984). The first term is a constant and accounts for short-range effects (this is the $\Phi_{ij}$ of Harvie, Møller, and Weare). The second term, which is the newer part, is entirely theoretical in nature and accounts for higher-order electrostatic effects. Only the $S\theta_{MM'}$ part is obtained by fitting. Corresponding to this is the equation:

$$\lambda_{MM'}(I) = S\lambda_{MM'} + E\lambda_{MM'}(I)$$  \hspace{1cm} (140)$$

The relevant mapping relation is then:

$$S\lambda_{MM'} = S\theta_{MM'}$$  \hspace{1cm} (141)$$

The $E\lambda_{MM'}(I)$ part is obtainable directly from theory (Pitzer, 1975):

$$E\lambda_{MM'} = \frac{z_{M}z_{M'}}{4l} \left( J(x_{MM'}) - \frac{J(x_{MM'})}{2} - \frac{J(x_{MM'})}{2} \right)$$  \hspace{1cm} (142)$$

where:

$$J(x) = \frac{1}{x} \int_{0}^{\infty} \left( 1 + q + \frac{q^2}{2} - e^{q} \right) y^2 dy$$  \hspace{1cm} (143)$$

in which:

$$q = -\left( \frac{x}{y} \right) e^{-y}$$  \hspace{1cm} (144)$$

and:

$$x_{ij} = 6z_{i}z_{j}A_{i}^{\Phi}A_{j}^{\Phi}$$  \hspace{1cm} (145)$$

The derivative of $E\lambda_{MM'}(I)$ is given by:
Expansion of $J(x)$ gives (Pitzer, 1975):

$$J(x) = -\left(\frac{x^2}{6}\right) (\ln x + 0.419711) + ...$$

Application of L'Hospital's rule shows that $J(x)$ goes to zero as $x$ goes to zero (hence also as the ionic strength goes to zero). $J(x)$ is a monotonically increasing function. So is $J'(x)$, which approaches a limiting value of 0.25 as $x$ goes to infinity. The function $J(x)$ and its derivative are approximated in EQ3/6 by a Chebyshev polynomial method suggested by Harvie and Weare (1980). This method is described in detail by Harvie (1981, Appendix B, in which $J(x)$ is referred to as $J_0(x)$); this method is also described in the review by Pitzer (1987, p. 131-132).

Pitzer (1979) showed that substitution of the observable interaction coefficients into the single-ion activity coefficient equation gives the following result for cation $M$:

$$\ln \gamma_M = z_M^2 \beta + 2 \sum_a m_a \left[ B_{Ma} + (\Sigma mz) C_{Ma} \right] +$$

$$2 \sum_c m_c \theta_{Mc} + \sum_a m_a \left[ z_M^2 B_{ca} + z_M C_{ca} + \Psi_{Mca} \right] +$$

$$\frac{1}{2} \sum_a m_a \left[ z_M^2 \theta_{aa} + \Psi_{Maa} \right] + \frac{z_M^2}{2} \sum_c m_c \left[ \psi_{cc} + \theta'_{cc} \right] +$$

$$z_M \left\{ \sum_c \frac{m_c \lambda_{cc}}{z_c} - \sum_a \frac{m_a \lambda_{aa}}{|z_a|} + \frac{3}{2} \sum_c \sum_a m_c m_a \left( \frac{\mu_{cca}}{z_c} - \frac{\mu_{ca}}{|z_a|} \right) \right\}$$

Here $a$ denotes anions, $c$ denotes cations, and:

$$f' = \frac{f}{2}$$

$$C_{MX} = \frac{c_{MX}}{2 \sqrt{z_M^2 x_M}}$$

$$\Sigma m_z = \sum_c m_c m_c$$
(The single-ion equation for an anion is analogous). As pointed out by Pitzer, the unobservability of single-ion activity coefficients in his model lies entirely in the last term (the fourth line) of the equation and involves the primitive interaction coefficients \( \lambda_{cc}, \lambda_{aa}, \mu_{ca}, \) and \( \mu_{ca}. \) His suggested conventional single-ion activity coefficient equation is obtained by omitting this part. This requires the affected primitive interaction coefficients to be treated exactly as in the previously adopted mapping equations. This approach could in fact have been used to derive them.

In theory, the relevant data required to evaluate Pitzer's equations for complex mixtures of relatively strong aqueous electrolytes can all be obtained from measurements of the properties of pure aqueous electrolytes (giving the observable interaction coefficients \( \beta^{(0)}_{MX}, \beta^{(1)}_{MX}, \beta^{(2)}_{MX}, \) and \( C_{MX}^\phi \)) and mixtures of two aqueous electrolytes having a common ion (\( S_{\theta_{MM'}} \) and \( \psi_{MM'X}. \))

There is one peculiarity in this fitting scheme in that \( S_{\theta_{MM'}} \) is obtainable from more than one mixture of two electrolytes having a common ion, because this parameter does not in theory depend on that ion. Thus, the value adopted may have to be arrived at by simultaneously considering the experimental data for a suite of such mixtures.

3.5.3. Solutions of Electrolytes and Nonelectrolytes

In general, it is necessary to consider the case of solutions containing nonelectrolyte solute species in addition to ionic species. Examples of such uncharged species include molecular species such as \( O_2(aq), \) \( CO_2(aq), \) \( CH_4(aq), \) \( H_2S(aq), \) \( C_2H_5OH(aq), \) and \( SiO_2(aq); \) strongly bound complexes, such as \( HgCl_2(aq) \) and \( UO_2^2(aq); \) and weakly bound ion pairs such as \( CaCO_3(aq), \) and \( CaSO_4(aq). \) The theoretical treatment of these kinds of uncharged species is basically the same. There are practical differences, however, in fitting the models to experimental data. This is simplest for the case of molecular neutral species. In the case of complexes or ion pairs, the models are complicated by the addition of corresponding mass action equations.

The treatment of solutions of electrolytes using Pitzer's equations is quite standardized. In such solutions, there is one generally accepted relation for describing single-ion activity coefficients, though it may be expressed in various equivalent forms. Thus, in such solutions there is only one implied "Pitzer" \( pH \) scale. Also, the set of parameters to be obtained by regressing experimental measurements is well established. Unfortunately, this is not the case for the treatment of solutions containing both electrolytes and nonelectrolytes.

Harvie, Möller, 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. Additional modification was made by Felmy and Weare (1986), who extended the Harvie, Möller, and Weare model to include borate as a component. The Felmy and Weare equation for the activity of water (obtained from their equation for the osmotic coefficient) is:
\[ \ln a_w = -\frac{\Sigma m}{\Omega} - \frac{2}{\Omega} \left( If - f \right) + \sum_c \sum_a m_c m_a (B_{ca}^\phi \Omega Z_{ca}) \]

\[ + \sum_c \sum_{c'>c} m_c m_{c'} (\Phi_{cc'}^\phi \Omega + \sum_a m_a \psi_{aa'c'}) \]

\[ + \sum_a \sum_{a'>a} m_a m_{a'} (\Phi_{aa'}^\phi \Omega + \sum_c m_c \psi_{cc'a'}) \]

\[ + \sum_n \sum_c m_n m_c \lambda_{nc} + \sum_n \sum_a m_n m_a \lambda_{na} + \sum_n \sum_c m_n m_c m_a \zeta_{nca} \]

(152)

In this equation, \( c \) denotes a cation and \( a \) an anion, and the following definitions are introduced:

\[ Z = \sum_i |z_i| m_i \]  

(153)

\[ \Phi_{ij} = S_{ij} + \sum \Psi_{ij} (I) + \sum I \Theta_{ij} (I) \]  

(154)

The first three lines are equivalent to the mixture formulation given by Pitzer (1979). The fourth line (last three terms) is the new part. Here \( n \) denotes a neutral species, \( \lambda_{nc} \) and \( \lambda_{na} \) are second order interaction coefficients describing neutral species-ion interactions, and \( \zeta_{nca} \) is an observable third order coefficient. These new interaction coefficients are treated as constants. The terms in \( \lambda_{nc} \) and \( \lambda_{na} \) were introduced by Harvie, Møller, and Weare (1984) to treat the species \( CO_2(aq) \). The term in \( \zeta_{nca} \) was put in by Felmy and Weare (1986) and is a third order interaction coefficient. It was necessary to include it in the equations to account for interactions involving the species \( B(OH)_3(aq) \).

The corresponding single-ion equation for cation \( M \) takes the following form:

\[ \ln \gamma_M = 2 \sum_c m_c (2 \Phi_{Mc} + \sum_a m_a \psi_{Mca}) \]

\[ + \sum_a m_a (2 \Phi_{Mc} + \sum_a m_a \psi_{Mca}) \]

\[ + \sum_a \sum_{a'>a} m_a m_{a'} \psi_{Maa'} + \sum_n \sum_c m_n m_c \zeta_{naM} \]

(155)
Here $\Phi_{ij}$ is the $\theta_{ij}$ of the earlier notation and:

$$F = \frac{1}{2} \sum_c \sum_a m_c m_a B'_{ca} + \sum_c \sum_{c' > c} m_c m_{c'} \Phi'_{cc'}$$

$$+ \sum_a \sum_{a' > a} m_a m_{a'} \Phi'_{aa'}$$

(156)

The first three lines are equivalent to Pitzer's suggested single-ion activity coefficient equation. The fourth line (last two terms) is the new part. The corresponding equation for anions is analogous. The corresponding equation for the $N$-th neutral species is:

$$\ln \gamma_N = 2 \sum_c m_c \lambda_{Nc} + 2 \sum_a m_a \lambda_{Na} + \sum_c \sum_a m_c m_a \zeta_{Nca}$$

(157)

To deal with the fact that $\lambda_{nc}$ and $\lambda_{na}$ are only observable in combination, Harvie, Møller, and Weare (1984) adopted the convention that:

$$\lambda_{N, H} = 0$$

(158)

These equations were presented for the modeling of specific systems, and are not completely general. They are missing some terms describing interactions involving neutral species. A set of complete equations is given by Clegg and Brimblecombe (1990). Their equation for the activity coefficient of a neutral solute species is:

$$\ln \gamma_N = 2 \sum_n m_n \lambda_{Nn} + 2 \sum_c m_c \lambda_{Nc} + 2 \sum_a m_a \lambda_{Na}$$

$$+ 6 \sum_n \sum_c m_n m_c \mu_{Nnc} + 6 \sum_n \sum_a m_n m_a \mu_{Nna}$$

$$+ 3 \sum_c m_c^2 \mu_{Ncc} + 3 \sum_a m_a^2 \mu_{Naa} + 6 \sum_c \sum_a m_c m_a \mu_{Nca}$$

$$+ 6 \sum_c \sum_{c' > c} m_c m_{c'} \mu_{Ncc'} + 6 \sum_{a' > a} m_a m_{a'} \mu_{Na'a}$$

$$+ 3 \sum_n m_n^2 \mu_{Nnn} + 6 \sum_{n \neq N} m_N m_n \mu_{NNn} + 6 \sum_{n \neq N} \sum_{n' \neq N} m_n m_{n'} \mu_{NNnn'}$$

(159)

This is a complete and general representation of the activity coefficient of a neutral species in terms of all possible second order and third order primitive interaction coefficients. The first line of this equation contains the same terms in $\lambda_{nc}$ and $\lambda_{na}$ as appear in the Felmy-Weare equation. This line is augmented by an addition term which describes second order interactions among neutral species (and which was also pointed out by Pitzer, 1987). The third line in this equation is
equivalent to the term in $\zeta_{Nca}$ that appears in the Felmy-Weare equation. Clegg and Brimblecombe (1990) have pointed out that this observable interaction coefficient is related to the corresponding primitive interaction coefficients by the relation:

$$\zeta_{NMX} = 6\mu_{NMX} + \frac{3|z_x|}{z_M} \mu_{NMN} + \frac{3z_M}{|z_x|} \mu_{NXX}$$

(160)

The second, fourth, and fifth lines consist of terms not found in the Felmy-Weare equation.

In a solution of a pure aqueous nonelectrolyte, the activity coefficient of the neutral species takes the form:

$$\ln \gamma_N = 2m_N \lambda_{NN} + 3m_N^2 \mu_{NNN}$$

(161)

This activity coefficient is directly observable. Hence the two interaction coefficients on the right hand side are also observable. In a study of the solubility of aqueous ammonia, Clegg and Brimblecombe (1989) found that the term including $\mu_{NNN}$ was significant only for concentrations greater than 25 molal (a solution containing more ammonia than water). They therefore dropped this term and reported model results only in terms of $\lambda_{NN}$. Similarly, Barta and Bradley (1985) found no need for a $\mu_{NNN}$ term to explain the data for pure solutions of $CO_2(aq)$, $H_2S(aq)$, and $CH_4(aq)$, and no such term was apparently required by Felmy and Weare (1986) to explain the data for $B(OH)_3(aq)$. Pitzer and Silvester (1976) report a significant $P_{NNN}$ term for undissociated phosphoric acid. This result now appears somewhat anomalous and has not been explained. The bulk of the available data, however, suggest that the $\mu_{NNN}$ term is generally insignificant in most systems of geochemical interest and can be ignored without loss of accuracy.

This result suggests that in more complex solutions, terms in $\lambda_{NN}$, $\mu_{NNN}$, $\mu_{NNN}$, and $\mu_{NNN}$ can also often be ignored. While there may be solutions in which the full complement of these terms are significant, one could argue that they must be so concentrated in nonelectrolyte components that they have little relevance to the study of surface waters and shallow crustal fluids (though some deep crustal fluids are rich in $CO_2$). Furthermore, one could argue that to address such solutions, it would be more appropriate to use a formalism based on a different kind of expansion than the one used in the present treatment (see Pabalan and Pitzer, 1990).

In an aqueous solution consisting of one nonelectrolyte and one electrolyte, the activity coefficient of the neutral species takes the form:

$$\ln \gamma_N = 2m_N \lambda_{NN} + 2(m_M \lambda_{NM} + m_X \lambda_{NX})$$

$$+ 6m_N (m_M \mu_{NNM} + m_X \mu_{NXX}) + m_M m_N \mu_{NMX} + 3m_N^2 \mu_{NNN}$$

(162)

Three new terms appear. The resemblance of the term in $\lambda_{NM}$ and $\lambda_{NX}$ to a traditional Setchenow term has been pointed out by various workers (e.g., Felmy and Weare, 1986; Pitzer, 1987). Work reported by Clegg and Brimblecombe (1989, 1990) for a number of such systems containing am-
monia showed that the most important of the three new terms were the second \((\lambda_{NM}, \lambda_{NX})\) term and the third \((\mu_{NNM}, \mu_{NNX})\) term. They defined these using the following conventions:

\[
\lambda_{N, CR} = 0 \quad (163)
\]

\[
\mu_{N, N, CR} = 0 \quad (164)
\]

Note that the first of these conventions conflicts with the corresponding convention adopted by Harvie, Möller, and Weare (1984), though it matches that proposed by Pitzer and Silvester (1976) in a study of the dissociation of phosphoric acid, a weak electrolyte. Clegg and Brimblecombe found that in one system, the use of the fourth \((\zeta_{NMX})\) term was also required, though the contribution was relatively small. No use was required of the last \((\mu_{NNN})\) term, as was shown by fitting the data for pure aqueous ammonia.

There seems to be some disagreement in the literature regarding the above picture of the relative significance of the \((\mu_{NNM}, \mu_{NNX})\) term versus that of the \((\zeta_{NMX})\) term, although the seemingly contradictory results involve nonelectrolytes other than ammonia. We have noted above that Felmy and Weare (1986) used a \((\zeta_{NMX})\) term to explain the behavior of boric acid-electrolyte mixtures. It is not clear if they considered the possibility of a \((\mu_{NNM}, \mu_{NNX})\) term. Pitzer and Silvester (1976) found no apparent need to include a \((\mu_{NNM}, \mu_{NNX})\) term or a \((\zeta_{NMX})\) term to explain the thermodynamics of phosphoric acid dissociation in electrolyte solutions. The data on aqueous silica in electrolyte solutions of Chen and Marshall (1981), discussed by Pitzer (1987), require a \((\zeta_{NMX})\) term, but no \((\mu_{NNM}, \mu_{NNX})\) term. A similar result was obtained by Barta and Bradley (1985) for mixtures of electrolytes with \(CO_2(aq), H_2S(aq)\), and \(CH_4(aq)\). Simonson et al. (1987) interpret data for mixtures of boric acid with sodium borate and sodium chloride and of boric acid with potassium borate and potassium chloride exclusively in terms of the first \((\lambda_{NN})\) and second \((\lambda_{NM}, \lambda_{NX})\) terms, using neither of the third order terms for nonelectrolyte-electrolyte interactions.

The \((\mu_{NNM}, \mu_{NNX})\) term can only be observed (and hence is only significant) when the concentrations of both the nonelectrolyte and the electrolyte are sufficiently high. In contrast, evaluating the \((\zeta_{NMX})\) term requires data for high concentrations of the electrolyte, but low concentrations of the nonelectrolyte will suffice. Some nonelectrolytes, such as aqueous silica, are limited to low concentrations by solubility constraints. Thus, the results of Chen and Marshall (1981) noted by Pitzer (1987) are not surprising. In the case of more soluble nonelectrolytes, the range of the available experimental data could preclude the evaluation of the \((\mu_{NNM}, \mu_{NNX})\) term. This may be why Pitzer and Silvester (1976) reported no need for such a term to describe the data for mixtures of electrolytes with phosphoric acid and why Barta and Bradley (1985) found no need for such a term for similar mixtures of electrolytes with \(CO_2(aq), H_2S(aq), \) and \(CH_4(aq)\). The data analyzed by Felmy and Weare (1986) correspond to boric acid concentrations of about one molal, which may not be high to observe this term (or require its use). In the case of Simonson et al. (1987), who also looked at mixtures of electrolytes and boric acid, the need for no third order terms describing nonelectrolyte-electrolyte interactions is clearly due to the fact that the concentrations of boric acid were kept low to avoid the formation of polyborate species.
The equations for solutions containing nonelectrolytes can be considerably simplified if the model parameters are restricted to those pertaining to solutions of pure aqueous nonelectrolytes and mixtures of one nonelectrolyte and one electrolyte. This is analogous to the usual restriction in treating electrolyte solutions, in which the parameters are restricted to those pertaining to solutions of two electrolytes with a common ion. Furthermore, it seems appropriate as well to drop the terms in $\mu_{NN}$. The equation for the activity coefficient of a neutral electrolyte in electrolyte-nonelectrolyte mixtures then becomes:

$$
\ln \gamma_N = 2m_N\lambda_{NN} + 2\left( \sum_c m_c\lambda_{NC} + \sum_a m_a\lambda_{Na} \right) + 6m_N \left( \sum_c m_c\mu_{NNc} + \sum_a m_a\mu_{NNa} \right) + \sum_c \sum_a m_c m_a \zeta_{Nca}
$$

(165)

The reduction in complexity is substantial. In the context of using Pitzer's equations in geochemical modeling codes, this level of complexity is probably quite adequate for dealing with non-electrolytes in a wide range of application.

If a higher level of complexity is required, the next step is probably to add in terms in $\mu_{NN}$ and $\lambda_{NN}$. The first of these has been discussed previously and is obtained from data on pure aqueous nonelectrolytes. The second must be obtained from mixtures of two aqueous electrolytes (one could argue that this is also analogous to the treatment of electrolytes). This higher level of complexity may suffice to deal with at least some CO$_2$-rich deep crustal fluids and perhaps other fluids of interest in chemical engineering. However, an even higher level of complexity would probably be best addressed by a formalism based on an alternate expansion, as noted earlier.

The observability and mapping issues pertaining to the remaining parameters may be dealt with as follows. In the case of $\lambda_{NN}$, no mapping relation is required because this parameter is directly observable. The same is true of $\mu_{NN}$ and $\lambda_{NN}$, if the higher level of complexity is required.

The $\lambda_{NM}$ and $\lambda_{NX}$, and $\mu_{NNM}$ and $\mu_{NNX}$, are only observable in combinations, but can be dealt with by adopting the following respective conventions:

$$
\lambda_{N,J} = 0
$$

(166)

$$
\mu_{N,N,J} = 0
$$

(167)

where $J$ is a reference ion ($J = H^+$ as suggested by Felmy and Weare, 1986; $J = Cl^-$ as suggested by Pitzer and Silvester, 1976, and Clegg and Brimblecombe, 1989, 1990). In any data file used to support code calculations, the choice of reference ion must be consistent. This may require the recalculation of some published data.

The $\zeta_{NNM}$ parameter is observable and can be mapped into primitive form by adopting the following conventions:

$$
\mu_{NNM} = 0
$$

(168)
These relations are analogous to those defined for the $C_{MX}^{\phi}$ parameter.

The above conventions correspond well with the current literature on the subject. However, the treatment of the $\lambda_{NM}$ and $\lambda_{NX}$, and $\mu_{NNM}$ and $\mu_{NNX}$, though valid and functional, still stands out in that it is not analogous to, or a natural extension of, the conventions which have been universally adopted in the treatment of electrolyte solutions. The logical extension, of course, is to define observable interaction coefficients to represent the primitive coefficients which can only be observed in combination, and to then follow Pitzer (1979) in determining exactly which parts of the theoretical equations constitute the non-observable part. The conventions would then be defined so as to make these parts have zero value.

The suggested process can be shown to be consistent with the above mapping conventions for all the other coefficients treated above, including $\zeta_{NMX}$. However, the process which worked so nicely for electrolytes fails to work for $\lambda_{NM}^{\phi} \lambda_{NX}$, and $\mu_{NNM}^{\phi} \mu_{NNX}$. We will demonstrate this for the case of the $\lambda_{NM}^{\phi} \lambda_{NX}$. Application of the above equation to the case of an aqueous mixture of a neutral species ($N$) and a neutral electrolyte ($MX$) immediately shows that the corresponding observable combination of primitive interaction coefficients is given by:

$$L_{NMX} = |z_X| \lambda_{NM} + z_M \lambda_{NX}$$

In such a system, the activity coefficient of the neutral species can be written as:

$$\ln \gamma_N = \frac{2}{z_M + |z_X|} \nu_{MX} L_{NMX}^{\phi NMX} m_{MX}$$

In the manner of Pitzer (1979), one can show that the relevant term in the single-ion activity coefficient for cation $M$ expands in the following manner:

$$2 \sum_{n} m_n \lambda_{nM} = 2 \sum_{n} m_n \frac{L_{nMX}^{\phi}}{|z_X|} - 2 \sum_{n} m_n \frac{z_M}{|z_X|} \lambda_{nX'}$$

where $X'$ is some reference anion. When $X'$ is $Cl^-$, we have the convention proposed by Pitzer and Silvester (1976) and followed by Clegg and Brimblecombe (1989, 1990). The first term on the right hand side is the relevant observable part; the second term is the non-observable part. Following the logic of Pitzer (1979), we could set the second term to zero. This would have the effect of defining the following mapping relations:

$$\lambda_{NX'} = 0$$
Although this makes the relevant non-observable part vanish in the single-ion activity coefficient equation for all cations, it forces the complementary part in the corresponding equation for anions to not vanish, as we will now show. The relevant part of the anion equation gives the following analogous result:

$$\lambda_{NM} = \frac{L_{NMX}^*}{|z_X|}$$  \hspace{1cm} (175)

where $M'$ is some reference cation. As before, the second term on the right hand side is the non-observable part. Using the above mapping equation for $X_{NM}$, this can be transformed to:

$$2\sum_n m_n \lambda_{nX} = 2\sum_n m_n \frac{L_{nM'X}}{z_{M'}} - 2\sum_n m_n \frac{|z_X|}{z_{M'}} \lambda_{nM'}$$  \hspace{1cm} (176)

Thus, under the conventions defined above, the non-observable part of the single-ion activity coefficient equation for anions does not vanish.

There are alternatives, but none are particularly outstanding. For example, one could reverse the situation and make analogous conventions so that the non-observable part of the anion equation vanishes, but then the non-observable part of the cation equation would not vanish. When $M'$ is $H^+$, we have the convention proposed by Felmy and Weare (1986). One could also try a symmetrical mapping, based on the following relation:

$$X_{NM} = \frac{X_{NX}}{z_X}$$  \hspace{1cm} (178)

This would lead to the following mapping relations:

$$\lambda_{NM} = \frac{z_M}{|z_X|} \lambda_{NX}$$  \hspace{1cm} (179)

$$\lambda_{NM} = \frac{z_M}{(z_M + |z_X|)} L_{NMX}$$

$$\lambda_{NX} = \frac{|z_X|}{(z_M + |z_X|)} L_{NMX}$$  \hspace{1cm} (180)

Unfortunately, this would lead to a non-vanishing non-observable part in the equations for both cations and anions.

### 3.5.4. Temperature and Pressure Dependence

Pitzer's equations were originally developed and applied to conditions of 25°C and atmospheric pressure (e.g., Pitzer and Kim, 1974). The formalism was subsequently applied both to activity coefficients under other conditions and also to related thermodynamic properties which reflect
the temperature and pressure dependence of the activity coefficients (see the review by Pitzer, 1987).

The first effort to extend the Pitzer formalism to high temperature was a detailed study of the properties of aqueous sodium chloride (Silvester and Pitzer, 1977). In this study, the data were fit to a complex temperature function with up to 21 parameters per observable interaction coefficient and which appears not to have been applied to any other system. In general, the early efforts concerning the temperature dependence of the activity coefficients focused mainly on estimating the first derivatives of the observable interaction coefficient parameters with respect to temperature (e.g., Silvester and Pitzer, 1978). The results of the more detailed study of sodium chloride by Silvester and Pitzer (1977; see their Figures 4, 5, and 6) suggest that these first derivatives provide an extrapolation that is reasonably accurate up to about 100°C.

In more recent work, the temperature dependence has been expressed in various 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-K-Mg-Cl-SO₄·OH-H₂O which appears to be generally valid up to about 200°C. Pabalan and Pitzer (1988) used equations of this type to build a model for the system Na-Cl-SO₄-OH-H₂O that extends to 300°C. Greenberg and Møller (1989), using an elaborate compound temperature function, have constructed a model for the Na-K-Cl-SO₄-H₂O 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-K-Ca-Mg-Cl-SO₄-H₂O system at temperatures in the range -60 to 25°C.

The pressure dependence of activity coefficients has also been looked at in the context of the Pitzer formalism. For descriptions of recent work, see Kumar (1986), Connaughton, Millero, and Pitzer (1989), and Monnin (1989).

3.5.5. Practical Aspects

In practice, the matter of obtaining values for the observable interaction coefficients is more complicated. Not all models based on Pitzer’s equations are mutually consistent. Mixing reported data can lead to inconsistencies. For the most part, differences in reported values for the same coefficient are functions of the exact data chosen for use in the fitting process, not just whose data, but what kind or kinds of data as well. Some older reported values for the mixture parameters (e.g., Pitzer, 1979) are based on fits not employing the $E_{\theta MM}$ formalism, which has become firmly entrenched in more recent work.

Some differences in the values of reported Pitzer parameters are due to minor differences in the values used for the $A^0$ Debye-Hückel parameter (e.g., 0.39 versus 0.392; see Plummer et al., 1988, p. 3, or Plummer and Parkhurst, 1990). The general problem of minor discrepancies in this and other limiting law slope parameters has been looked at in some detail by Ananthaswamy and Atkinson (1984). Recently, Archer (1990) has also looked at this problem and proposed a method for adjusting reported Pitzer coefficients for minor changes in Debye-Hückel parameters without resorting to refitting the original experimental data.
There has also been some occasional modification of the basic activity coefficient equations themselves. For example, in treating the activity coefficients of alkali sulfate salts at high temperature, Holmes and Mesmer (1986a, 1986b) changed the recommended value of the $\alpha$ parameter from 2.0 to 1.4. Also Kodytek and Dolejs (1986) have proposed a more widespread usage of the $\beta^{(2)}_{M^2X}$ parameter, based on the empirical grounds that better fits can be obtained for some systems. The usage of this parameter was originally restricted to the treatment of 2:2 electrolytes (Pitzer and Mayorga, 1973).

The formal treatment of speciation in the solutions (assumptions of which species are present) can also lead to different models. Association phenomena were first recognized in the Pitzer formalism in order to deal with phosphoric acid (Pitzer and Silvester, 1976) and sulfuric acid (Pitzer, Roy, and Silvester, 1977). In general, ion pairs have been treated formally as non-existent. An exception is in the model of Harvie, Møller, and Weare (1984), who employ three ion pair species: $CaCO_3(aq)$, $MgCO_3(aq)$, and $MgOH^+$. Components which form strong complexes have received relatively little attention in the Pitzer formalism, presumably because of the much greater experimental data requirements necessary to evaluate the greater number of parameters associated with the greater number of species. However, Millero and Byrne (1984) have used Pitzer's equations to develop a model of activity coefficients and the formation of lead chloro complexes in some concentrated electrolyte solutions. Huang (1989) has also recently looked at some examples of complex formation in the context of the Pitzer formalism. However, because strong complexing cannot be represented even mathematically by the interaction coefficient formalism without taking explicit account of the associated chemical equilibria, and because such models are more difficult to develop, the practical application of the Pitzer formalism remains limited mostly to systems of relatively strong electrolytes, molecular nonelectrolytes, and a few weak nonelectrolytes.

3.5.6. Pitzer's Equations in EQ3/6: Current Status

The present treatment of Pitzer's equations in EQ3/6 is somewhat limited, particularly in regard to some of the advances that have been made with these equations in the past few years. These limitations have to do with the state of the existing data files which support the use of Pitzer's equations, the treatment of the temperature dependence of the interaction coefficients, and the treatment of neutral solute species.

The **hmw** data file is an implementation of the model of Harvie, Møller, and Weare (1984). This model is restricted to 25°C. The **pit** data file is based mostly on the data summarized by Pitzer (1979). These data include the first order temperature derivatives of the interaction coefficients. The nominal temperature range of this data file is 0-100°C. These data are not based on the currently universally accepted $E^0$ formalism introduced by Pitzer (1975).

EQ3/6 uses or ignores the $E^0$ formalism, depending on the value of a flag parameter on the data file. The temperature dependence, if any, is handled by using first and second order temperature derivatives of the interaction coefficients, which are expected for use at temperatures other than 25°C. The code permits a $\beta^{(2)}_{M^2X}$ parameter to be specified on the data file for any electrolyte. The
α parameters are also provided on the data file for each electrolyte. Thus, non-standard values can be employed if desired.

The temperature dependence is presently limited to a representation in terms of a second-order Taylor’s series in temperature. This requires the presence on the supporting data file of first and second temperature derivatives (see the EQPT User’s Guide, Daveler and Wolery, 1992). No provision has yet been made for the more sophisticated representations proposed for example by Pabalan and Pitzer (1987) or Spencer, Møller, and Weare (1990).

EQ3/6 is presently quite limited in terms of the treatment of nonelectrolyte components by means of Pitzer’s equations. This limitation is expressed in the structure of the data files and the mapping relations presently built into the EQPT data file preprocessor. These are presently set up to deal only with electrolyte parameters. However, it is possible to enter \( \lambda_{NN}, \lambda_{NN'}, \lambda_{NM}, \) and \( \lambda_{NX} \) parameters as though they were \( \beta_{MK}^{(0)} \) parameters. The \( \lambda_{MM} \) and \( \lambda_{NY} \) parameters that are part of the model of Harvie, Møller, and Weare (1984) are included on the hmw data file in this manner.

The present version of EQPT can not handle the \( \xi_{MNX} \) interaction coefficient; however.

The means of storing and representing interaction coefficient data in EQ3/6 deserves some comment. There is a natural tendency to represent \( \lambda_{ij} \) by a two-dimensional array, and \( \mu_{ijk} \) by a three-dimensional array. However, arrays of this type would be sparse (for example, \( \lambda_{ij} = 0 \) for many \( i, j \)). and many of the entries would be duplicates of others (\( \lambda_{ij} = \lambda_{ji}, \) etc.). Therefore, the \( \lambda_{ij} \) are represented instead by three parallel one-dimensional arrays. The first contains the \( \lambda_{ij} \) values themselves, the second contains indices identifying the \( i \)-th species, and the third identifies the \( j \)-th species. The treatment is analogous for \( \mu_{ijk} \), which only requires an additional array to identify the \( k \)-th species. These arrays are constructed from data listed on the data0 data files. Coefficients which must be zero by virtue of the mapping relations or other conventions are not included in the constructed arrays. Also, the storage scheme treats for example \( \lambda_{ij} \) and \( \lambda_{ji} \) as one coefficient, not two.
4. Activity Coefficients of Solid Solution Components

4.1. Introduction

The thermodynamic activities \(a_i\) of solid solution components are always defined on the basis of mole fractions. Thus, they can be described by the product of their mole fractions \(x_i\) and their rational (mole fraction) activity coefficients \(\lambda_i\):

\[
a_i = x_i \lambda_i \tag{181}
\]

The same treatment is typically applied to all components in non-aqueous liquid phases. It is also applied to water in aqueous solutions (cf. Chapter 3).

Mole fraction ideality is the reference ideality when dealing with solid solutions. Therefore, the corresponding excess Gibbs energy is \(G^{EXx}\) (see Chapter 3). The relevant differential equation linking this with the mole fraction activity coefficients is:

\[
\ln \lambda_i = \frac{1}{RT} \frac{\partial G^{EXx}}{\partial n_i}
\]

where \(R\) is the gas constant and \(T\) the absolute temperature. Given an expression for the excess Gibbs energy, this equation gives a guaranteed route to thermodynamically consistent results (cf. Wolery, 1990).

Problems involving the thermodynamic consistency of activity coefficients in non-aqueous phases seem to be uncommon. However, consistency may be tested using various relations, such as the following form of the cross-differentiation rule (cf. Wolery, 1990):

\[
\frac{\partial \ln \lambda_i}{\partial n_j} = \frac{\partial \ln \lambda_j}{\partial n_i} \tag{183}
\]

The issue of sufficiency in proving consistency using this and related equations (Gibbs-Duhem equations and sum rules) is addressed by Wolery (1990).

In most speciation-solubility calculations, the activity coefficients of solid solution components only affect the corresponding calculated saturation indices; they do not change the model of the aqueous solution itself (i.e., the speciation). However, if an equilibrium relation involving a solid solution phase is used as a constraint in defining a speciation-solubility problem, all of the model results may be affected by the choice of activity coefficient model. The results may similarly affected when such a constraint is used in mass transfer calculations including reaction path calculations.

Mixing tends to stabilize a solid solution relative to its end-member components. Thus, an aqueous solution may be supersaturated with respect to a solid solution, yet undersaturated with respect to each of the pure end members. Consequently, a solid solution may form in a system in which some or none of the pure end members would form. This effect is true in the ideal case, in
which the activity coefficient has a value of unity. If the activity coefficient is less than unity, this stabilizing effect is increased. If it is greater than unity, it is lessened.

In general, the activity coefficient of a solid solution component depends on the composition of the solid solution. This is in turn normally expressed in terms of the mole fractions of the components. In order to use an equilibrium constraint involving a solid solution component in a speciation-solubility calculation, the user must provide this composition in order to allow calculation of the activity coefficient of the component involved. In mass transfer calculations involving solid solutions in equilibrium with an aqueous solution, the solid solution composition is itself a subset of the unknowns to be calculated. In speciation-solubility and other kinds of equilibrium calculations, it is necessary to calculate a saturation index for a solid solution which is not presumed to be in equilibrium with the aqueous phase. This presents a problem, because no composition is defined. This is solved in EQ3/6 by finding the composition which maximizes the computed saturation index (Bourcier, 1985, 1989).

In liquid solutions, the solutes may mix over the whole volume of the solution. This type of mixing is sometimes referred to as molecular mixing. It is commonly applied to non-aqueous liquids, such as a solution composed of hydrocarbons. In the ideal case, the activity coefficient of each component is unity. In aqueous solutions and other solutions involving a solvent with a high dielectric constant, this concept is modified to account for ionic dissociation. The concept of molecular mixing has been applied many times to solid solutions (cf. the examples presented later in this chapter), and is predicated on the use of end-member components (for example, calcite \([\text{CaCO}_3]\) and magnesite \([\text{MgCO}_3]\) in magnesian calcite \([\text{Ca,MgCO}_3]\)). The activity coefficients of these components in the non-ideal case are then described using interaction coefficients more or less resembling those used in Pitzer's equations to describe the activity coefficients of aqueous species.

In crystalline solids, mixing tends rather strongly to occur over well-defined sites in the crystal structure (see for example Wood and Fraser, 1977, or Nordstrom and Munoz, 1985). Some ions may mix over more than one kind of site. Vacancies may be involved in the mixing process. They may be created or destroyed by substitutions of one ion for another of different ionic charge. Mixing which takes account of such effects is referred to as site mixing. 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. However, 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 site-mixing models that have been proposed for the various 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 Chapters 3 and 4 of the EQPT User's Guide, Daveler and Wolery, 1992). At present (through the R16 set of data files), only the coin file contains any solid solutions. All of these are treated with ideal site-mixing models (the exception being olivine, which is treated according to a binary 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 cpx array. The elements of this array are represented below as $p_{k\psi}$. In EQ3NR and EQ6, solid solutions are presently ignored unless the option switch iopt4 is set to a value greater than or equal to 1.

The various models presently treated in EQ3/6 are discussed in the following sections. To avoid confusion, we will write the activity, mole fraction, activity coefficient, and related parameters of a solid solution component with a “σψ” subscript in place of “i.” Here σ denotes 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).

### 4.2. 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):

$$ a_{\sigma\psi} = \frac{N_\psi}{x_{\sigma\psi}} $$

(184)

where $N_\psi$ is the site mixing parameter. This formulation is equivalent to:

$$ \log \lambda_{\sigma\psi} = (N_\psi - 1) \log x_{\sigma\psi} $$

(185)

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

The $N_\psi$ 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 $N_\psi = 1$, 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 (184) and (185), 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 $N_\psi$ parameter is obtained from the parameters read from the data file according to:
4.3. **Third-Order Maclaurin Model for a Binary Solution**

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

\[
\begin{align*}
\log \lambda_{1\psi} &= \frac{1}{2.303RT} \left[ -\left( \frac{W_{2\psi}}{2} \right) x_2^2 - \left( \frac{W_{3\psi}}{3} \right) x_2^3 \right] \\
\log \lambda_{2\psi} &= \frac{1}{2.303RT} \left[ -\left( \frac{W_{2\psi} + W_{3\psi}}{2} \right) x_1^2 + \left( \frac{W_{3\psi}}{3} \right) x_1^3 + (W_{1\psi} + \frac{W_{2\psi}}{2} + \frac{W_{3\psi}}{6}) \right]
\end{align*}
\]

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 (187) and (188) 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:

\[
W_{1\psi} = -\frac{W_{2\psi}}{2} - \frac{W_{3\psi}}{6}
\]

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

\[
\begin{align*}
W_{1\psi} &= P_{1\psi} \\
W_{2\psi} &= P_{2\psi} \\
W_{3\psi} &= P_{3\psi}
\end{align*}
\]

However, $W_{1\psi}$ is actually recalculated using eq (189).

4.4. **Regular Solution Model for a Binary Solution**

The regular solution model for a binary solution corresponds to $j_{\text{sol}} = 3$. 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:

\[
\begin{align*}
\log \lambda_{1\psi} &= \frac{1}{2.303RT} W_{\psi} x_2^2 \\
\log \lambda_{2\psi} &= \frac{1}{2.303RT} W_{\psi} x_1^2
\end{align*}
\]
Here $W_\psi$ 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:

$$W_\psi = p_1\psi + p_2\psi T + p_3\psi P$$

Thus, the interaction coefficient in this model can be treated as a function of temperature and pressure. On the 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 $p_3\psi$ parameter, but this is not used.

4.5. Cubic Maclaurin Model for a Binary Solution

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

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

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

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:

$$W_{1\psi} = p_1\psi + p_2\psi T + p_3\psi P$$

$$W_{2\psi} = p_4\psi + p_5\psi T + p_6\psi P$$

4.6. Guggenheim Polynomial Model for a Binary Solution

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

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

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

\[
W_{1\psi} = p_{1\psi} + p_{2\psi}T + p_{3\psi}T^2 \tag{202}
\]

\[
W_{2\psi} = p_{4\psi} + p_{5\psi}T + p_{6\psi}T^2 \tag{203}
\]

\[
W_{3\psi} = p_{7\psi} + p_{8\psi}T + p_{9\psi}T^2 \tag{204}
\]

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.

4.7. Regular Solution Model for a Ternary Solution

The regular solution model for a ternary solution corresponds to $\text{jsol} = 6$. 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:

\[
\log \lambda_{1\psi} = \frac{1}{2.303RT} \left[ W_{12\psi}x_2^2 + W_{13\psi}x_3^2 + (W_{12\psi} - W_{23\psi} + W_{13\psi})x_2x_3 \right] \tag{205}
\]

\[
\log \lambda_{2\psi} = \frac{1}{2.303RT} \left[ W_{12\psi}x_1^2 + W_{23\psi}x_3^2 + (W_{12\psi} - W_{13\psi} + W_{23\psi})x_1x_3 \right] \tag{206}
\]

\[
\log \lambda_{3\psi} = \frac{1}{2.303RT} \left[ W_{13\psi}x_1^2 + W_{23\psi}x_2^2 + (W_{13\psi} - W_{12\psi} + W_{23\psi})x_1x_2 \right] \tag{207}
\]

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:

\[
W_{12\psi} = p_{1\psi} \tag{208}
\]

\[
W_{13\psi} = p_{2\psi} \tag{209}
\]

\[
W_{23\psi} = p_{3\psi} \tag{210}
\]
5. Basis Species: Key Concepts

5.1. Basis Species

In the EQ3/6 system, there is a set of master or basis species. In Chapter 2, this concept was introduced via the notion that one such species is associated with each chemical element and its associated mass balance (e.g., \( Na^+ \) for Na). If oxidation-reduction is considered, one additional species such as \( O_{2(g)} \) for \( e^- \) must be added, which is associated with charge balance. Every remaining species (aqueous, mineral, or gas) is formally associated with a reaction which destroys it. For example, an aqueous complex is paired with its dissociation reaction, and a mineral with its dissolution reaction. The basis species are used as a set of generalized "building blocks" in writing chemical reactions. The reactions are then written in terms of only the single associated species and the set of basis aqueous species.

We will call a basis set as defined above a strict basis set. It is the minimal basis set required for chemical modeling. The number of species in this set, in the general case including a redox species, is given by:

\[
s_B = \varepsilon_T + 1
\]

where \( \varepsilon_T \) is the number of chemical elements in the system of interest. The redox species itself will be denoted as the \( s_B \)-th species. In the case of systems in which there is no oxidation-reduction, we will simply treat the redox species as being inactive.

A speciation-solubility problem concerning an aqueous solution deals only with mass balances involving species in one (aqueous) phase. Therefore, the basis set in EQ3NR consists entirely of aqueous species. These are defined (at least initially) on the supporting data file. One is \( H_2O_{(l)} \), the solvent. The redox species used in EQ3/6 is \( O_{2(g)} \), which is treated in this context as a fictive aqueous species; the conventional \( e^- \) used by some other modeling codes is another example of such. The other basis species are simple species likely to dominate their respective mass balance relationships, at least in many instances.

Basis species are usually chosen as mono-elemental species such as \( Na^+ \) and \( Ca^{2+} \). Some are also comprised of oxygen and/or hydrogen (e.g., \( SO_4^{2-} \) and \( B(OH)_3(aq) \)). No basis species on a supporting data file is permitted to be comprised of more than one chemical element other than oxygen or hydrogen. The purpose of this restriction is to avoid certain problems that would otherwise arise in defining the total concentrations of the basis species. Such problems do not arise in the case of dealing with elemental oxygen and hydrogen because no meaningful analytical values exist for the total concentrations of the associated basis species, \( H_2O_{(l)} \) and \( H^+ \) or of these elements themselves. The concentration of water as measured by its mole fraction is implicitly fixed by the concentrations of the solute components. The concentration of the hydrogen ion is analytically determined via the \( pH \) or some other approach not involving a total concentration.

Using a strict basis set, all mass balance relationships can be defined in terms of chemical elements and the coefficients describing the elemental compositions of all species. The charge bal-
ance relationship can be defined in terms of the electrical charges of the species. All non-basis species appearing in these balance equations are related to the basis species via the associated chemical reactions. The concentrations of these non-basis species are then determined by the concentrations of the basis species through the associated mass action equations, assuming that the activity coefficients appearing in these equations are known. Thus, if the concentrations of the basis species are known, they may be used to span (compute) the complete speciation of the system. In mathematics, a set with such properties is usually called a basis, which is actually where the term basis set in the present context is derived.

In thermodynamic modeling, one deals in an algebraic sense with \( n \) equations in \( n \) unknowns. The use of a basis set which is strict requires assuming that the concentration of every non-basis species appearing in a balance equation satisfies a corresponding mass action equation. This has the effect of requiring the modeled system to be in a complete state of internal chemical equilibrium. There is simply no mechanism in this construction to deal with even one simple reaction in a state of disequilibrium. The concept of internal equilibrium as used here refers to a system which excludes any non-basis species that do not appear in the balance equations. Thus, an aqueous solution may be in a state of internal equilibrium, but still supersaturated with respect to calcite. The mineral in this context is a non-basis species, but it does not appear in the balance equations which describe the aqueous solution. The system consisting of the same aqueous solution plus the mineral, however, is not in a state of internal equilibrium.

In EQ3NR, the modeled system consists exclusively of the aqueous solution. Systems including other phases are treated in EQ6. Nevertheless, it is apparent from the above example that in order to model systems with some internal disequilibrium, one must expand the basis set beyond the confines of the strict basis. In the example given above, we would make the mineral a basis species. However, since the associated reaction is presumed to be in disequilibrium, the associated mass action equation is not used as a governing constraint. In order to maintain a balance of \( n \) equations in \( n \) unknowns, it is necessary to introduce a mass new balance equation for the new basis species. In the present example, this is just a statement of how much of the mineral is present in the system. Note that this is a new kind of mass balance relation not related to a chemical element.

The same principle holds in modeling an aqueous solution. One might wish to compute a model in which \( Fe^{3+} \) is not in equilibrium with \( Fe^{2+} \). If \( Fe^{2+} \) is already in the strict basis set, one must add \( Fe^{3+} \) to the basis set (or vice versa). In this case, the situation is more complicated, as the new basis species may have its own ion pairs and complexes appearing in the associated mass balance. This is a simple concept. However, it requires rethinking the description of mass balances, as the number of mass balance equations now exceeds the number of chemical elements. As we will show, a better concept is to associate the mass balance relations with corresponding basis species, not with the chemical elements.

We now show how to develop this more generalized concept for defining mass balance relations. Consider the following reaction:

\[
HgCl_3 = Hg^{2+} + 3Cl^-
\] (212)
This is represented in the software by paired arrays of reaction coefficients (floating point numbers) and names of the corresponding species (character variables). If you ask the question, how many chlorides is the non-basis species on the left hand side equivalent to, a human being will invariably answer the question by looking at the subscript “3” in the chemical formula of the species. In the software, this is equivalent to looking up the elemental composition of the species in the appropriate data array. Thus, this mechanism produces the required coefficient for evaluating the contribution of this species to a mass balance relation based on a chemical element. This is really the answer to the question, to how many chlorines (not chlorides) is this species equivalent. This is not what is presently desired, and a different approach is required.

The original question can be more accurately answered by looking at the reaction coefficients. Since reactions must satisfy mass and charge balance to be valid, the required information must be available there. A human being would probably answer the question by looking at the coefficient on the right hand side of the reaction. However, the coefficient of the non-basis species on the left hand side must also be considered to obtain the correct answer in the general case. To emphasize this, we note that the reaction can also be written as:

$$2HgCl_3 = 2Hg^{2+} + 6Cl^-$$  \hspace{1cm} (213)

Although a reaction whose coefficients have not been reduced to the lowest common denominator is unlikely to be written in any of the EQ3/6 data files, it is not prohibited. Also, some reactions written with a unit coefficient for the associated non-basis species require fractional coefficients. An example is:

$$Fe^{3+} + \frac{1}{2}H_2O \quad (l) = Fe^{2+} + H^+ + \frac{1}{4}O_2 \quad (g)$$  \hspace{1cm} (214)

One might reasonably wish to avoid the fractions and write instead:

$$4Fe^{3+} + 2H_2O \quad (l) = 4Fe^{2+} + 4H^+ + O_2 \quad (g)$$  \hspace{1cm} (215)

Furthermore, certain actions taken by the code as it executes, such as basis switching, may cause a reaction to be rewritten, and there is no general restriction requiring the new reaction to have a unit coefficient for the associated non-basis species.

In the software, the coefficients of products are defined as positive numbers and those of reactants as negative ones. For the basis species, these coefficients are symbolized by $b_{s'r}$, where $s'$ denotes a basis species and $r$ the reaction. The non-basis species associated with the $r$-th aqueous reaction is denoted by $s''$, and its reaction coefficient is symbolized by $b_{s''r}$. Thus, the factor giving the stoichiometric equivalence of such a species to the $s'$-th basis species is given by:

$$u_{s''s'} = \frac{b_{s'r}}{b_{s''r}}$$  \hspace{1cm} (216)

In a speciation-solubility problem, the mass balance equation for the $s'$-th basis species is the...
\[ m_{T,s'} = m_s' + \sum_{r=1}^{r_T} u_{s''} s' m_s'' \]  

(217)

where \( r \) is the reaction associated with the \( s'' \)-th species \( (r = s'' - s_B; \) see Section 9.2) and \( r_T \) is the number of reactions for the dissociation of non-basis aqueous species. Considerable care must be used in the application of such a formulation. Mathematically, it is quite rigorous. Physically, however, there are some potential problems. The quantity on the left hand side may or may not correspond to something that can be obtained by chemical analysis and therefore have physical as well as mathematical meaning. The formulation can be applied to any basis species. In the case of \( O_{2(g)} \) or \( e^- \), these have no physical meaning, as these are only hypothetical aqueous species in the first place. In the case of \( H^+ \), the total concentration has no physical significance. Its value is uniquely established only because one normally chooses to put this species in the basis set instead of \( OH^- \). In the case of \( H_2O(g) \), the computed total concentration is also technically non-physical and depends on which of \( H^+ \) or \( OH^- \) is chosen as a basis species.

It was pointed out earlier that basis species on the EQ3/6 data files are restricted in composition to no more than one chemical element other than oxygen and hydrogen. This is done to protect the physical meaning of the total concentrations of basis species other than \( H_2O(g), H^+, \) and \( O_{2(g)} \), for which there is no possibility of physical meaning, anyway. To illustrate the problem, consider the following three reactions in which \( HgCl_3^- \) is used as a basis species in place of \( Hg^{2+} \):

\[ Hg^{2+} + 3Cl^- = HgCl_3^- \]  

(218)

\[ HgBr_3^- + 3Cl^- = HgCl_3^- + 3Br^- \]  

(219)

Consider the mass balance of chloride and the contribution to it from \( Hg^{2+} \). Applying eq (216) to the first reaction above gives a stoichiometric coefficient of -3. The same result is obtained for the bromide complex in the second reaction. The chloride complex itself has a stoichiometric coefficient of zero.

In EQ3NR and EQ6, the chloride complex in the above example is likely to strongly dominate the mass balance of dissolved mercury, giving an incentive to consider switching it into the basis in place of the mercuric ion. The codes deal with this situation by continuing to define the stoichiometric factors appearing in the mass balance relations in terms the reactions as they were written prior to basis switching, modified only for stoichiometric factors relating the new basis species to the old ones.

### 5.2. Organization and Treatment of Basis Species

The set of basis species on an EQ3/6 data file is divided into two parts: the strict basis and the auxiliary basis. The species in the strict basis set correspond one-to-one with the chemical elements, except for \( O_{2(g)} \), which is used as a hypothetical aqueous species, and which corresponds to charge balance. These species appear first in the overall list of aqueous species. The solvent,
H₂O(l) is the first aqueous species. The hypothetical aqueous species O₂(g) is the last. The species in the strict basis set are not associated with any reactions, as are all other species.

The auxiliary basis species follow the strict basis species. For the most part, they represent chemical elements in different oxidation states. However, they may also include any species which do not readily equilibrate with other basis species according to the associated reactions. Auxiliary basis species are used like strict basis species as “building blocks” in writing reactions for various species on the data file. In EQ3NR, an auxiliary basis species may be treated as either a basis species or a non-basis species. The choice is up to the user in each case. By default, an auxiliary basis species is eliminated from the active basis set (except for O₂(aq) and H₂(aq), which are special cases). Any reactions for other species written in terms of this species will be rewritten to reflect this. However, an auxiliary basis species is treated as an active basis species if the user provides an appropriate matching input on the input file, such as a total concentration. The non-basis aqueous species follow the auxiliary basis species. In the present version of EQ3/6, a species defined as a non-basis species on the data file can not be treated as an active basis species unless it is switched with an existing member of this set. This prevents defining an additional mass balance relation for this species. If it is desired to use such a species in the active basis set for the purpose of defining an additional such relation, it is necessary to modify the data file, moving the species into the auxiliary basis set.

An input model constraint, such as a total concentration, is required for each master aqueous species in order to perform a speciation-solubility calculation. However, as discussed in Chapter 6, there are limitations on the constraints that can be placed on a given basis species, depending on whether it is in the strict basis or the auxiliary basis. The user needs to be keenly aware of which species are in which set. Users should consult either the relevant data file or the slist (species list) file written by EQPT when it processes this file.

The user may specify selected examples of basis-switching on the input file. This provides a means of changing the set of basis species at run time. For example, a strict basis species may be exchanged with an auxiliary basis species. This puts the latter in the strict basis, the former in the auxiliary set. A basis species may also be switched with a non-basis species. A basis switch causes reactions to be re-written in terms of the new basis set. Judicious basis switching can improve the code numerics, sometimes making the difference in whether the iteration converges or not. As a general rule, a basis species should not make up an insignificant part of the associated mass balance when a total concentration is used as the input constraint. The compositional restrictions on basis species on the EQ3/6 data file do not apply to basis switching made when running EQ3NR or EQ6.

A basis switch involving a non-basis species causes the corresponding input constraints (such as those represented by the csp and uphase parameters; see Chapter 6), to be reassigned to the species brought into the basis set. For example, if Al(OH)₄⁻ is to be switched into the basis set in place of Al³⁺, for which jflag = 16 (log activity constant) and esp = -5.0 (the desired value), the model actually specified is one in which the log activity of Al(OH)₄⁻ is -5.0. In this case, specifying a basis switch actually changes the definition of the problem. However, in a switch involving a basis species constrained to satisfy a specified total concentration, the total concentration is
recomputed by a stoichiometric adjustment to match the species moved into the basis. In this case, the problem itself is not really changed; it is merely expressed in different terms.

Setting the \( j\text{flag} = 30 \) for an auxiliary basis species causes the species to be eliminated from the active basis set. As noted above, this is the default condition for most such species. Elimination from the active basis set causes reactions originally written in terms of the eliminated species to be rewritten. For example, consider the following reaction:

\[
\text{FeSO}_4^+ = \text{Fe}^{3+} + \text{SO}_4^{2-}
\]

Elimination of \( \text{Fe}^{3+} \) from the basis set causes this to be rewritten as:

\[
\text{FeSO}_4^+ + \frac{1}{2} \text{H}_2\text{O}(l) = \text{Fe}^{2+} + \text{H}^+ + \frac{1}{4} \text{O}_2(g) + \text{SO}_4^{2-}
\]

Thus, \( \text{FeSO}_4^+ \) now appears to be, and is treated as, a complex of \( \text{Fe}^{2+} \). Elimination thus has the effect of combining mass balances. In this case, \( \text{Fe}^{1+} \) and its complexes are folded into the mass balance for \( \text{Fe}^{2+} \). Note that the reaction for \( \text{FeSO}_4^+ \) on the data file must be the first, not the second, of the two above reactions. Otherwise, \( \text{FeSO}_4^+ \) would have been considered a complex of \( \text{Fe}^{2+} \) from the start. If one did not eliminate \( \text{Fe}^{3+} \) from the active basis set, \( \text{FeSO}_4^+ \) would be incorrectly folded into the mass balance for \( \text{Fe}^{2+} \), and missing from that of \( \text{Fe}^{3+} \).

In the majority of cases, there are only one or two auxiliary basis species for a given chemical element. When there is more than one such auxiliary basis species, the species can be “chained.” The first such species must be related through its associated reaction to the corresponding strict basis species. This can also be done in the case of the second, third, etc., such basis species. However, the second such auxiliary basis species could be directly related to the first such auxiliary basis species. The third could be directly related to the first or second, etc. Of course, a non-basis species can be directly related to any basis species.

Chaining is not significant in the case of most chemical elements. Carbon, however, is an exception. A large number of organic species are now present on the \text{com} and \text{sup} data files because of the inclusion of such in SUPCRT92 from the work of Schock and Helgeson (1990). Several of these are treated as auxiliary basis species, the majority as non-basis species of which all are directly related to one of the organic species in the auxiliary basis. The basic problem with organics in a geochemical modeling code is that they may often be treated as complexes of \( \text{HCO}_3^- \) when this is not what is desired. In the “R7” versions of the \text{com} and \text{sup} data files, each of the several organic species in the auxiliary basis set is directly related to \( \text{HCO}_3^- \). In order to model organic-free systems without the unexpected appearance of organics in the model, it is necessary to enter on the input file a zero concentration for each organic species in the auxiliary basis set. In future versions of the data files, one such species (probably 'acetic acid(aq)') may be set up as a sort of master organic species. Only this organic species will be directly related to \( \text{HCO}_3^- \). All other organic species in the auxiliary basis set will be directly related to this master organic spe-
cies. Then all organics can be kept out of a computed model by entering on the input file a zero concentration for just the master organic species.

5.3. Stoichiometric Conversions of Analytical Data

The analytical data used to define speciation-solubility problems in EQ3NR pertain to the basis species on the supporting data file employed in a given run. To use the code correctly, one must know what the species are, and it is often necessary to correct the analytical data one is provided in order to provide a stoichiometric match.

For example, the river water test case of Nordstrom et al. (1979) includes the following data:

- Si 8.52 mg/L.
- B 0.050 mg/L.
- PO₄³⁻ 0.210 mg/L.

The species on the data0.com data file which respectively correspond to these components are SiO₂(aq), B(OH)₃(aq), and HPO₄²⁻. The problem is that, for example, 8.52 mg/L of Si is not equivalent to 8.52 mg/L of SiO₂(aq). A stoichiometric conversion, of the sort common in analytical chemistry, must be done. This is illustrated in the present case by:

\[
C_{\text{mg/L}, \text{SiO}_2(aq)} = \frac{M_w, \text{SiO}_2(aq)}{M_w, \text{Si}} C_{\text{mg/L}, \text{Si}}
\]

(222)

where \(M_w,i\) is the molecular weight of the component labeled \(i\). The atomic weight of \(Si\) is 28.086 g/mole and that of \(O\) is 15.999 g/mole. The molecular weight of SiO₂(aq) is therefore 60.0840 g/mole. The ratio of the molecular weights is therefore 2.1393, and the 8.52 mg/L of Si is therefore equivalent to 18.23 mg/L of SiO₂(aq). By following this method, it can be shown that the 0.050 mg/L of B is equivalent to 0.286 mg/L of B(OH)₃(aq), and that the 0.210 mg/L of PO₄³⁻ is equivalent to 0.212 mg/L of HPO₄²⁻. Corrections are analogous if the data are concentrations in mg/kg of solution.

The situation is much simpler if the analytical data are reported as molalities or molarities, as no conversion is generally necessary. For example, 0.0001 molal Si is equivalent to 0.0001 molal SiO₂(aq).

The code user must make any necessary stoichiometric conversions before entering the data on the input file. EQ3NR contains no provisions for direct input of data corresponding to dissolved components other than the basis species appearing on the data file used, so it is not possible for it to make these conversions for the user.
6. The EQ3NR Input File: Setting up the Problem

6.1. Input File Characteristics and Contents

We examine in this chapter the EQ3NR input file. This file is the means by which the user specifies a problem to be solved by the code. The user must supply a compatible data1 file, and the results obtained may differ if the problem is run with more than one such data file. Some examples of EQ3NR input files are presented in this chapter, and the reader will find more examples, along with the corresponding output files, in Chapter 7. Still more examples are given in Appendix F of the EQ6 Theoretical Manual and User's Guide (Wolery and Daveler, 1992).

The EQ3NR input file presently exists in one of two formats. The first is of the type used in previous versions of the code (e.g., Wolery, 1983). This is a compact form more suitable for use by experienced users. We will refer to this as the "W" format. A newer optional form (Daveler and Bourcier, unpublished) has a menu-style format that is much less compact, but which may be easier to use for less experienced users. We will refer to this as the "D" format. The present manual will focus more on the "W" format, as this naturally leads into a discussion of the relevant code variables. Some examples will be given of problems presented in both formats.

The recommended way of creating a new input file is to use an old one as a template. This works best if the old one is as close as possible to the desired new one. To this end, a representative selection of sample input files is included in the distribution package for EQ3/6 (Wolery and Daveler, 1992a). The distribution package also includes some software which converts input files in "W" format to "D" format. Using this template approach reduces the necessary knowledge a user must have concerning input file formats, and minimizes the need to consult the related documentation.

The "W" format input file is read by the code module readx.f. The source code for this module is extensively documented internally by of comment lines. On-line access to the source code of this module may helpful to users, serving as a kind of on-line documentation. The "D" format input file is read by the module rdninp.f, which calls a number of other modules in carrying out this function (the EQ3NR modules rdtyp1.f, rdtyp2.f, rd3uds.f, rdtyp4.f, rdtyp5.f, and rdtyp9.f, and the EQLIB modules rdtyp0.f, rdtyp6.f, rdtyp7.f, and rdtyp8.f). The source codes of these modules may also be helpful to users as on-line documentation.

An input file of either format contains a title field to provide space for internal documentation. In addition, an input file may contain remarks in comment lines. These are marked by an asterisk in column one and are analogous to comment lines in FORTRAN source code. They may appear anywhere in the input file.

Regardless of which format of input files is used, EQ3NR writes an "instant echo" of the input file on the output file. That is to say, after the code has read a line or closely related group of lines, it echoes their contents. This is particularly helpful in identifying the causes of read format errors, which most commonly occur when a line is missing or out of the proper sequence. This feature also provides a record of the input file used for a given run. However, it does not include comment lines. If necessary, a lost input file may be recovered (less comment lines) by extracting the echo from the output file.
The user is cautioned that the number of lines in an EQ3NR input file in either format is variable. Whether or not some potential lines appear in a given file depends upon the contents of other lines. Some items, such as the constraints applied to the basis species, appear on successive lines until a terminator appears. Certain options, if invoked, require corresponding additional lines of input. The file structure has been chosen so that the size of the input file reflects the size of the problem.

There are no species index numbers for users to bother with. Internally, EQ3NR sets up its own internal indexing schemes at run time. Users deal with species in terms of their names, which are 24-byte character variables. These are much easier to remember and are instantly recognizable. However, the names must match perfectly with those on the data file used or EQ3NR will not recognize them. In such a case, the code will write an error message and terminate activity on the current problem input.

EQ3NR input problems may be stacked on the input file so that the code will read one problem, solve it, read another, solve it, and so on, in one job. In most cases, if an error is caught in one problem input, the code will proceed to the next problem input, if any.

A short summary of the contents of the EQ3NR input file in “W” format is given in on the following pages. Parameters for which default values are recommended are marked with an asterisk. To take the default for a given parameter, leave the corresponding input field blank. Following the short summary is a discussion of the input file parameters themselves. The user need not enter values for all of these. Some may not appear on specific examples of input files, depending on other parameters. This summary is followed by an example of an EQ3NR input file in both “W” and “D” formats (more examples are given in Chapter 7).

**Short Summary of the EQ3NR input file (“W” format):**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Format</th>
</tr>
</thead>
<tbody>
<tr>
<td>Do n from 1, ending with the string 'endit.' in column 1:</td>
<td>(a80)</td>
</tr>
<tr>
<td>util(n)</td>
<td>(a80)</td>
</tr>
<tr>
<td>End do</td>
<td></td>
</tr>
<tr>
<td>tempc</td>
<td>(12x,e12.5)</td>
</tr>
<tr>
<td>rho, tdspkg, tdspl</td>
<td>(3(12x,e12.5))</td>
</tr>
<tr>
<td>(enter only one of tdspkg, tdspl)</td>
<td></td>
</tr>
<tr>
<td>fep, uredox</td>
<td>(12x,e12.5,12x,a24)</td>
</tr>
<tr>
<td>(enter either fep or uredox)</td>
<td></td>
</tr>
<tr>
<td>tolbt(<em>), toldt(</em>), tolsat(*)</td>
<td>(3(12x,e12.5))</td>
</tr>
<tr>
<td>itermx(*)</td>
<td>(12x,i2)</td>
</tr>
<tr>
<td>iopt1 - iopt10</td>
<td>(12x,10i5)</td>
</tr>
</tbody>
</table>
If nxmod > 0:
  Do n = 1, nxmod:
    uxmod(j,n), j = 1, 3) (12x,i24),
    jxmod(n), kxmod(n), xikmod(n) (12x,i2,22x,i2,22x,e12.5)
  End do
End if

Do until 'endit.' starting in column 1 of the ubasis line is encountered:
  ubasis(n) (26x,a24)
  uspecb(n) (24x,a24)
  jflag(n), csp(n) (10x,i2,8x,e12.5)

If jflag(n) ≥ 17 and jflag(n) ≤ 21:
  uphas1(n), uphas2(n) (10x,a24,11x,a24)
End if
End do

If lopt4 = 2:
  Do until 'endit.' starting in column 4 of the usolb line is encountered:
    usolb(n) (3x,a24)
  Do until 'endit.' starting in column 7 of the umemb line is encountered:
    (umemb(i,n), xbarb(i,n)) (6x,a24,3x,f10.4)
  End do
End do
End if

(*) Default values are recommended (i.e., leave these blank on the input file)
Summary of EQ3NR input file parameters:

- **util1**: Up to 100 lines of text that describe the input problem, terminated by an 'endit.' beginning in column 1.

- **tempc**: Temperature, °C.

- **rho**: Aqueous solution density, g/ml. The default value is 1.0.

- **tdspkg**: Total dissolved salts, mg/kg of solution.

- **tdspl**: Total dissolved salts, mg/L (do not enter both of tdspkg and tdspl).

- **fep**: Redox parameter:
  - \( = pe \) if \( iopt1 = -2 \).
  - \( = Eh \) if \( iopt1 = -1 \).
  - \( = \text{log oxygen fugacity} \) if \( iopt1 = 0 \).

- **ur:dox**: Name of an auxiliary master species; this defines a redox couple that specifies the oxygen fugacity (\( iopt2 = 1 \); enter only one of fep, ur:dox).

- **tolbt**: Convergence tolerance on Newton-Raphson residual functions. The default value is \( 1 \times 10^{-6} \).

- **toldl**: Convergence tolerance on Newton-Raphson correction terms. The default value is \( 1 \times 10^{-6} \).

- **tolsat**: Saturation tolerance; this only determines whether or not a mineral is listed as "saturated" on the output file; it has no effect on Newton-Raphson iteration. The default value is 0.5 kcal; reasonable values range from 0.1 kcal to 1.0 kcal.

- **itermx**: Limit on the number of Newton-Raphson iterations. The default value is 30.

- **iopt1**: Option switch for determining the redox parameter input:
  - -3 = This option instructs the code to look for an input constraint on \( O_2(g) \); a normal constraint block for a basis species (see uspecb, jflag, esp, uphas1, and uphas2 below; in this case, uspecb ='o2(g)'). By choosing jflag = 19, 20, or 21, the oxygen fugacity can be fixed by a heterogeneous reaction for a mineral, solid solution end-member component, or gas species, respectively (defined by the uphas1 and uphas2 inputs, see below).
  - -2 = The \( pe \) is specified in fep.
  - -1 = The \( Eh \) is specified in fep.
  - 0 = The log oxygen fugacity is specified in fep.
  - 1 = An aqueous redox couple identified by the ur:dox variable constrains the oxygen fugacity.

- **iopt2**: Option switch for automatic basis switching:
  - 0 = Turns it off.
  - 1 = Turns it on.

- **iopt3**: Option switch for writing a pickup file for input to EQ6:
  - -1 = No pickup file is generated.
  - 0 = A pickup file is generated.
iopt4  Option switch for solid solutions:
   0 = Solid solutions are ignored.
   1 = Only solid solutions for which compositions are given on the input file are considered.
   2 = Both input and hypothetical solid solutions are considered.

iopt5  Option switch, not currently used.

iopt6  Option switch, controls convergence testing:
   -1 = Only residual functions are tested.
   0 = Both residual functions and correction terms are tested.

iopt7  Option switch, determines pickup file format:
   0 = Normal version 7.0 format.
   1 = Post-7.0 version format (do not use).

iopt8 - iopt10 Option switches, not currently used.

iopt1 Activity coefficient option switch- choice of basic equations:
   -1 = Use the Davies equation.
   0 = Use the B-dot equation.
   1 = Use Pitzer’s equations.

   Caution: a compatible data file must be used.

iopt2 Activity coefficient option switch- choice of pH scale:
   -1 = Evaluate single-ion expressions and use as is.
   0 = Convert results from single-ion expressions to the NBS pH scale.
   1 = Convert results from single-ion expressions to the scale on which logy H+ = 0.

iopt3 Print option switch for reactions read from the data file:
   0 = Do nothing.
   1 = Print all reactions (this can be extremely lengthy).

iopt4 Print option ordering switch for the aqueous species distribution table:
   0 = Present in order of decreasing concentration.
   1 = Present in the order in which the species appeared on the data file.

iopt5 Print option cutoff switch for the aqueous species distribution table:
0 = Print all aqueous species.
1 = Print only those with concentrations greater than $1 \times 10^{-20}$ molal.
2 = Print only those with concentrations greater than $1 \times 10^{-12}$ molal.
3 = Do not print the aqueous species distribution.

**iopr5**  Print option cutoff switch for the mass balance percentage tables:
-1 = Do not print.
  0 = Print, cutting off at 99% of the total for each table.
  1 = Print all species in each table.

**iopr6**  Print option switch for the mean ionic properties table:
  0 = Do nothing.
  1 = Print the table.

**iopr7**  Print option for mineral affinity/saturation index tables:
-1 = Do not print.
  0 = Print, excluding minerals whose affinities are less than -10 kcal.
  1 = Print data for all minerals.

**iopr8**  Print option for hard core diameters and hydration numbers of aqueous species:
-1 = Do not print.
  0 = Print, these data.

**iopr9**  Print option switch for Pitzer interaction coefficients:
  0 = Print only warnings, if any.
  1 = Print the species in the model and the number of coefficients.
  2 = Print the species and the associated pairs and triplets of species for which the coefficients are defined.

**iopr10**  Print option switch for the mean ionic properties table:
  0 = Do nothing.
  1 = Print the stoichiometric concentrations of the basis species.

**iopr11 - iopr20**  Print option switches, not currently used.

**iodb1**  Debugging print option switch for general informational messages:
  0 = Do nothing.
  1 = Print certain messages which may be of diagnostic value.
  2 = Print a higher level of such messages.

**iodb2**  Debugging print option switch for pre-Newton-Raphson optimization:
  0 = Do nothing.
1 = Print a summary of the optimization process.
2 = Print a more detailed summary.

iodb3 Option switch for the iteration variable kill option:
0 = Do nothing.
1 = Invoke the killer option (this is intended for the use of code developers only).

iodb4 Debugging print option switch for Newton-Raphson iteration:
0 = Print a summary of the process.
1 = Print a more detailed summary of the process.

iodb5 Debugging print option switch for stoichiometric equivalence factors:
0 = Do nothing.
1 = Print the equivalence factors for oxygen and hydrogen mass balances only.
2 = Print the equivalence factors for all mass balances.

iodb6 Debugging print option switch for calculation of equivalence factors:
0 = Do nothing.
1 = Print details of these calculations.

iodb7 Debugging print option switch for reactions:
0 = Do nothing.
1 = Print the reactions on a file called rlist, before and after any basis switching operations (intended for use only by code developers).

iodb8 - iodb10 Debugging print option switches, not currently used.

uebal Name of ionic species for electrical balancing; if uebal is 'pick1', the code picks a species; if uebal is blank, no electrical balancing is done. In most instances, users should not have the code do electrical balancing.

nxmod Number of alter/suppress options (number of species to be suppressed or whose log K values are to be modified).

uxmod Name of a species to be suppressed or whose corresponding equilibrium constant is to be modified for use in the current run.
0 = pure mineral.
1 = solid solution.
2 = special reactant.
3 = aqueous species.
4 = gas.

kxmod The nxmod alter/suppress option (see jxmod and uxmod):
-1 = Suppress.
0 = Replace the \( \log K \) by \( xlkmod \).
1 = Augment the \( \log K \) by \( xlkmod \) units.
2 = The \( \log K \) changed as if the corresponding Gibbs energy of reaction were decremented by \( xlkmod \) kcal/mole.

\( xlkmod \) Equilibrium constant alteration function (see above).
\( ubasis \) The name of a run-time basis species (if not the same as uspecb, the name of the species to switch into the basis set in place of the species whose name is input in uspecb).
\( uspecb \) The name of a data file basis species.
\( jflag \) The option flag which defines the type of input constraint (see below).
\( csp \) A floating point datum whose meaning is determined by the corresponding value of the \( jflag \) option flag; usually this is a concentration of some type.
\( uphas1 \) The name of an aqueous basis species or a mineral, solid solution, or gas species required to define an input constraint under the \( jflag = 17, 18, 19, 20, \) and \( 21 \) options.
\( uphas2 \) The name of solid solution end-member component required to define an input constraint under the \( jflag = 20 \) option.
\( usolb \) The name of a solid solution for which a composition is entered for the purpose of computing the corresponding affinity and saturation index.
\( umemb \) The name of an end-member component of the solid-solution whose name is input in \( usolb \).
\( xbarb \) The mole fraction of a solid solution end-member component whose name is input in \( umemb \).

Table of \( jflag \) Options:

<table>
<thead>
<tr>
<th>( jflag )</th>
<th>( csp )</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>Suppression option- no ( csp ) input.; This has the same effect as entering a concentration of zero. This is a convenient way to keep unwanted auxiliary basis species from appearing in the model.</td>
</tr>
<tr>
<td>0</td>
<td>Total molality.</td>
</tr>
<tr>
<td>1</td>
<td>Total molarity.</td>
</tr>
<tr>
<td>2</td>
<td>Total concentration, mg/L.</td>
</tr>
<tr>
<td>3</td>
<td>Total concentration, mg/kg of solution.</td>
</tr>
<tr>
<td>4</td>
<td>Free molality.</td>
</tr>
<tr>
<td>5</td>
<td>Free molarity.</td>
</tr>
<tr>
<td>6</td>
<td>Free concentration, mg/L.</td>
</tr>
<tr>
<td>7</td>
<td>Free concentration, mg/kg of solution.</td>
</tr>
</tbody>
</table>
Free concentration, cm$^3$(STP)/cm$^3$ solution.

The log activity. This is the means of entering pH ($-pH = \log a_{H^+}$).

Combination log activity function- enter the name of the corresponding ion as uphas1. This is the means of entering pHCl ($-pHCl = \log a_{H^+} + \log a_{Cl^-}$).

Mean log activity- enter name of corresponding ion as uphas1.

Equilibrium with a pure mineral- no csp input; enter name of mineral as uphas1.

Equilibrium with a solid solution end-member component- no csp input; enter name of the solid solution as uphas1 and the name of the end member as uphas2.

Equilibrium with gas- enter the log fugacity of the gas as csp; enter the name of the gas as uphas1.

Equilibrium with other basis species, but unconstrained by any mass balance relations- no csp input; this option is available only for auxiliary basis species. This is the default for $O_{2(aq)}$ and $H_{2(aq)}$.

Eliminate an auxiliary basis species from the active basis set- no csp input. This is the default for all auxiliary basis species other than $O_{2(aq)}$ and $H_{2(aq)}$.

Example of an EQ3NR input file in "W" format.

EQ3NR input file name- sunaj.13
Description- "Sea water, major ions only"
Version number= 3245 Stage number= 01
Created 06/08/90 Creator= T.J. Wolery
Revised 06/08/90 Revisor= T.J. Wolery

Sea water, including only the major ions. This is a considerably pared-down version of swtst.31, which contains the full benchmark sea water test case of Nordstrom et al. (1979, Table III).

Purpose: to test the code on a small problem involving a moderately concentrated solution. The activity coefficients of the aqueous species are calculated from the B-dot equation and related equations.

References

endit.

-86-
The EQ3NR input file in "D" format is illustrated by the following example, which contains the same problem that was just presented in "W" format. The mapping between the two is largely self-evident. The most immediately obvious characteristic of an input file in "D" format is its use of the "|" character to delimit fields in which data are entered. Note that an asterisk ("*") is used to mark the choice of units for entering total dissolved salts. It may also be used to choose among two of the options for electrical balancing ("code selects" and "not performed"). If electrical balancing is to be done on a specified ion, the name of the ion should simply be entered in the field provided. The principal option switches are set in blocks in which an asterisk is used to mark the desired choice. If more than one choice is marked for the same option, the code writes an error message and execution stops. In the case of debugging option switches, the user enters a numerical input of 0, 1, or 2. If 2 is a valid input, a "2" appears on the line following the final "|". When EQ3NR reads an input file in "D" format, it immediately checks the range limits and notes discrepancies in the instant echo on the output file. When the code reads an input file in "W" format, such checks are made after the input file has been read.

Note that the iopt1 option is handled in a special way. It does not appear in the options block, but in the block of inputs for the basis species. Here it appears as a "species" called 'REDOX'. This is used in the example to input the \( \text{Eh} \) by entering the corresponding string 'EH'. The available options are as follows:

<table>
<thead>
<tr>
<th>iopt1</th>
<th>&quot;D&quot; format string</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>-3</td>
<td>'REDOX COUPLE'</td>
<td>A normal basis species input line for ( \text{O}_2 ) is expected to immediately follow the 'REDOX' input line. The &quot;D&quot; format string for this option is not descriptive of the actual option; something like 'O2 INPUT' would have been a better choice.</td>
</tr>
<tr>
<td>-2</td>
<td>'PE'</td>
<td>( \text{pe} ).</td>
</tr>
<tr>
<td>-1</td>
<td>'EH'</td>
<td>( \text{Eh} ), volts.</td>
</tr>
<tr>
<td>0</td>
<td>'LOGFO2'</td>
<td>log oxygen fugacity.</td>
</tr>
<tr>
<td>1</td>
<td>'REDOX COUPLE'</td>
<td>Use redox couple defined by \text{uredox} input. The auxiliary basis species corresponding to the \text{uredox} variable is defined by the species on the species input line immediately following the 'REDOX' input line. It is not defined in the constraint field on the 'REDOX' input line itself, as one might expect.</td>
</tr>
</tbody>
</table>

Although these strings are listed here in upper case, the code does not consider case in interpreting them. Similar strings noted below are treated in the same manner.
Instead of entering a \texttt{kxmod} number to define the type of an \texttt{nxmod} alter/suppress option, one uses one of the following strings:

<table>
<thead>
<tr>
<th>\texttt{kxmod}</th>
<th>\texttt{&quot;D&quot; format string}</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>'SUPPRESS'</td>
<td>Suppress the phase/reaction.</td>
</tr>
<tr>
<td>0</td>
<td>'REPLACE'</td>
<td>Replace the log $K$.</td>
</tr>
<tr>
<td>1</td>
<td>'AUGMENTK'</td>
<td>Augment the log $K$.</td>
</tr>
<tr>
<td>2</td>
<td>'AUGMENTG'</td>
<td>The log $K$ changed as if the corresponding Gibbs energy of reaction were decremented by $x\text{kmod}$ kcal/mole.</td>
</tr>
</tbody>
</table>

The \texttt{jflag} options are also handled in "D" format by character strings. These are listed in the following table.

<table>
<thead>
<tr>
<th>\texttt{jflag}</th>
<th>\texttt{&quot;D&quot; format string}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>'MOLALITY'</td>
</tr>
<tr>
<td>1</td>
<td>'MOLARITY'</td>
</tr>
<tr>
<td>2</td>
<td>'MG/L'</td>
</tr>
<tr>
<td>3</td>
<td>'MG/KG'</td>
</tr>
<tr>
<td>4</td>
<td>'FREE MOLAL'</td>
</tr>
<tr>
<td>5</td>
<td>'FREE MOLAR'</td>
</tr>
<tr>
<td>6</td>
<td>'FREE MG/L'</td>
</tr>
<tr>
<td>7</td>
<td>'FREE MG/KG'</td>
</tr>
<tr>
<td>8</td>
<td>'FREE CM3/CM' (*)</td>
</tr>
<tr>
<td>16</td>
<td>'LOG ACTIVITY (+)</td>
</tr>
<tr>
<td>17</td>
<td>'LOG ACTIVITY COMBO' (††)</td>
</tr>
<tr>
<td>18</td>
<td>'LOG MEAN ACTIVITY'</td>
</tr>
<tr>
<td>19</td>
<td>'MINERAL'</td>
</tr>
<tr>
<td>20</td>
<td>'SOLID SOLUTION'</td>
</tr>
<tr>
<td>21</td>
<td>'GAS'</td>
</tr>
<tr>
<td>27</td>
<td>'DEPENDENT'</td>
</tr>
<tr>
<td>30</td>
<td>'ELIMINATED'</td>
</tr>
</tbody>
</table>

(*) This is a typographical error in the code.

(†) One may use the string 'PH' to enter the pH.

(††) One may use the string 'PHCL' to enter the pHCl.
Example of the same EQ3NR input file in “D” format.

EQ3NR input file name= swwmaj.3i
Description= "Sea water, major ions only"
Version number= 3245 Stage number= 01
Created 06/08/90 Creator= T.J. Kolery
Revised 06/08/90 Revisor= T.J. Kolery

Sea water, including only the major ions. This is a considerably pared-down version of swwtst.3i, which contains the full benchmark sea water test case of Nordstrom et al. (1979, Table III).

Purpose: to test the code on a small problem involving a moderately concentrated solution. The activity coefficients of the aequous species are calculated from the B-dot equation and related equations.

References

Temperature (C) 25.00
Density (gm/cm3) 1.02336

Total Dissolved Salts

Electrical Balancing on

SPECIES BASIS SWITCH/CONSTRAINT CONCENTRATION UNITS OR TYPE

redox 0.5000 eb
na+ 10.7189 mg/kg
k+ 399.10 mg/kg
ca++ 412.30 mg/kg
mg++ 1291.3 mg/kg
hr 8.2200 rh
necl 0.20220E-02 molality
ct 27353.0 mg/kg
so4-- 2712.0 mg/kg

Input Solid Solutions
none

SUPPRESSED SPECIES (suppress,replace,augment,augmentg) value
none

OPTIONS

SOLID SOLUTIONS
* ignore solid solutions
process hypothetical solid solutions
process input and hypothetical solid solutions

LOADING OF SPECIES INTO MEMORY
* does nothing
lists species loaded into memory

ECO DATABASE INFORMATION
* does nothing
lists all reactions
lists reactions and log K values
lists reactions, log K values and polynomial coeff.

LIST OF AQUEOUS SPECIES (ordering)
* in order of decreasing concentration
in same order as input file

LIST OF AQUEOUS SPECIES (concentration limit)
* all species
only species > 10**-20 molal
only species > 10**-12 molal
not printed

LIST OF AQUEOUS SPECIES (by element)
* print major species
print all species
don't print

MINERAL SATURATION STATES
* print if affinity > 10 kJals
print all
* don't print

PH SCALE CONVENTION
* modified NBS
internal
rational

ACTIVITY COEFFICIENT OPTIONS
* use B-dot equation
EQ3NR input files in "D" format are treated differently from ones in "W" format in one important way. The input from files in "D" format are checked against allowed range limits, where such exist, as soon as the relevant lines of data are read. Error or warning messages may therefore appear right after these lines in the instant echo portion of the output file. Essentially the same checks are made for input in "W" format, but after the current problem has been read from the input file. Any relevant error or warning messages therefore appear after the instant echo on the output file.

6.2. Cautions

In the absence of analytical data, it is recommended that users take the default condition of jflag = 27 for the auxiliary basis species O_2(aq) and H_2(aq). The reason is that one (or the other) will then usually have a low but sufficiently high concentration to insure some poising of the oxygen fugacity. This has little significance if one is not passing the solution model on to EQ6. However, if one does, this is helpful in avoiding computational difficulties in that code which may arise in trying to treat very ill-poised systems. As an example, a user might be interested in the dissolution of a feldspar in CO_2-charged water. This problem appears to have no redox aspect, but EQ6 expects a problem to have a redox aspect unless the user invokes special options. If some O_2(aq) is not present in the modeled solution and these special options are not invoked, the code will run with very small step sizes, trying to do the nearly impossible job of accurately calculating the oxygen fugacity when there is hardly anything present to define it. If on running EQ3NR one sets iopt1 = 0 and sets fep to -0.700, the oxygen fugacity will at the atmospheric value and a concen-
tration of $O_{2(aq)}$ will be computed which is in equilibrium with this. This is enough to poise the system in the example cited, and EQ6 can then be run quite nicely without having to invoke the above noted special options.

If the user creates an aqueous system model in which data are input for an auxiliary basis species but not for the corresponding strict basis species, the results from the code calculation may not be what the user intended. Suppose an analyst reports $2 \text{ mg/L}$ of dissolved $Fe$ for some water. On all of the existing EQ3/6 data files, $Fe^{2+}$ is the strict basis species and $Fe^{3+}$ is in the auxiliary basis. Generally speaking, the quantity reported by the analyst really means total dissolved iron of either form. To input this correctly, the user must enter $2 \text{ mg/L}$ for $Fe^{2+}$. Then letting $jflag$ for $Fe^{3+}$ default to $30$, the mass balances for the two forms are combined and the calculation is done correctly. On the other hand, if the user inputs $2 \text{ mg/L}$ for $Fe^{3+}$, the $jflag$ value for $Fe^{2+}$ will default to $-1$, an internal value equivalent to $jflag = 0$ and $csp = 0$. In other words, $Fe^{2+}$ (and its associated ion pairs and complexes) will be absent from the model, and the input total concentration will be distributed only among $Fe^{3+}$ and its ion pairs and complexes.

As a general rule, it is not wise to create EQ3NR models in which an auxiliary basis species is present in the absence of the corresponding strict basis species. The calculations may be valid. However, the resulting aqueous solution model can not be input to EQ6. In situations in which an auxiliary basis species is present in the actual absence of the corresponding strict basis species, the roles of these species should be reversed by a basis switch. The instructions for the switch and the desired $jflag$ and $csp$ values should be entered on the input file as input for the original strict basis species. As the $csp$ input is initially interpreted in terms of this species, and will then be recalculated by the code for stoichiometric equivalence with the species switched into the strict basis set, it may be necessary to recalculate the analytical data for stoichiometric equivalence with the original basis species. The code will then invert this same calculation when it makes the basis switch.
7. Sample Problems: Inputs and Outputs

7.1. Introduction

This chapter presents the input and output files for several speciation-solubility modeling problems that are successfully executed by EQ3NR. Each example begins with a short discussion. The input file and output files are then presented. The reader is encouraged to compare the input file examples presented here with the input file description presented in Chapter 6. Note that each output file begins with an “instant” echo of the input file. The examples presented here were run on a Sun SPARCstation IPC using optimized code, using the “W” format input files and the “R10” com and hmw data files. More examples of EQ3NR input files can be found in Appendix F of the EQ6 Theoretical Manual and User’s Guide (Wolery and Daveler, 1992). The examples presented here are relatively simple. Two input files addressing more complex problems are presented without external comments or computed results in Appendix E.

On the output files one will occasionally see “+999” and “-999”. These are respectively treated in EQ3/6 as the logarithms of plus infinity and zero, respectively. In the context of their appearance in these files, they generally signify a condition of “no data.”

7.2. Sea Water Test Case, with Major Cations and Anions Only

The first sample problem is the sea water test case from Nordstrom et al. (1979), but in which only the major cations and anions are included. This simplified test case is a classic example in geochemistry (Garrels and Thompson, 1962; Garrels and Christ, 1965). The input file was presented in both “W” and “D” formats in the previous chapter, and will not be repeated here. We will here focus on the output file. The corresponding pickup file is presented in Chapter 8. The data file used is the com file, and the activity coefficients are computed from the B-dot equation (lop1 = 0).

The output file for this problem is presented in its entirety. The output begins with the name of the code and the version identification (“EQ3NR, version 3245.1090R124”). This is followed by a copyright notice and a set of disclaimers. This in turn is followed by a time and data stamp (“Run 09:31 3Dec91”).

The instant echo of the input file appears following the line, “--- reading the input file ---”. The input file contents appear shifted one character to the right, to be consistent with the use of older carriage control conventions. If all goes well this is followed by a blank line and the message, “--- the input file has been successfully read ---”.

The next action of the code is to read the data file. Note that the code prints messages when it starts (“--- reading the data file ---”) and finishes (“--- the data file has been successfully read ---”) this action.

This is followed by “EQ3NR” in large block letters. The code name and version identification are given, along with the version identification for the EQLIB library. The title from the input file is printed, followed by the name and version identification of the supporting data file. Problem and data file statistics are then printed, followed by a list of the problem inputs, including any default values or truncated values taken by the code. The table appearing under the header
"--- input constraints ---" is part of this summary. It is followed by a table headed by "--- inactive aqueous species ---". The entries in this table, if any, correspond to species which are either lacking thermodynamic data or have been suppressed by user options on the input file.

This is followed by the table headed by "--- modified input constraints ---". This lists the model inputs as they have been modified by the program before Newton-Raphson iteration commences. The modified constraints may differ from the original ones in several ways. They include all conversions of concentration units to the molal scale, any defaults provided by the program, and the effects of any basis switching. This table also shows the status of any auxiliary basis species that pertain to the model but which were not listed on the input file. Users should make it a point to examine this table to ensure that the model they are getting is indeed the one they want.

At this point, the code has set up the problem and is ready to solve it. The code then sets up starting estimates and refines them somewhat according to a pre-Newton-Raphson optimization algorithm described in Chapter 9. If this is successful, the code writes, "--- optimization ended within requested limits ---". This step is not always successful, which leads to the appearance of a message to that effect. However, this does not mean that the code has or will fail to solve the problem. It only means that the optimization algorithm failed to satisfy a set of tolerances before handing the problem over to hybrid Newton-Raphson iteration.

Some data are then printed showing the progress of hybrid Newton-Raphson iteration. The user does not need to be concerned with these data as long as the iteration process succeeds. The printing of these data on the output file is primarily done to provide an obvious break between the problem setup and the problem results. If iteration is successful, a message is printed to that effect ("Hybrid newton-raphson iteration converged in 4 steps.").

The data that follow should all be self-explanatory. Note that in the table headed by "----- distribution of aqueous species -----" many organic species appear. This occurs because the code is treating these species as complexes of $HCO_3^-$. This problem was discussed in Chapter 5 (at the end of Section 5.2). The R10 versions of the com and sup data files have a small number of organic species are in the auxiliary basis. There is a larger number of non-basis organic species, which are related by their associated reactions to these auxiliary basis species. These in turn are each related to $HCO_3^-$. Looking in the table headed by "--- modified input constraints ---", we see what the species are and that their $jflag$ values have been assigned default values of 30. This eliminates them from the active basis set and causes them and all related non-basis organic species to be treated as complexes of $HCO_3^-$

Knowing what these auxiliary basis species are, one could go back and enter $jflag = 0$ and $csp = 0$ for each of them, and then no organic species would appear in the computed model, which is really what one might normally desire. However, in this case, the results are not sensibly different from those that were desired anyway. Because the oxygen fugacity is high, the computed concentrations of all of these organic species are vanishingly small from a practical point of view.
Organic species can be more easily kept out of a speciation model using the newer R16 data files. The species 'acetic acid(aq)', one of the organics in the auxiliary basis, is now treated as the "mother" of all other organics. This was accomplished by writing the reactions of the other organic auxiliary basis species so that these species are converted to acetic acid instead of bicarbonate. Thus, entering jflag = 0 and csp = 0 for acetic acid suffices to prevent the appearance of any organic species (caution: the species CH₄(aq) is not treated as an organic; enter jflag = 0 and csp = 0 for it as well if this species is not desired). Similarly, on the R16 data files, the species S₂⁻ is the "mother" of other polysulfide species such as S₃²⁻ and S₄²⁻, and S₂O₅²⁻ is the "mother" of similar partially oxidized sulfur species such as S₂O₄²⁻ and S₂O₅²⁻. The R16 data files became available close to the publication deadline for this series of reports. It was not feasible to update the examples using these data files.

In the "summary of aqueous redox reactions" we see that the tabulated redox parameters have the same values for all of the redox couples in the table. This indicates that all these couples are in mutual equilibrium. This is not a scientific conclusion about the chemistry of sea water. Rather, it is an example that what comes out of a model must be consistent with what went into it. The input constraints for this problem assumed this equilibrium.

In the "summary of stoichiometric mineral saturation states", note that low to moderate supersaturations are predicted for several carbonate minerals, including calcite and aragonite. These are to be expected for surface sea water at 25°C (see for example, Berner, 1971).

Note that when the code is done with this problem, it looks for another on the input file. Not finding any, it terminates by writing run time statistics.

The EQ3NR output file for the sea water test case:
or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or the University of California, and shall not be used for advertising or product endorsement purposes.

**LLNL Yucca Mountain Project Disclaimer**

The Lawrence Livermore National Laboratory, a participant in the Yucca Mountain Project, has not determined that this software constitutes "approved code" for the conduct of "quality affecting work" for the Yucca Mountain Project.

Run 09:31 30ee91

--- reading the input file ---

EQN3I input file name- swnaj.3i
Description: "Sea water, major ions only"
Version number= 3245 Screen number- 01
Created 06/08/90 Creator- T.J. Wolery
Revised 06/08/90 Reviser- T.J. Wolery

Sea water, including only the major ions. This is a considerably pared-down version of swnaj.3i, which contains the full benchmark sea water test case of Nordstrom et al. (1979, Table III).

Purpose: to test the code on a small problem involving a moderately concentrated solution. The activity coefficients of the aqueous species are calculated from the B-dot equation and related equations.

References


endit.

temp = 0.25000E+02
t = 0.10234E+01
tdspl = 0.00000E+00
tdspi = 0.00000E+00
tdspp = 0.00000E+00
tdspp = 0.00000E+00
tdspl = 0.00000E+00
tdspl = 0.00000E+00
tdspl = 0.00000E+00
tdspl = 0.00000E+00
iterm = 0
iop1-10 = 1 2 3 4 5 6 7 8 9 10
iop2-10 = 0 0 0 0 0 0 0 0 0 0
iop3-10 = 0 0 0 0 0 0 0 0 0 0
iop4-10 = 0 0 0 0 0 0 0 0 0 0
iop5-10 = 0 0 0 0 0 0 0 0 0 0
iop6-10 = 0 0 0 0 0 0 0 0 0 0
iop7-10 = 0 0 0 0 0 0 0 0 0 0
iop8-10 = 0 0 0 0 0 0 0 0 0 0
iop9-10 = 0 0 0 0 0 0 0 0 0 0
iop10-10 = 0 0 0 0 0 0 0 0 0 0

--- the input file has been successfully read ---

--- reading the data file ---

--- the data file has been successfully read ---

* note: (eqlib/inbdot) The following aqueous species have been assigned a default hard core diameter of 4.000 Angstroms.-

calc2(eq)
caco3(aq)  
caso4(aq)  
li(aq)  
hso4(aq)  
koh(aq)  
mgco3(aq)  
na2hco3(aq)

eeqnrs.3245.r153

EQNR input file name= seaqma.3i
Description= "Sea water, major ions only"
Version number= 3245 Stage number= 01
Created 06/08/90 Creator= T.J. Wolery
Revised 06/08/90 Revisor= T.J. Wolery

Sea water, including only the major ions. This is a considerably pared-down version of swst.3i, which contains the full benchmark sea water test case of Nordstrom et al. (1979, Table III).

Purpose: to test the code on a small problem involving a moderately concentrated solution. The activity coefficients of the aqueous species are calculated from the B-dot equation and related equations.

References

data0.com.R10

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

the activity coefficients of aqueous solute species
and the activity of water are calculated according to the b-dot equation plus others

temperature= 25.00 degrees celsius
pressure= 1.0132 bars

78 elements are in the data base
100 elements can be loaded into memory
9 elements are active in this problem

852 aqueous species are in the data base
255 aqueous species were loaded into memory
800 aqueous species can be loaded into memory
133 aqueous species are active in this problem

771 aqueous reactions are in the data base
179 aqueous reactions were loaded into memory
699 aqueous reactions can be loaded into memory

886 minerals are in the data base
84 minerals were loaded into memory
859 minerals can be loaded into memory
84 minerals are active in this problem

12 solid solutions are in the data base
50 solid solutions can be loaded into memory

76 gases are in the data base
16 gases were loaded into memory
80 gases can be loaded into memory
16 gases are active in this problem
solution density = 1.02336 g/ml

total dissolved salts = 0.00 mg/kg solution

total dissolved salts = 0.00 mg/l

tolbt = 0.1000E-05 (convergence tolerance on residual functions)
toldl = 0.1000E-05 (convergence tolerance on correction terms)
tolsat = 0.5000E+00 (phase saturation tolerance, does not affect convergence)

--- input constraints ---

<table>
<thead>
<tr>
<th>species</th>
<th>csp</th>
<th>jflag</th>
<th>input type/co-species</th>
</tr>
</thead>
<tbody>
<tr>
<td>na+</td>
<td>1.07638E+04</td>
<td>3</td>
<td>tot conc, mg/kg</td>
</tr>
<tr>
<td>k+</td>
<td>3.9109E+02</td>
<td>3</td>
<td>tot conc, mg/kg</td>
</tr>
<tr>
<td>ca++</td>
<td>4.1235E+02</td>
<td>3</td>
<td>tot conc, mg/kg</td>
</tr>
<tr>
<td>mg++</td>
<td>1.2913E+03</td>
<td>3</td>
<td>tot conc, mg/kg</td>
</tr>
<tr>
<td>h+</td>
<td>-0.2200E+00</td>
<td>16</td>
<td>log activity</td>
</tr>
<tr>
<td>h2o</td>
<td>2.0220E-03</td>
<td>0</td>
<td>tot conc, molal</td>
</tr>
<tr>
<td>cl-</td>
<td>1.9359E+04</td>
<td>3</td>
<td>tot conc, mg/kg</td>
</tr>
<tr>
<td>so4++</td>
<td>2.7120E+03</td>
<td>3</td>
<td>tot conc, mg/kg</td>
</tr>
</tbody>
</table>

--- inactive aqueous species ---

(a-path) benzene(aq)
--- modified input constraints ---

<table>
<thead>
<tr>
<th>species</th>
<th>cap</th>
<th>jflag</th>
<th>input type/co-species</th>
</tr>
</thead>
<tbody>
<tr>
<td>ca**</td>
<td>1.02074E-02</td>
<td>0</td>
<td>tot conc. molal</td>
</tr>
<tr>
<td>cl-</td>
<td>5.45802E-01</td>
<td>0</td>
<td>tot conc. molal</td>
</tr>
<tr>
<td>hr</td>
<td>-9.22006E+00</td>
<td>16</td>
<td>log activity</td>
</tr>
<tr>
<td>hco3-</td>
<td>7.02206E-03</td>
<td>0</td>
<td>tot conc. molal</td>
</tr>
<tr>
<td>k+</td>
<td>1.02076E-02</td>
<td>0</td>
<td>tot conc. molal</td>
</tr>
<tr>
<td>mg**</td>
<td>3.31496E-02</td>
<td>0</td>
<td>tot conc. molal</td>
</tr>
<tr>
<td>na+</td>
<td>4.68302E-01</td>
<td>0</td>
<td>tot conc. molal</td>
</tr>
<tr>
<td>so4--</td>
<td>2.82113E-02</td>
<td>0</td>
<td>tot conc. molal</td>
</tr>
<tr>
<td>(o-phth)~</td>
<td>0.00000E+00</td>
<td>30</td>
<td>eliminated species</td>
</tr>
<tr>
<td>acetic acid(aq)</td>
<td>0.00000E+00</td>
<td>30</td>
<td>eliminated species</td>
</tr>
<tr>
<td>acetone(aq)</td>
<td>0.00000E+00</td>
<td>30</td>
<td>eliminated species</td>
</tr>
<tr>
<td>benzene(aq)</td>
<td>0.00000E+00</td>
<td>30</td>
<td>eliminated species</td>
</tr>
<tr>
<td>cfo</td>
<td>0.00000E+00</td>
<td>30</td>
<td>eliminated species</td>
</tr>
<tr>
<td>co2(aq)</td>
<td>0.00000E+00</td>
<td>30</td>
<td>eliminated species</td>
</tr>
<tr>
<td>co3--</td>
<td>0.00000E+00</td>
<td>30</td>
<td>eliminated species</td>
</tr>
<tr>
<td>cthane(aq)</td>
<td>0.00000E+00</td>
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<td>eliminated species</td>
</tr>
<tr>
<td>h2(aq)</td>
<td>0.00000E+00</td>
<td>30</td>
<td>eliminated species</td>
</tr>
<tr>
<td>hso3--</td>
<td>0.00000E+00</td>
<td>30</td>
<td>eliminated species</td>
</tr>
<tr>
<td>methano(aq)</td>
<td>0.00000E+00</td>
<td>30</td>
<td>eliminated species</td>
</tr>
<tr>
<td>methanol(aq)</td>
<td>0.00000E+00</td>
<td>30</td>
<td>eliminated species</td>
</tr>
<tr>
<td>o2(aq)</td>
<td>0.00000E+00</td>
<td>30</td>
<td>eliminated species</td>
</tr>
<tr>
<td>oh-</td>
<td>0.00000E+00</td>
<td>30</td>
<td>eliminated species</td>
</tr>
<tr>
<td>so3--</td>
<td>0.00000E+00</td>
<td>30</td>
<td>eliminated species</td>
</tr>
</tbody>
</table>

--- optimization ended within requested limits ---

iter= 0
del( conc so4-- ) => 0.00000E+00, delfn= 0.00000E+00
beta(conc so4-- ) => 7.30728E-02, betfn= 0.00000E+00
bbig= 7.30728E-02, ubbig= so4--
bneg= 0.00000E+00, ubneg= none
bgam= -1.52413E-04, ubgam= mg4(oh)4++++
bgam= 0.00000E+00
bx= 0.00000E+00
bfcnr= 0.00000E+00

iter= 1
del(conc so4-- ) => -2.71023E-02, delfn= 0.00000E+00
beta(conc so4-- ) => 4.33286E-03, betfn= 9.40705E-01
bbig= 4.33286E-03, ubbig= so4--
bneg= 0.00000E+00, ubneg= none
bgam= -1.79456E-03, ubgam= mg4(oh)4++++
bgam= -4.72140E-03
bx= -7.47492E-03
bfcnr= 9.66315E-01

iter= 2
del(conc so4-- ) => -1.78199E-03, delfn= 9.34443E-01
beta(conc so4-- ) => 8.88639E-05, betfn= 9.79919E-01
bbig= 8.88639E-05, ubbig= so4--
bneg= 0.00000E+00, ubneg= none
bgam= -1.61627E-04, ubgam= mg4(oh)4++++
bgam= -1.18720E-04
bx= -7.19716E-04
bfcnr= 9.97035E-01

iter= 3
del(conc so4-- ) => -3.60694E-05, delfn= 9.79759E-01
beta(conc so4-- ) => 1.86766E-06, betfn= 9.78926E-01
bbig= 1.86766E-06, ubbig= so4--
bneg= 0.00000E+00, ubneg= none
bgam= -3.78999E-06, ubgam= mg4(oh)4++++
bgam= -1.09320E-06
bx= -7.18463E-06
bfcnr= 9.40734E-01

iter= 4
del(conc so4-- ) => -7.53517E-07, delfn= 9.79109E-01
beta(conc so4-- ) => 4.07346E-08, betfn= 9.78180E-01
bbig= 4.07346E-08, ubbig= so4--
bneg= 0.00000E+00, ubneg= none
bgam= -1.06804E-08, ubgam= mg4(oh)4++++
bgam= -4.06804E-08
bx= -1.63586E-07
bfcnr= 9.98647E-01

Hybrid Newton-Raphson iteration converged in 4 steps.

--- Summary of the Aqueous Phase ---
### Elemental composition of the aqueous phase ###

<table>
<thead>
<tr>
<th>element</th>
<th>mg/l</th>
<th>mg/kg</th>
<th>moles/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.91000E+06</td>
<td>0.89000E+06</td>
<td>0.5562741837E+02</td>
</tr>
<tr>
<td>Ca</td>
<td>421.93</td>
<td>412.30</td>
<td>0.1028743950E+01</td>
</tr>
<tr>
<td>Cl</td>
<td>19805.</td>
<td>19353.</td>
<td>0.5458822668E+00</td>
</tr>
<tr>
<td>H</td>
<td>0.11451E+06</td>
<td>0.11319E+06</td>
<td>0.1110187334E+03</td>
</tr>
<tr>
<td>C</td>
<td>24.834</td>
<td>24.286</td>
<td>0.0202000001E+02</td>
</tr>
<tr>
<td>K</td>
<td>408.42</td>
<td>399.10</td>
<td>0.1020760495E-01</td>
</tr>
<tr>
<td>Mg</td>
<td>1322.0</td>
<td>1291.8</td>
<td>0.5314955494E-01</td>
</tr>
<tr>
<td>Na</td>
<td>11020.</td>
<td>10768.</td>
<td>0.4693824210E+00</td>
</tr>
<tr>
<td>S</td>
<td>926.41</td>
<td>905.26</td>
<td>0.2823129792E-01</td>
</tr>
</tbody>
</table>

### Elemental composition as strict basis species ###

<table>
<thead>
<tr>
<th>species</th>
<th>moles/kg H2O</th>
<th>moles/kg H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O</td>
<td>0.10256E+07</td>
<td>0.10021E+07</td>
</tr>
<tr>
<td>Ca++</td>
<td>431.03</td>
<td>412.30</td>
</tr>
<tr>
<td>Cl-</td>
<td>19063.</td>
<td>19353.</td>
</tr>
<tr>
<td>H+</td>
<td>0.11451E+06</td>
<td>0.11319E+06</td>
</tr>
<tr>
<td>HCO3-</td>
<td>126.26</td>
<td>121.38</td>
</tr>
<tr>
<td>Mg++</td>
<td>408.42</td>
<td>399.10</td>
</tr>
<tr>
<td>Na+</td>
<td>1322.0</td>
<td>1291.8</td>
</tr>
<tr>
<td>SO4--</td>
<td>2775.4</td>
<td>2712.0</td>
</tr>
</tbody>
</table>

### Equivalent composition of the aqueous phase (cete balances) ###

<table>
<thead>
<tr>
<th>species</th>
<th>moles/kg H2O</th>
<th>moles/kg H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O</td>
<td>0.5562741837E+02</td>
<td>0.5562741837E+02</td>
</tr>
<tr>
<td>Ca++</td>
<td>0.1028743950E+01</td>
<td>0.1028743950E+01</td>
</tr>
<tr>
<td>Cl-</td>
<td>0.5458822668E+00</td>
<td>0.5458822668E+00</td>
</tr>
<tr>
<td>H+</td>
<td>0.1110187334E+03</td>
<td>0.1110187334E+03</td>
</tr>
<tr>
<td>HCO3-</td>
<td>0.2020000001E+02</td>
<td>0.2020000001E+02</td>
</tr>
<tr>
<td>Mg++</td>
<td>0.5314955494E-01</td>
<td>0.5314955494E-01</td>
</tr>
<tr>
<td>Na+</td>
<td>0.4693824210E+00</td>
<td>0.4693824210E+00</td>
</tr>
<tr>
<td>SO4--</td>
<td>0.2823129792E-01</td>
<td>0.2823129792E-01</td>
</tr>
</tbody>
</table>

---

**Activity of water** = 0.99233

**Log activity of water** = -0.00774

**True osmotic coefficient** = 0.91574

**Stoichiometric osmotic coefficient** = 0.86520

**Sum of true molalities** = 1.08092608297521

**Sum of stoichiometric molalities** = 1.118217202006

**True ionic strength** = 0.6226746935852

**Stoichiometric ionic strength** = 0.6966516633063

### Electrical balance totals ###

**Equivalent/eq**

| sigma(mg) cations | 0.5599123587E+00 |
| sigma(mg) anions | -0.5599123587E+00 |
| total charge     | 0.1118971109E+01 |
| mean charge      | 0.5599123587E+00 |
| charge imbalance | 0.2540965850E-03 |

**Total charge** = **sigma(mg) cations** + abs( **sigma(mg) anions** )

**Mean charge** = 1/2 total charge

**The electrical imbalance is**

0.853E-03 per cent of the total charge
### Activity Ratios of Ions

<table>
<thead>
<tr>
<th>Species</th>
<th>log activity</th>
<th>log conc</th>
<th>log g</th>
<th>Activity (log)</th>
</tr>
</thead>
<tbody>
<tr>
<td>act(oh)</td>
<td>0.9981E-02</td>
<td>-2.0008</td>
<td>-0.2180</td>
<td>0.6629E-02</td>
</tr>
<tr>
<td>act(h+)</td>
<td>0.1710E-02</td>
<td>-2.1772</td>
<td>-0.1559</td>
<td>0.6444E-02</td>
</tr>
<tr>
<td>act(h2o4)</td>
<td>0.5789E-12</td>
<td>-3.2237</td>
<td>-0.1599</td>
<td>0.5890E-12</td>
</tr>
<tr>
<td>o2(aq)</td>
<td>0.4564E-29</td>
<td>-29.3808</td>
<td>0.0508</td>
<td>0.4671E-29</td>
</tr>
<tr>
<td>h2o2(aq)</td>
<td>0.6468E-20</td>
<td>-20.0722</td>
<td>0.0000</td>
<td>0.8468E-20</td>
</tr>
<tr>
<td>clo2</td>
<td>0.8399E-25</td>
<td>-25.0758</td>
<td>-0.1599</td>
<td>0.3868E-25</td>
</tr>
<tr>
<td>hclo(aq)</td>
<td>0.1309E-25</td>
<td>-25.0832</td>
<td>0.0000</td>
<td>0.1309E-25</td>
</tr>
<tr>
<td>h2o2</td>
<td>0.2519E-29</td>
<td>-29.5988</td>
<td>-0.1599</td>
<td>0.1759E-29</td>
</tr>
<tr>
<td>formate</td>
<td>0.9274E-36</td>
<td>-36.0320</td>
<td>-0.1599</td>
<td>0.6476E-36</td>
</tr>
<tr>
<td>h2(aq)</td>
<td>0.3561E-36</td>
<td>-36.5001</td>
<td>0.0508</td>
<td>0.2535E-36</td>
</tr>
<tr>
<td>h2o5</td>
<td>0.2356E-37</td>
<td>-37.6279</td>
<td>-0.1599</td>
<td>0.1645E-37</td>
</tr>
<tr>
<td>so2</td>
<td>0.1452E-38</td>
<td>-38.0381</td>
<td>-0.1599</td>
<td>0.2628E-39</td>
</tr>
<tr>
<td>hso3</td>
<td>0.3733E-40</td>
<td>-40.4302</td>
<td>-0.1599</td>
<td>0.2539E-40</td>
</tr>
<tr>
<td>formic acid(aq)</td>
<td>0.2209E-40</td>
<td>-40.6558</td>
<td>0.0000</td>
<td>0.2209E-40</td>
</tr>
<tr>
<td>clo2</td>
<td>0.1780E-42</td>
<td>-42.7473</td>
<td>-0.1599</td>
<td>0.1250E-42</td>
</tr>
<tr>
<td>hclo3</td>
<td>0.2073E-46</td>
<td>-46.5652</td>
<td>-0.1599</td>
<td>0.1250E-46</td>
</tr>
<tr>
<td>h2o3+</td>
<td>0.1592E-46</td>
<td>-46.7900</td>
<td>0.0000</td>
<td>0.1592E-46</td>
</tr>
<tr>
<td>so3-</td>
<td>0.1153E-46</td>
<td>-46.9642</td>
<td>0.0000</td>
<td>0.1153E-46</td>
</tr>
<tr>
<td>hso4</td>
<td>0.1114E-47</td>
<td>-47.7642</td>
<td>0.0000</td>
<td>0.1114E-47</td>
</tr>
<tr>
<td>clo-</td>
<td>0.8163E-53</td>
<td>-53.0002</td>
<td>-0.7334</td>
<td>0.1508E-53</td>
</tr>
<tr>
<td>hclo-</td>
<td>0.2241E-54</td>
<td>-54.6404</td>
<td>-0.1599</td>
<td>0.1464E-54</td>
</tr>
<tr>
<td>clo-</td>
<td>0.5643E-05</td>
<td>-0.85.2385</td>
<td>-0.7334</td>
<td>0.1043E-05</td>
</tr>
<tr>
<td>methanol(aq)</td>
<td>0.6522E-120</td>
<td>-120.1095</td>
<td>0.0000</td>
<td>0.5227E-120</td>
</tr>
<tr>
<td>h2so4(aq)</td>
<td>0.8468E-20</td>
<td>-20.0722</td>
<td>0.0000</td>
<td>0.8468E-20</td>
</tr>
<tr>
<td>mg4&lt;oh&gt;4+</td>
<td>0.1250E-31</td>
<td>-31.8904</td>
<td>-2.7012</td>
<td>0.3561E-14</td>
</tr>
<tr>
<td>clo-</td>
<td>0.2519E-29</td>
<td>-29.5988</td>
<td>-0.1599</td>
<td>0.1759E-29</td>
</tr>
<tr>
<td>clo-</td>
<td>0.170 per cent of the mean charge</td>
<td>0.170 per cent of sigma(mg) cations</td>
<td>0.171 per cent of sigma(mg) anions</td>
<td></td>
</tr>
<tr>
<td>Species</td>
<td>log conc</td>
<td>log g</td>
<td>Activity (log)</td>
<td></td>
</tr>
</tbody>
</table>

### Distribution of Aqueous Species

<table>
<thead>
<tr>
<th>species</th>
<th>log conc</th>
<th>log g</th>
<th>Activity (log)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hcl(aq)</td>
<td>0.1411E-09</td>
<td>-9.3552</td>
<td>0.3416E-08</td>
</tr>
<tr>
<td>h2sio3</td>
<td>0.1900E-111</td>
<td>-111.7213</td>
<td>0.0000</td>
</tr>
<tr>
<td>h2so3</td>
<td>0.8468E-20</td>
<td>-20.0722</td>
<td>0.0000</td>
</tr>
<tr>
<td>h2o</td>
<td>0.8163E-53</td>
<td>-53.0002</td>
<td>-0.7334</td>
</tr>
<tr>
<td>h2o</td>
<td>0.2241E-54</td>
<td>-54.6404</td>
<td>-0.1599</td>
</tr>
<tr>
<td>h2o</td>
<td>0.5643E-05</td>
<td>-0.85.2385</td>
<td>-0.7334</td>
</tr>
<tr>
<td>h2o</td>
<td>0.6522E-120</td>
<td>-120.1095</td>
<td>0.0000</td>
</tr>
<tr>
<td>h2o</td>
<td>0.8468E-20</td>
<td>-20.0722</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

---

*Note: The table contains log activity values for various aqueous species, along with their corresponding log conc and log g values.
### Alkaline Earth Metals

<table>
<thead>
<tr>
<th>Species</th>
<th>Mol Conc</th>
<th>Per Cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca**</td>
<td>0.9368E-02</td>
<td>90.09</td>
</tr>
<tr>
<td>CaSO4(aq)</td>
<td>0.6712E-03</td>
<td>6.52</td>
</tr>
<tr>
<td>CaCl2(aq)</td>
<td>0.2271E-02</td>
<td>2.21</td>
</tr>
<tr>
<td>CaCO3(aq)</td>
<td>0.5676E-04</td>
<td>0.55</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>99.37</td>
</tr>
</tbody>
</table>

### Chloride

<table>
<thead>
<tr>
<th>Species</th>
<th>Mol Conc</th>
<th>Per Cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl-</td>
<td>0.5344E-00</td>
<td>96.05</td>
</tr>
<tr>
<td>NaCl(aq)</td>
<td>0.1648E-01</td>
<td>3.02</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>99.07</td>
</tr>
</tbody>
</table>

### Total Carbonic Acid

<table>
<thead>
<tr>
<th>Species</th>
<th>Mol Conc</th>
<th>Per Cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCO3-</td>
<td>0.1201E-02</td>
<td>63.36</td>
</tr>
<tr>
<td>NaHCO3(aq)</td>
<td>0.3672E-03</td>
<td>18.18</td>
</tr>
<tr>
<td>MgHCO3-</td>
<td>0.1394E-03</td>
<td>8.87</td>
</tr>
</tbody>
</table>
### Aqueous Species Accounting for 99% or More of $K^+$

<table>
<thead>
<tr>
<th>Species</th>
<th>Molal Conc</th>
<th>Molar Conc</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K^+$</td>
<td>0.9981E-02</td>
<td>97.78</td>
</tr>
<tr>
<td>$KNO_3^-$</td>
<td>0.1001E-03</td>
<td>1.57</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>99.35</strong></td>
</tr>
</tbody>
</table>

### Aqueous Species Accounting for 99% or More of $Mg^{2+}$

<table>
<thead>
<tr>
<th>Species</th>
<th>Molal Conc</th>
<th>Molar Conc</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Mg^{2+}$</td>
<td>0.4072E-01</td>
<td>76.62</td>
</tr>
<tr>
<td>$MgSO_4(aq)$</td>
<td>0.7531E-02</td>
<td>14.17</td>
</tr>
<tr>
<td>$MgCl^+$</td>
<td>0.4638E-02</td>
<td>8.73</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>99.92</strong></td>
</tr>
</tbody>
</table>

### Aqueous Species Accounting for 99% or More of $Na^+$

<table>
<thead>
<tr>
<th>Species</th>
<th>Molal Conc</th>
<th>Molar Conc</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Na^+$</td>
<td>0.4449E+00</td>
<td>94.90</td>
</tr>
<tr>
<td>$NaCl(aq)$</td>
<td>0.1648E-01</td>
<td>3.52</td>
</tr>
<tr>
<td>$NaSO_4^-$</td>
<td>0.6650E-02</td>
<td>1.42</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>99.92</strong></td>
</tr>
</tbody>
</table>

### Aqueous Species Accounting for 99% or More of $SO_4^{2-}$

<table>
<thead>
<tr>
<th>Species</th>
<th>Molal Conc</th>
<th>Molar Conc</th>
</tr>
</thead>
<tbody>
<tr>
<td>$SO_4^{2-}$</td>
<td>0.1322E-01</td>
<td>46.82</td>
</tr>
<tr>
<td>$MgSO_4(aq)$</td>
<td>0.7531E-02</td>
<td>26.68</td>
</tr>
<tr>
<td>$NaSO_4^-$</td>
<td>0.6650E-02</td>
<td>23.26</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>99.92</strong></td>
</tr>
</tbody>
</table>

### Summary of Aqueous Redox Reactions

<table>
<thead>
<tr>
<th>Couple</th>
<th>$E_h$, Volts</th>
<th>PE</th>
<th>$log fO_2$</th>
<th>$ah$, Kcal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Default</td>
<td>0.500</td>
<td>0.8452E-01</td>
<td>-16.432</td>
<td>11.531</td>
</tr>
<tr>
<td>Acetic $a/hCO_3^-$</td>
<td>0.500</td>
<td>0.8452E-01</td>
<td>-16.432</td>
<td>11.531</td>
</tr>
<tr>
<td>Acetone $a/hCO_3^-$</td>
<td>0.500</td>
<td>0.8452E-01</td>
<td>-16.432</td>
<td>11.531</td>
</tr>
<tr>
<td>Clo2 $/hClO_3^-$</td>
<td>0.500</td>
<td>0.8452E-01</td>
<td>-16.432</td>
<td>11.531</td>
</tr>
<tr>
<td>Ethanol $a/hCO_3^-$</td>
<td>0.500</td>
<td>0.8452E-01</td>
<td>-16.432</td>
<td>11.531</td>
</tr>
<tr>
<td>$H_2O$ /$H_2$</td>
<td>0.500</td>
<td>0.8452E-01</td>
<td>-16.432</td>
<td>22.552</td>
</tr>
<tr>
<td>$H_2S$ /$SO_2$</td>
<td>0.500</td>
<td>0.8452E-01</td>
<td>-16.432</td>
<td>11.531</td>
</tr>
<tr>
<td>Methane $a/hCO_3^-$</td>
<td>0.500</td>
<td>0.8452E-01</td>
<td>-16.432</td>
<td>11.531</td>
</tr>
<tr>
<td>Methanol $a/hCO_3^-$</td>
<td>0.500</td>
<td>0.8452E-01</td>
<td>-16.432</td>
<td>11.531</td>
</tr>
<tr>
<td>$CO_2(aq)$ /$H_2O$</td>
<td>0.500</td>
<td>0.8452E-01</td>
<td>-16.432</td>
<td>11.531</td>
</tr>
<tr>
<td>$SO_3^2-$ /$SO_4^{2-}$</td>
<td>0.500</td>
<td>0.8452E-01</td>
<td>-16.432</td>
<td>11.531</td>
</tr>
</tbody>
</table>

### Summary of Aqueous Non-Equilibrium Non-Redox Reactions

<table>
<thead>
<tr>
<th>Couple</th>
<th>Affinity, Kcal</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td></td>
</tr>
</tbody>
</table>

### Summary of Stoichiometric Mineral Saturation States

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Log $q/k$</th>
<th>Aff, Kcal</th>
<th>State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anhydrite</td>
<td>-0.978</td>
<td>-1.334</td>
<td></td>
</tr>
<tr>
<td>Aragonite</td>
<td>-5.249</td>
<td>-7.161</td>
<td></td>
</tr>
<tr>
<td>Basanite</td>
<td>-1.621</td>
<td>-2.219</td>
<td></td>
</tr>
<tr>
<td>Bloodite</td>
<td>1.706</td>
<td>-7.880</td>
<td></td>
</tr>
<tr>
<td>Calcite</td>
<td>0.651</td>
<td>0.000</td>
<td>ssatd</td>
</tr>
<tr>
<td>Dolomite</td>
<td>3.235</td>
<td>4.414</td>
<td>ssatd</td>
</tr>
<tr>
<td>Dolomite-ord</td>
<td>4.325</td>
<td>4.144</td>
<td>ssatd</td>
</tr>
<tr>
<td>Gaylodolite</td>
<td>-4.623</td>
<td>-6.297</td>
<td></td>
</tr>
<tr>
<td>Gypsum</td>
<td>-0.817</td>
<td>-1.115</td>
<td></td>
</tr>
</tbody>
</table>

### Minerals with Affinities (10 Kcal are Not Listed)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Log $q/k$</th>
<th>Aff, Kcal</th>
<th>State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aragonite</td>
<td>-1.928</td>
<td>-2.631</td>
<td></td>
</tr>
<tr>
<td>Basanite</td>
<td>-7.292</td>
<td>-9.940</td>
<td></td>
</tr>
<tr>
<td>Bloodite</td>
<td>-1.766</td>
<td>-2.450</td>
<td></td>
</tr>
<tr>
<td>Calcite</td>
<td>1.600</td>
<td>2.307</td>
<td></td>
</tr>
<tr>
<td>Dolomite</td>
<td>-2.627</td>
<td>-3.538</td>
<td></td>
</tr>
<tr>
<td>Dolomite-ord</td>
<td>-3.509</td>
<td>-4.787</td>
<td></td>
</tr>
<tr>
<td>Gypsum</td>
<td>-2.592</td>
<td>-3.536</td>
<td></td>
</tr>
<tr>
<td>Mineral</td>
<td>Pitzer</td>
<td>Harvie</td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td>--------</td>
<td>--------</td>
<td></td>
</tr>
<tr>
<td>f</td>
<td>m</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>m.g. 5so4(ch)</td>
<td>0.055</td>
<td>0.055</td>
<td></td>
</tr>
<tr>
<td>m.g. 5co3:3so4</td>
<td>0.022</td>
<td>0.022</td>
<td></td>
</tr>
<tr>
<td>m.g. 4co3:2so4</td>
<td>0.250</td>
<td>0.250</td>
<td></td>
</tr>
<tr>
<td>m.g. 3co3:2so4</td>
<td>0.500</td>
<td>0.500</td>
<td></td>
</tr>
</tbody>
</table>

2 approx. saturated pure minerals
0 approx. saturated end-members of specified solid solutions
0 saturated end-members of hypothetical solid solutions

7 supersaturated pure minerals
0 supersatd. end-members of specified solid solutions
0 supersatd. hypothetical solid solution phases

### summary of gases

<table>
<thead>
<tr>
<th>Gas</th>
<th>Fugacity</th>
<th>Log Fugacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>c(g)</td>
<td>0.195644-173</td>
<td>-173.70853</td>
</tr>
<tr>
<td>c(g)</td>
<td>0.219654-141</td>
<td>-141.65826</td>
</tr>
<tr>
<td>co2(g)</td>
<td>0.375270-03</td>
<td>-3.44700</td>
</tr>
<tr>
<td>h2o(g)</td>
<td>0.452523-33</td>
<td>-33.24436</td>
</tr>
<tr>
<td>h2o(g)</td>
<td>0.255180-01</td>
<td>-1.95314</td>
</tr>
<tr>
<td>h2o(g)</td>
<td>0.104994-110</td>
<td>-110.73308</td>
</tr>
<tr>
<td>h2o(g)</td>
<td>0.101490-14</td>
<td>-14.49950</td>
</tr>
<tr>
<td>k(g)</td>
<td>0.174855-70</td>
<td>-70.77473</td>
</tr>
<tr>
<td>mg(g)</td>
<td>0.030804-12</td>
<td>-11.88050</td>
</tr>
<tr>
<td>na(g)</td>
<td>0.434634-68</td>
<td>-68.34180</td>
</tr>
<tr>
<td>o2(g)</td>
<td>0.370023-16</td>
<td>-16.43177</td>
</tr>
<tr>
<td>so2(g)</td>
<td>0.372234-180</td>
<td>-180.42918</td>
</tr>
</tbody>
</table>

7.3. The Sea Water Test Case, Using Pitzer's Equations

The preceding test case can also be run using Pitzer's equations. The results presented here were obtained using the bmw data file, which is based on Harvie, Mallr, and Weare (1984). The only functional difference between the input file used here and that in the previous case is that *iopgl = 1* in the present case. The input files are shown in both "W" and "D" formats. The output file is reproduced here beginning with the message announcing the end of Newton-Raphson iteration.

The results differ from those in the previous section because the underlying models are different. In fact, some quantities, including individual species molalities and activity coefficients, cannot be compared in a meaningful way. This is due to the fact that the models utilize different sets of species to represent the systems. Note that far fewer species appear in the present case. The only
ion pairs represented are $CaCO_3^{aq}$, $MgCO_3^{aq}$, and $MgOH^+$. Also note that no organics appear on the present output file, as there are none in this model.

Some parameters which can be compared are the activities and activity coefficients of the electrically neutral species common to both models (mostly basis species). For the ions, electrically neutral combinations of these parameters can also be compared. The single-ion activities and activity coefficients themselves can be compared, but not in a truly exact sense. Note that in both the present case and the previous one, the $iopgl$ option switch is set to 0, causing all single-ion activities and activity coefficients to be normalized to the NBS $pH$ scale. However, the exact definition of this scale in a solution as concentrated as sea water has some ionic strength dependence, and the ionic strength of this water is slightly different in the two models (0.6964 versus 0.6227 molal). The saturation indices of the various minerals common to both models can be compared with no problem. In the present case, the $SI$ for calcite is +0.645; in the previous case, it was +0.651. This is reasonably good agreement, though the results in the present case are without doubt more accurate.

The EQ3NR input file (swmaip.3i), the sea water benchmark test case using Pitzer’s equations ("W" format):

EQ3NR input file name= swmaip.3i
Description= "Sea water, major ions only, using Pitzer’s equations"
Version number= 3245 Stage number= 01
Creator= 06/08/90 Creator= T.J. Koltery
Revision= 06/08/90 Revisor= T.J. Koltery

Sea water, including only the major ions. This is a considerably pared-down version of sw3st.31, which contains the full benchmark sea water test case of Nordstrom et al. (1979, Table III).

Purpose: to test the code on a small problem involving a moderately concentrated solution, using Pitzer’s equations to calculate the activity coefficients of the aqueous species. Input file swmaaj.31 runs the same problem using the $S$-dot equation and related equations instead of Pitzer’s equations. Input file swmajd.31 runs the same problem using the Davies equation.

This problem is best addressed using the thermodynamic data base of Harvie, Moller, and Weare (1984).

References

The EQ3NR input file (swmain.3i), sea water benchmark test case using Pitzer's equations ("D" format):

```
EQ3NR input file name= swmain.3i
Description= "Sea water, major ions only, using Pitzer's equations"
Version number= 3245  Stage number= 01
Created 06/08/90 Creator= T.J. Moler
Revised 06/00/90 Revisor= T.J. Moler

Sea water, including only the major ions. This is a considerably pared-down version of swtst.3i, which contains the full benchmark sea water test case of Nordstrom et al. (1979, Table III).

Purpose: to test the code on a small problem involving a moderately concentrated solution, using Pitzer's equations to calculate the activity coefficients of the aqueous species. Input file swmaj.3i runs the same problem using the B-dot equation and related equations instead of Pitzer's equations. Input file swmajd.3i runs the same problem using the Davies equation.

This problem is best addressed according to Holler, and Weare (1984).

References
Harvie, C. E., Moller, N., and Weare, J. H., 1984, The prediction of mineral solubilities in natural waters: The Na-K-Ca[K]-Cl-SO4-
OH-HCO3-CO3-CO2-H2O system to high ionic strengths at 25 C;
Nordstrom, D. K., et al., 1979, A comparison of computerized chemical models for equilibrium calculations in aqueous systems, in Jenne,
```

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>25.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (gm/cm3)</td>
<td>1.02356</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Total Dissolved Salts</th>
<th>mg/kg</th>
<th>mg/l</th>
<th>*not used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical Balancing on</td>
<td>code selects</td>
<td>*not performed</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SPEC</th>
<th>BASIS SWITCH/CONSTRAINT</th>
<th>CONCENTRATION</th>
<th>UNITS OR TYPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>redox na+</td>
<td>0.3000</td>
<td>eH</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1068.</td>
<td>mg/kg</td>
<td></td>
</tr>
<tr>
<td></td>
<td>399.10</td>
<td>mg/kg</td>
<td></td>
</tr>
<tr>
<td>ca++</td>
<td>412.30</td>
<td>mg/kg</td>
<td></td>
</tr>
<tr>
<td>mg++</td>
<td>1291.0</td>
<td>mg/kg</td>
<td></td>
</tr>
<tr>
<td>h+</td>
<td>18.220</td>
<td>pH</td>
<td></td>
</tr>
<tr>
<td>hco3-</td>
<td>0.002022</td>
<td>molality</td>
<td></td>
</tr>
<tr>
<td>cl-</td>
<td>1915.3</td>
<td>mg/kg</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Input Solid Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SUPPRESSED SPECIES (suppress, replace, augment) value</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
</tr>
</tbody>
</table>

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OPTIONS

- **SOLID SOLUTIONS**
  - ignore solid solutions
  - process hypothetical solid solutions
  - process input and hypothetical solid solutions
- **LOADING OF SPECIES INTO MEMORY**
  - does nothing
  - lists species loaded into memory
- **ECO DATABASE INFORMATION**
  - does nothing
  - lists all reactions
  - lists reactions and log K values
  - lists reactions, log K values and polynomial coeff.
- **LIST OF AQUEOUS SPECIES (ordering)**
  - in order of decreasing concentration
  - in same order as input file
- **LIST OF AQUEOUS SPECIES (concentration limit)**
  - all species
  - only species > 10^{-20} molal
  - only species > 10^{-12} molal
  - not printed
- **LIST OF AQUEOUS SPECIES (by element)**
  - print major species
  - print all species
  - don't print
- **MINERAL SATURATION STATES**
  - print if affinity > -10 kcals
  - print all
  - don't print
- **pH SCALE CONVENTION**
  - modified NBS
  - internal
  - rational
- **ACTIVITY COEFFICIENT OPTIONS**
  - use B-dot equation
  - Davies' equation
  - Pitzer's equations
- **AUTO BASIS SWITCHING**
  - off
  - on
- **PITZER DATABASE INFORMATION**
  - print only warnings
  - print species in model and number of Pitzer coefficients
  - print species in model and names of Pitzer coefficients
- **PICKUP FILE**
  - write pickup file
  - don't write pickup file
- **LIST MEAN IONIC PROPERTIES**
  - don't print
  - print
- **LIST AQUEOUS SPECIES, ION SIZES, AND HYDRATION NUMBERS**
  - print
  - don't print
- **CONVERGENCE CRITERIA**
  - test both residual functions and correction terms
  - test only residual functions

DEBUGGING SWITCHES (o-off, 1,2-on, default is off)

<table>
<thead>
<tr>
<th>SWITCH</th>
<th>DESCRIPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>generic debugging information</td>
</tr>
<tr>
<td>0</td>
<td>print details of pre-Newton-Raphson iteration</td>
</tr>
<tr>
<td>0</td>
<td>print details of Newton-Raphson iteration</td>
</tr>
<tr>
<td>0</td>
<td>print details of stoichiometric factors</td>
</tr>
<tr>
<td>0</td>
<td>print details of stoichiometric factors calculation</td>
</tr>
<tr>
<td>0</td>
<td>write reactions on RLST</td>
</tr>
<tr>
<td>0</td>
<td>list stoichiometric concentrations of master species</td>
</tr>
<tr>
<td>0</td>
<td>request iteration variables to be killed</td>
</tr>
</tbody>
</table>

DEVELOPMENT OPTIONS (used for code development)

- none

TOLERANCES (desired values) (defaults)

<table>
<thead>
<tr>
<th>TOLERANCE</th>
<th>DESIRED VIEW</th>
<th>DEFAULT VIEW</th>
</tr>
</thead>
<tbody>
<tr>
<td>residual functions</td>
<td>1.0e-10</td>
<td>1.0e-10</td>
</tr>
<tr>
<td>correction terms</td>
<td>1.0e-10</td>
<td>1.0e-10</td>
</tr>
<tr>
<td>saturation state</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>number of N-W iterations</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The E03NR output file (swmaip.3p), the sea water benchmark test case using Pitzer's equations (beginning with the message announcing the end of Newton-Raphson iteration):

```
Hybrid newton-raphson iteration converged in 4 steps.
```

--- Summary of the Aqueous Phase ---

### Elemental composition of the aqueous phase

<table>
<thead>
<tr>
<th>Element</th>
<th>mg/l</th>
<th>mg/kg</th>
<th>moles/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>o</td>
<td>0.21080E+06</td>
<td>0.19960E+06</td>
<td>0.5526242039E+02</td>
</tr>
<tr>
<td>ca</td>
<td>4.2193</td>
<td>412.30</td>
<td>0.1028743949E+01</td>
</tr>
<tr>
<td>cl</td>
<td>19803.</td>
<td>19333.</td>
<td>0.4459872606E+04</td>
</tr>
<tr>
<td>h</td>
<td>0.11451E+06</td>
<td>0.11100E+06</td>
<td>0.311495770E+01</td>
</tr>
<tr>
<td>c</td>
<td>24.304</td>
<td>24.306</td>
<td>0.512694932E+00</td>
</tr>
<tr>
<td>k</td>
<td>408.42</td>
<td>399.30</td>
<td>0.1020640493E+01</td>
</tr>
<tr>
<td>mg</td>
<td>132.10</td>
<td>129.18</td>
<td>0.3011495770E+01</td>
</tr>
<tr>
<td>na</td>
<td>110.90</td>
<td>107.60</td>
<td>0.2823129677E+01</td>
</tr>
</tbody>
</table>

--- Elemental composition as strict basis species ---

<table>
<thead>
<tr>
<th>Species</th>
<th>mg/l</th>
<th>mg/kg</th>
<th>moles/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>h2o</td>
<td>0.10256E+07</td>
<td>0.10001E+07</td>
<td>0.5526242039E+02</td>
</tr>
<tr>
<td>ca++</td>
<td>4.2192</td>
<td>412.30</td>
<td>0.1028743949E+01</td>
</tr>
<tr>
<td>cl-</td>
<td>19805.</td>
<td>19333.</td>
<td>0.545872606E+00</td>
</tr>
<tr>
<td>br</td>
<td>0.11451E+06</td>
<td>0.11100E+06</td>
<td>0.311495770E+01</td>
</tr>
<tr>
<td>hco3-</td>
<td>126.26</td>
<td>123.38</td>
<td>0.2022000000E+02</td>
</tr>
<tr>
<td>k+</td>
<td>408.42</td>
<td>399.30</td>
<td>0.1020640493E+01</td>
</tr>
<tr>
<td>mg++</td>
<td>132.00</td>
<td>129.18</td>
<td>0.3011495770E+01</td>
</tr>
<tr>
<td>na+</td>
<td>110.90</td>
<td>107.60</td>
<td>0.2823129677E+01</td>
</tr>
</tbody>
</table>

--- Equivalent composition of the aqueous phase (cte balances) ---

<table>
<thead>
<tr>
<th>Species</th>
<th>moles/kg</th>
<th>h2o</th>
<th>moles/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>h2o</td>
<td>0.5526242039E+02</td>
<td>h2o</td>
<td>0.5526242039E+02</td>
</tr>
<tr>
<td>ca++</td>
<td>0.1028743949E+01</td>
<td>ca++</td>
<td>0.1028743949E+01</td>
</tr>
<tr>
<td>cl-</td>
<td>0.545872606E+00</td>
<td>cl-</td>
<td>0.545872606E+00</td>
</tr>
<tr>
<td>br</td>
<td>0.311495770E+01</td>
<td>br</td>
<td>0.311495770E+01</td>
</tr>
<tr>
<td>hco3-</td>
<td>0.2022000000E+02</td>
<td>hco3-</td>
<td>0.2022000000E+02</td>
</tr>
<tr>
<td>k+</td>
<td>0.1020640493E+01</td>
<td>k+</td>
<td>0.1020640493E+01</td>
</tr>
<tr>
<td>mg++</td>
<td>0.3011495770E+01</td>
<td>mg++</td>
<td>0.3011495770E+01</td>
</tr>
<tr>
<td>na+</td>
<td>0.2823129677E+01</td>
<td>na+</td>
<td>0.2823129677E+01</td>
</tr>
</tbody>
</table>

--- Single ion activities and activity coefficients are here defined with respect to the modified nbs ph scale ---

```
--- modified nbs ph scale ---
```

```
pH = 8.6722
```

```
activity of water = 0.98198
log activity of water = -0.009790
true osmotic coefficient = 0.90273
stoichiometric osmotic coefficient = 0.90273
sum of true molalities = 1.1805795259E+07
sum of stoichiometric molalities = 1.1805795259E+07
true ionic strength = 0.59643948915726
stoichiometric ionic strength  0.6967640957883

----- electrical balance totals -----

  equiv/kg  
  \( \sigma_{(\text{mz})} \) cations =  0.6052455191E+00  
  \( \sigma_{(\text{mz})} \) anions  =  0.6043365394E+00  
  total charge  =  0.1209502077E+01  
  mean charge  =  0.6047910387E+00  
  charge imbalance  =  0.909906644E-03

  total charge = \( \sigma_{(\text{mz})} \) cations + abs ( \( \sigma_{(\text{mz})} \) anions )
  mean charge = 1/2 total charge

the electrical imbalance is
  0.752E-01 per cent of the total charge
  0.150 per cent of the mean charge
  0.150 per cent of \( \sigma_{(\text{mz})} \) cations
  0.150 per cent of abs ( \( \sigma_{(\text{mz})} \) anions )

----- activity ratios of ions -----  

\[
\begin{align*}
\log ( \text{act}(\text{ca}^+) ) / \log(\text{act}(\text{h}^+)) & = 13.7845 \\
\log ( \text{act}(\text{hco}_3^-) ) / \log(\text{act}(\text{h}^+)) & = -8.6722 \\
\log ( \text{act}(\text{h}^+) ) / \log(\text{act}(\text{h}^+)) & = 6.0291 \\
\log ( \text{act}(\text{na}^+) ) / \log(\text{act}(\text{h}^+)) & = -11.2062 \\
\log ( \text{act}(\text{mg}^+)) / \log(\text{act}(\text{h}^+)) & = -4.0291 \\
\log ( \text{act}(\text{so}_4^{2-}) ) / \log(\text{act}(\text{h}^+)) & = 14.5357 \\
\log ( \text{act}(\text{co}_3^{2-}) ) / \log(\text{act}(\text{h}^+)) & = 7.2243 \\
\log ( \text{act}(\text{co}_2^{(aq)}) ) / \log(\text{act}(\text{h}^+)) & = -19.0096 \\
\log ( \text{act}(\text{oh}^-)) / \log(\text{act}(\text{h}^+)) & = -4.8609 \\
\log ( \text{act}(\text{oh}^-)) / \log(\text{act}(\text{h}^+)) & = -14.0046
\end{align*}
\]

----- distribution of aqueous species -----  

  species  | molal conc | \log conc | \log g  | activity  | \log act  
  ------ | ---------- | --------- | ------- | --------- | --------- 
  \( \text{cl}^- \)  | 0.5459E+00  | -0.2629   | -0.1893 | 0.3530E+00 | -0.4522   
  \( \text{na}^+ \)  | 0.4668E+00  | -0.3294   | -0.1653 | 0.3134E+00 | -0.4957   
  \( \text{mg}^2- \) | 0.5306E-01  | -1.2752   | -0.6201 | 0.1247E-01 | -1.3015   
  \( \text{ca}^{2-} \) | 0.1026E-01  | -1.9887   | -0.6660 | 0.2210E-02 | -2.0555   
  \( \text{h}^+ \)   | 0.1021E-01  | -1.9911   | -1.0598 | 0.6444E-02 | -2.1909   
  \( \text{hco}_3^- \)| 0.1816E-02  | -2.7409   | -0.2426 | 0.1032E-02 | -2.3862   
  \( \text{co}_3^{2-} \)| 0.8641E-04  | -4.0535   | -1.0420 | 0.7044E-05 | -5.1055   
  \( \text{mgco}_3^{(aq)} \) | 0.8293E-04 | -4.0813   | 0.0000  | 0.8292E-04 | -4.0813   
  \( \text{caco}_3^{(aq)} \) | 0.2456E-04 | -4.6097   | 0.0000  | 0.2456E-04 | -4.6097   
  \( \text{co}_2^{(aq)} \) | 0.1224E-04 | -4.9121   | 0.0512  | 0.1378E-04 | -4.8609   
  \( \text{mgoh}^- \) | 0.3162E-05 | -5.4735   | -0.0279 | 0.3152E-05 | -5.5014   
  \( \text{oh}^- \)   | 0.1029E-02  | -5.2168   | -0.2656 | 0.1642E-05 | -5.7546   
  \( \text{h}^+ \)   | 0.7706E-08  | -6.1132   | -0.6068 | 0.6026E-08 | -8.2200   
  \( \text{hso}_4^- \) | 0.2332E-08  | -6.6322   | -0.1786 | 0.1545E-08 | -8.8110   

----- major aqueous species contributing to mass balances ----- 

aqueous species accounting for 99% or more of ca++
   species  molal conc per cent  
    ca++ | 0.1026E+01  99.76  
    total | 99.76  

aqueous species accounting for 99% or more of cl-
   species  molal conc per cent  
    cl-  | 0.5459E+00  100.00  
    total | 100.00  

aqueous species accounting for 99% or more of hco3-
   species  molal conc per cent  
    hco3- | 0.2616E-02  89.82  
    co3-  | 0.8641E-01  4.27  
    mgco3^{(aq)} | 0.8293E-04  4.10  
    caco3^{(aq)} | 0.2456E-04  1.21  
    total | 99.39  

---
aqueous species accounting for 99% or more of k+

<table>
<thead>
<tr>
<th>species</th>
<th>molal conc</th>
<th>per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>k+</td>
<td>0.1021E-01</td>
<td>100.00</td>
</tr>
<tr>
<td>total</td>
<td></td>
<td>100.00</td>
</tr>
</tbody>
</table>

daqueous species accounting for 99% or more of mg++

<table>
<thead>
<tr>
<th>species</th>
<th>molal conc</th>
<th>per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg++</td>
<td>0.5306E-01</td>
<td>99.84</td>
</tr>
<tr>
<td>total</td>
<td></td>
<td>99.84</td>
</tr>
</tbody>
</table>

daqueous species accounting for 99% or more of na+

<table>
<thead>
<tr>
<th>species</th>
<th>molal conc</th>
<th>per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>na+</td>
<td>0.4684E+00</td>
<td>100.00</td>
</tr>
<tr>
<td>total</td>
<td></td>
<td>100.00</td>
</tr>
</tbody>
</table>

daqueous species accounting for 99% or more of so4--

<table>
<thead>
<tr>
<th>species</th>
<th>molal conc</th>
<th>per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>so4--</td>
<td>0.2832E-01</td>
<td>100.00</td>
</tr>
<tr>
<td>total</td>
<td></td>
<td>100.00</td>
</tr>
</tbody>
</table>

--- summary of aqueous redox reactions ---

couple eh, volts pe- log fo2 ah, kcal

default 0.500 0.8452E+01 -16.432 11.531

--- summary of aqueous non-equilibrium non-redox reactions ---

couple affinity, kcal

none

--- summary of stoichiometric mineral saturation states ---

(minerals with affinities > -10 kcal are not listed)

<table>
<thead>
<tr>
<th>mineral</th>
<th>log q/k</th>
<th>aff, kcal state</th>
<th>mineral</th>
<th>log q/k</th>
<th>aff, kcal state</th>
</tr>
</thead>
<tbody>
<tr>
<td>anhydrite</td>
<td>-0.863</td>
<td>ssatd</td>
<td>aragonite</td>
<td>0.438</td>
<td>ssatd</td>
</tr>
<tr>
<td>aragonite</td>
<td>-1.177</td>
<td></td>
<td>bischofite</td>
<td>-7.311</td>
<td>ssatd</td>
</tr>
<tr>
<td>bischofite</td>
<td>-7.060</td>
<td></td>
<td>brucite</td>
<td>-2.389</td>
<td>ssatd</td>
</tr>
<tr>
<td>calcite</td>
<td>-7.803</td>
<td></td>
<td>dolomite</td>
<td>2.312</td>
<td>ssatd</td>
</tr>
<tr>
<td>dolomite</td>
<td>0.880</td>
<td>ssatd</td>
<td>euglyptite</td>
<td>-4.476</td>
<td>-5.107</td>
</tr>
<tr>
<td>euglyptite</td>
<td>-3.412</td>
<td></td>
<td>gypsum</td>
<td>-0.460</td>
<td>ssatd</td>
</tr>
<tr>
<td>halite</td>
<td>-4.832</td>
<td></td>
<td>bezhohydrate</td>
<td>-2.886</td>
<td>-3.938</td>
</tr>
<tr>
<td>kainite</td>
<td>-3.436</td>
<td></td>
<td>kainite</td>
<td>-5.458</td>
<td>-7.447</td>
</tr>
<tr>
<td>kieserite</td>
<td>-2.518</td>
<td></td>
<td>kieserite</td>
<td>-0.460</td>
<td>ssatd</td>
</tr>
<tr>
<td>kieserite</td>
<td>-3.446</td>
<td></td>
<td>magnesite</td>
<td>0.824</td>
<td>1.244</td>
</tr>
<tr>
<td>mirabilite</td>
<td>-5.309</td>
<td></td>
<td>na2co3:7h2o</td>
<td>-5.652</td>
<td>-7.765</td>
</tr>
<tr>
<td>na2co3:7h2o</td>
<td>-3.293</td>
<td></td>
<td>na2co3:7h2o</td>
<td>-1.079</td>
<td>-4.200</td>
</tr>
<tr>
<td>natron</td>
<td>-5.351</td>
<td></td>
<td>natron</td>
<td>-1.079</td>
<td>-4.200</td>
</tr>
<tr>
<td>oxychloride-mg</td>
<td>-5.686</td>
<td></td>
<td>oxychloride-mg</td>
<td>-1.079</td>
<td>-4.200</td>
</tr>
<tr>
<td>pinzonite</td>
<td>-3.446</td>
<td></td>
<td>pinzonite</td>
<td>-3.543</td>
<td>-4.834</td>
</tr>
<tr>
<td>syngenite</td>
<td>-5.458</td>
<td></td>
<td>syngenite</td>
<td>-3.543</td>
<td>-4.834</td>
</tr>
<tr>
<td>thenardite</td>
<td>-4.346</td>
<td></td>
<td>thenardite</td>
<td>-3.274</td>
<td>-4.466</td>
</tr>
</tbody>
</table>

0 approx. saturated pure minerals
0 approx. saturated end-members of specified solid solutions
0 saturated end-members of hypothetical solid solutions

4 supersaturated pure minerals
0 supersatd. end-members of specified solid solutions
0 supersatd. hypothetical solid solution phases

--- summary of gases ---

gas | fugacity | log fugacity

- 109 -
7.4. Using Mineral Solubility Constraints: An Example

This test case is taken from INTERA (1983), which used it to compare EQ3/6 with PHREEQE (Parkhurst, Plummer, and Thorstenson, 1980). In it, dissolved calcium is constrained to satisfy equilibrium with calcite and dissolved iron is constrained to satisfy equilibrium with hematite. The bicarbonate is constrained to satisfy an equilibrium CO₂ fugacity of 10⁻² bar. On top of that, the pH is adjusted to satisfy electrical balance. The input files are presented here in both formats. The output file is presented beginning with the message announcing the end of Newton-Raphson iteration. The results shown were obtained using the com data file. The activity coefficients were computed from the B-dot equation. Note the appearance of the organic species, which all have negligible concentrations at the relatively high oxygen fugacity.

Note that the calculated saturation indices for calcite and hematite written on the output file are indeed zero. Similarly, the calculated equilibrium CO₂ fugacity is 10⁻² bar. The pH adjustment is relatively minor. In problems such as this, if the input pH value is too far off the mark (usually more than 1-3 pH units), convergence problems are likely to occur. More than that, problems using some of the kind of constraints used here, especially in combination, may be ill-defined and have no realistic solution.

The EQ3NR input file (oxcalhem.3i), mineral solubility equilibrium test case (“W” format):

References


The EQ3NR input file (oxcalhem.3i), mineral solubility equilibrium test case ("D" format):

```
endit.

Temperature (C) | 25.00 | Density (g/cm^3) | 1.00000
Total Dissolved Salts | not used
Electrical Balancing on | not performed
SPECIES | BASIS SWITCH/CONSTRAINT | CONCENTRATION | UNITS OR TYPE
```

References


Input Solid Solutions

| none |

SUPPRESS SPECIES (suppress, replace, augment) value

| none |

OPTIONS

- SOLID SOLUTIONS -
  * ignore solid solutions
  process input and hypothetical solid solutions

- LOADING OF SPECIES INTO MEMORY -
  * does nothing
  lists species loaded into memory

- ECHO DATABASE INFORMATION -
  * does nothing
  lists all reactions
  lists reactions and log K values
  lists reactions, log K values and polynomial coefficients

- LIST OF AQUEOUS SPECIES (ordering) -
  * in order of decreasing concentration
  in same order as input file

- LIST OF AQUEOUS SPECIES (concentration limit) -
  * all species
  only species > 10^-20 molal
  only species > 10^-12 molal
  not printed

- LIST OF AQUEOUS SPECIES (by element) -
  * print major species
  print all species
  don't print

- MINERAL SATURATION STATES -
  * print if affinity > -10 kcales
  print all
  don't print

- pH SCALE CONVENTION -
  * modified NBS
  internal
  rational

- ACTIVITY COEFFICIENT OPTIONS -
  * use h-dot equation
  Davies' equation
  Pitzer's equations

- AUTO BASIS SWITCHING -
  * off
onces

- PITZER DATABASE INFORMATION -
  * print only warnings
  print species in model and number of Pitzer coefficients
  print species in model and names of Pitzer coefficients

- PICKUP FILE -
  * write pickup file
  don't write pickup file

- LIST MEAN IONIC PROPERTIES -
  * don't print
  print

- LIST AQUEOUS SPECIES, ION SIZES, AND HYDRATION NUMBERS -
  * print
  don't print

- CONVERGENCE CRITERIA -
  * test both residual functions and correction terms
  test only residual functions

DEBUGGING SWITCHES (o-off, 1,2-on, default is off)

0 generic debugging information
0 print details of pre-Newton-Raphson iteration
0 print details of Newton-Raphson iteration
0 print details of stoichiometric factors calculation
0 write reactions on BLIST
0 list stoichiometric concentrations of master species
0 request iteration variables to be killed

DEVELOPMENT OPTIONS (used for code development)

TOLERANCES (desired values) (defaults)
The EQ3NR output file (oxcalhem3o), mineral solubility equilibrium test case (beginning with the message announcing the end of Newton-Raphson iteration):

* *
* *
* *
(Material deleted)
* *
* *
Hybrid newton-raphson iteration converged in 6 steps.

----- Summary of the Aqueous Phase -----

----- Elemental composition of the aqueous phase -----  

<table>
<thead>
<tr>
<th>element</th>
<th>mg/l</th>
<th>mg/kg</th>
<th>moles/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>o</td>
<td>0.88836E+06</td>
<td>0.88836E+06</td>
<td>0.5552474398E+02</td>
</tr>
<tr>
<td>ca</td>
<td>74.248</td>
<td>74.248</td>
<td>0.3852584728E+02</td>
</tr>
<tr>
<td>cl</td>
<td>177.26</td>
<td>177.26</td>
<td>0.50660000000E+02</td>
</tr>
<tr>
<td>fe</td>
<td>0.50317E+07</td>
<td>0.50317E+07</td>
<td>0.9009750988E+12</td>
</tr>
<tr>
<td>h</td>
<td>0.11194E+06</td>
<td>0.11194E+06</td>
<td>0.1110204565E+03</td>
</tr>
<tr>
<td>c</td>
<td>40.264</td>
<td>40.264</td>
<td>0.40199986372E+02</td>
</tr>
<tr>
<td>na</td>
<td>160.03</td>
<td>160.03</td>
<td>0.70000000000E+02</td>
</tr>
<tr>
<td>s</td>
<td>33.866</td>
<td>33.866</td>
<td>0.1000000001E+02</td>
</tr>
<tr>
<td>u</td>
<td>9.5212</td>
<td>0.5212</td>
<td>0.3999999985E-04</td>
</tr>
</tbody>
</table>

----- elemental composition as strict basis species -----  

<table>
<thead>
<tr>
<th>species</th>
<th>mg/l</th>
<th>mg/kg</th>
<th>moles/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>h2o</td>
<td>0.10003E+07</td>
<td>0.10003E+07</td>
<td>0.5552474398E+02</td>
</tr>
<tr>
<td>ca**</td>
<td>74.248</td>
<td>74.248</td>
<td>0.1852584728E+02</td>
</tr>
<tr>
<td>cl-</td>
<td>177.26</td>
<td>177.26</td>
<td>0.50000000000E+02</td>
</tr>
<tr>
<td>fe**</td>
<td>0.50317E+07</td>
<td>0.50317E+07</td>
<td>0.9009750988E+12</td>
</tr>
<tr>
<td>h**</td>
<td>0.11194E+06</td>
<td>0.11194E+06</td>
<td>0.1110204565E+03</td>
</tr>
<tr>
<td>hco3-</td>
<td>245.29</td>
<td>245.29</td>
<td>0.4019986372E+02</td>
</tr>
<tr>
<td>as+</td>
<td>160.53</td>
<td>160.53</td>
<td>0.70000000000E+02</td>
</tr>
<tr>
<td>so4**</td>
<td>96.064</td>
<td>96.064</td>
<td>0.1000000001E+02</td>
</tr>
<tr>
<td>uo2++</td>
<td>10.801</td>
<td>10.801</td>
<td>0.3999999985E-04</td>
</tr>
</tbody>
</table>

----- equivalent composition of the aqueous phase (cta balances) -----  

<table>
<thead>
<tr>
<th>species</th>
<th>moles/kg h2o</th>
<th>h2o</th>
<th>species</th>
<th>moles/kg h2o</th>
</tr>
</thead>
<tbody>
<tr>
<td>h2o**</td>
<td>0.5552474398E+02</td>
<td>h2o</td>
<td>0.5552474398E+02</td>
<td></td>
</tr>
<tr>
<td>ca**</td>
<td>0.1852584728E+02</td>
<td>ca**</td>
<td>0.1852584728E+02</td>
<td></td>
</tr>
<tr>
<td>cl-</td>
<td>0.50000000000E+02</td>
<td>cl-</td>
<td>0.50000000000E+02</td>
<td></td>
</tr>
<tr>
<td>fe**</td>
<td>0.9009750988E+12</td>
<td>fe**</td>
<td>0.9009750988E+12</td>
<td></td>
</tr>
<tr>
<td>h**</td>
<td>0.1110204565E+03</td>
<td>h**</td>
<td>0.1110204565E+03</td>
<td></td>
</tr>
<tr>
<td>hco3-</td>
<td>0.4019986372E+02</td>
<td>hco3-</td>
<td>0.4019986372E+02</td>
<td></td>
</tr>
<tr>
<td>as+</td>
<td>0.70000000000E+02</td>
<td>as+</td>
<td>0.70000000000E+02</td>
<td></td>
</tr>
<tr>
<td>so4**</td>
<td>0.1000000001E+02</td>
<td>so4**</td>
<td>0.1000000001E+02</td>
<td></td>
</tr>
<tr>
<td>uo2++</td>
<td>0.3999999985E-04</td>
<td>uo2++</td>
<td>0.3999999985E-04</td>
<td></td>
</tr>
</tbody>
</table>

Single ion activity and activity coefficients are here defined with respect to the modified nbs ph scale

<table>
<thead>
<tr>
<th>ph</th>
<th>ch</th>
<th>pe</th>
</tr>
</thead>
<tbody>
<tr>
<td>modified nbs ph scale</td>
<td>7.3308</td>
<td>0.7862</td>
</tr>
<tr>
<td>rational ph scale</td>
<td>7.2655</td>
<td>0.7899</td>
</tr>
</tbody>
</table>

pHcl = 2.6524
activity of water = 0.99968
log activity of water = -0.00014

true osmotic coefficient = 0.95018
stoichiometric osmotic coefficient = 0.99417

sum of true molalities = 0.02080594407872
sum of stoichiometric molalities = 0.0198469598020

true ionic strength = 0.0131467506839
stoichiometric ionic strength = 0.0139741601186

----- electrical balance totals -----

equiv/kg

sigma(mz) cations = 0.104283E-01
sigma(mz) anions = -0.104283E-01
total charge = 0.208576827E-01
charge imbalance = 0.785843393E-12

total charge = sigma(mz) cations + abs ( sigma(mz) anions )
mean charge = 1/2 total charge

the electrical imbalance is

0.377E-08 per cent of the total charge
0.754E-08 per cent of the mean charge
0.754E-08 per cent of sigma(mz) cations
0.754E-08 per cent of abs ( sigma(mz) anions )

electrical balancing on h+

log activity
input -7.4000
final -7.3108
avg 0.69175E-01

----- activity ratios of ions -----

log ( act(ca++) ) / act(h+)xx 2 ) = 11.6624
log ( act(cl-) ) x act(h+)xx 1 ) = -9.6624
log ( act(co2aq) ) / act(h+)xx 2 ) = -7.5360
log ( act(hco3- ) / act(h+)xx 1 ) = -9.0137
log ( act(na+ ) / act(h+)xx 1 ) = 5.0998
log ( act(so42- ) / act(h+)xx 2 ) = -17.8693
log ( act(acetic acid(aq) ) / act(h+)xx 2 ) = 3.8852
log ( act(diacetone(aq) ) / act(h+)xx 2 ) = -154.4231
log ( act(ethanol(aq) ) / act(h+)xx 1 ) = -20.1425
log ( act(ethene(aq) ) x act(h+)xx 1 ) = -114.6231
log ( act(fe3+ ) / act(h+)xx 3 ) = 0.0545
log ( act(h2aq) ) / act(h+)xx 1 ) = -44.3076
log ( act(h- ) / act(h+)xx 1 ) = -148.9896
log ( act(h2o) ) / act(h+)xx 3 ) = -146.7584
log ( act(methanol(aq) ) / act(h+)xx 1 ) = -132.3211
log ( act(o2aq) ) / act(h+)xx 1 ) = -12.9952
log ( act(oh-) ) / act(h+)xx 1 ) = -114.0000
log ( act(so32- ) ) / act(h+)xx 2 ) = 62.6945
log ( act(uo2++ ) / act(h+)xx 3 ) = -58.4613
log ( act(uo2+++ ) / act(h+)xx 4 ) = -28.2603
log ( act(uo22+ ) / act(h+)xx 1 ) = -15.2316

----- distribution of aqueous species -----
<table>
<thead>
<tr>
<th>Compound</th>
<th>pK value</th>
<th>pH value</th>
<th>pOH value</th>
<th>pOH value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane (aq)</td>
<td>-146.7584</td>
<td>-146.7584</td>
<td>0.0000</td>
<td>0.1744</td>
</tr>
<tr>
<td>Methanol (aq)</td>
<td>-122.3211</td>
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<td>0.0000</td>
<td>0.4774</td>
</tr>
<tr>
<td>Acetate</td>
<td>-151.8695</td>
<td>-151.8695</td>
<td>0.0000</td>
<td>0.1351</td>
</tr>
<tr>
<td>Hydrogen Sulfide</td>
<td>-147.3031</td>
<td>-147.3031</td>
<td>0.0000</td>
<td>0.4977</td>
</tr>
<tr>
<td>Hydrogen Sulfide</td>
<td>-142.0019</td>
<td>-142.0019</td>
<td>0.0000</td>
<td>0.9956</td>
</tr>
<tr>
<td>Sulfate</td>
<td>-134.1756</td>
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<td>0.0000</td>
<td>0.6674</td>
</tr>
<tr>
<td>Sulfur Dioxide</td>
<td>-53.6283</td>
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<td>0.2351</td>
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<tr>
<td>Hydrogen Chlorine</td>
<td>-44.3076</td>
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<tr>
<td>Chlorine Chloride</td>
<td>-43.5091</td>
<td>-43.5091</td>
<td>0.0000</td>
<td>0.3097</td>
</tr>
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<td>Formic Acid</td>
<td>-47.0670</td>
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<td>0.0000</td>
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<td>Iron (II)</td>
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<tr>
<td>Iron (IIIO)</td>
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<td>-30.4525</td>
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<td>Iron (IIIO)</td>
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<td>Iron (IIIO)</td>
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<td>Iron (IIIO)</td>
<td>-22.9485</td>
<td>-22.9485</td>
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<td>Iron (IIIO)</td>
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<td>Iron (IIIO)</td>
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<td>Iron (IIIO)</td>
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<td>Iron (IIIO)</td>
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<tr>
<td>Iron (IIIO)</td>
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<td>Iron (IIIO)</td>
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<tr>
<td>Iron (IIIO)</td>
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<tr>
<td>Iron (IIIO)</td>
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<td>-17.2633</td>
<td>0.0000</td>
<td>0.2543</td>
</tr>
<tr>
<td>Iron (IIIO)</td>
<td>-16.7576</td>
<td>-16.7576</td>
<td>0.0000</td>
<td>0.1811</td>
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<tr>
<td>Iron (IIIO)</td>
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<td>-16.2522</td>
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</tr>
<tr>
<td>Iron (IIIO)</td>
<td>-15.7008</td>
<td>-15.7008</td>
<td>0.0000</td>
<td>0.1269</td>
</tr>
<tr>
<td>Iron (IIIO)</td>
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<td>-15.1497</td>
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<tr>
<td>Iron (IIIO)</td>
<td>-14.5933</td>
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<tr>
<td>Iron (IIIO)</td>
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<td>0.1936</td>
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<tr>
<td>Iron (IIIO)</td>
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<td>-13.4413</td>
<td>0.0000</td>
<td>0.1936</td>
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<tr>
<td>Iron (IIIO)</td>
<td>-12.8499</td>
<td>-12.8499</td>
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<td>0.1369</td>
</tr>
<tr>
<td>Iron (IIIO)</td>
<td>-12.2580</td>
<td>-12.2580</td>
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<td>0.2767</td>
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<tr>
<td>Iron (IIIO)</td>
<td>-11.6762</td>
<td>-11.6762</td>
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<td>0.1909</td>
</tr>
<tr>
<td>Iron (IIIO)</td>
<td>-11.0929</td>
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<td>0.1200</td>
</tr>
<tr>
<td>Iron (IIIO)</td>
<td>-10.5085</td>
<td>-10.5085</td>
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<td>0.1200</td>
</tr>
<tr>
<td>Iron (IIIO)</td>
<td>-9.9140</td>
<td>-9.9140</td>
<td>0.0000</td>
<td>0.9136</td>
</tr>
<tr>
<td>Iron (IIIO)</td>
<td>-9.3001</td>
<td>-9.3001</td>
<td>0.0000</td>
<td>0.9136</td>
</tr>
<tr>
<td>Iron (IIIO)</td>
<td>-8.6673</td>
<td>-8.6673</td>
<td>0.0000</td>
<td>0.9136</td>
</tr>
<tr>
<td>Iron (IIIO)</td>
<td>-8.0234</td>
<td>-8.0234</td>
<td>0.0000</td>
<td>0.9136</td>
</tr>
<tr>
<td>Iron (IIIO)</td>
<td>-7.3786</td>
<td>-7.3786</td>
<td>0.0000</td>
<td>0.9136</td>
</tr>
<tr>
<td>Iron (IIIO)</td>
<td>-6.7238</td>
<td>-6.7238</td>
<td>0.0000</td>
<td>0.9136</td>
</tr>
<tr>
<td>Iron (IIIO)</td>
<td>-6.0682</td>
<td>-6.0682</td>
<td>0.0000</td>
<td>0.9136</td>
</tr>
<tr>
<td>Iron (IIIO)</td>
<td>-5.4126</td>
<td>-5.4126</td>
<td>0.0000</td>
<td>0.9136</td>
</tr>
<tr>
<td>Iron (IIIO)</td>
<td>-4.7562</td>
<td>-4.7562</td>
<td>0.0000</td>
<td>0.9136</td>
</tr>
<tr>
<td>Iron (IIIO)</td>
<td>-4.0998</td>
<td>-4.0998</td>
<td>0.0000</td>
<td>0.9136</td>
</tr>
<tr>
<td>Iron (IIIO)</td>
<td>-3.4430</td>
<td>-3.4430</td>
<td>0.0000</td>
<td>0.9136</td>
</tr>
<tr>
<td>Iron (IIIO)</td>
<td>-2.7862</td>
<td>-2.7862</td>
<td>0.0000</td>
<td>0.9136</td>
</tr>
<tr>
<td>Iron (IIIO)</td>
<td>-2.1294</td>
<td>-2.1294</td>
<td>0.0000</td>
<td>0.9136</td>
</tr>
<tr>
<td>Iron (IIIO)</td>
<td>-1.4725</td>
<td>-1.4725</td>
<td>0.0000</td>
<td>0.9136</td>
</tr>
<tr>
<td>Iron (IIIO)</td>
<td>-0.8156</td>
<td>-0.8156</td>
<td>0.0000</td>
<td>0.9136</td>
</tr>
<tr>
<td>Iron (IIIO)</td>
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<td>-0.1587</td>
<td>0.0000</td>
<td>0.9136</td>
</tr>
<tr>
<td>Iron (IIIO)</td>
<td>0.5137</td>
<td>0.5137</td>
<td>0.0000</td>
<td>0.9136</td>
</tr>
<tr>
<td>Iron (IIIO)</td>
<td>0.8568</td>
<td>0.8568</td>
<td>0.0000</td>
<td>0.9136</td>
</tr>
<tr>
<td>Iron (IIIO)</td>
<td>1.1999</td>
<td>1.1999</td>
<td>0.0000</td>
<td>0.9136</td>
</tr>
<tr>
<td>Species</td>
<td>Molal Conc</td>
<td>Per Cent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------------------------</td>
<td>------------</td>
<td>----------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca⁺</td>
<td>0.1721E-02</td>
<td>92.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na⁺(aq)</td>
<td>0.0021E-04</td>
<td>4.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CI⁻</td>
<td>0.4336E-04</td>
<td>2.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>99.6%</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

--- Major aqueous species contributing to mass balances ---

<table>
<thead>
<tr>
<th>Aqueous species accounting for 99% or more of Ca⁺</th>
<th>Molal Conc</th>
<th>Per Cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca²⁺</td>
<td>0.1721E-02</td>
<td>92.89</td>
</tr>
<tr>
<td>Na⁺(aq)</td>
<td>0.0021E-04</td>
<td>4.34</td>
</tr>
<tr>
<td>CI⁻</td>
<td>0.4336E-04</td>
<td>2.34</td>
</tr>
<tr>
<td><strong>Total</strong> have a Na⁺ molal conc of 100.0% or more</td>
<td><strong>99.6%</strong></td>
<td></td>
</tr>
</tbody>
</table>

--- Aqueous species accounting for 99% or more of CI⁻ | Molal Conc | Per Cent |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CI⁻</td>
<td>0.4994E-02</td>
<td>99.89</td>
</tr>
<tr>
<td><strong>Total</strong> CI⁻</td>
<td><strong>99.89</strong></td>
<td></td>
</tr>
</tbody>
</table>
aqueous species accounting for 99% or more of \( \text{HCO}_3^- \)

<table>
<thead>
<tr>
<th>Species</th>
<th>Molal Conc</th>
<th>Per Cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{HCO}_3^- )</td>
<td>0.351E-02</td>
<td>87.33</td>
</tr>
<tr>
<td>( \text{CO}_2(\text{aq}) )</td>
<td>0.338E-03</td>
<td>8.43</td>
</tr>
<tr>
<td>( \text{CNO}^+ )</td>
<td>0.433E-04</td>
<td>1.08</td>
</tr>
<tr>
<td>( \text{NaNO}_3(\text{aq}) )</td>
<td>0.275E-04</td>
<td>0.69</td>
</tr>
<tr>
<td>( \text{UO}_2(\text{CO}_3)^{2-} )</td>
<td>0.245E-04</td>
<td>1.22</td>
</tr>
<tr>
<td>( \text{UO}_2(\text{CO}_3)^{3-} )</td>
<td>0.123E-04</td>
<td>0.92</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>0.351E-02</strong></td>
<td><strong>99.67</strong></td>
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</tbody>
</table>

aqueous species accounting for 99% or more of \( \text{Na}^+ \)

<table>
<thead>
<tr>
<th>Species</th>
<th>Molal Conc</th>
<th>Per Cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Na}^+ )</td>
<td>0.694E-02</td>
<td>99.17</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>0.694E-02</strong></td>
<td><strong>99.17</strong></td>
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</tbody>
</table>

aqueous species accounting for 99% or more of \( \text{SO}_4^{2-} \)

<table>
<thead>
<tr>
<th>Species</th>
<th>Molal Conc</th>
<th>Per Cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{SO}_4^{2-} )</td>
<td>0.894E-03</td>
<td>89.41</td>
</tr>
<tr>
<td>( \text{CASO}_4(\text{aq}) )</td>
<td>0.802E-04</td>
<td>8.02</td>
</tr>
<tr>
<td>( \text{NASO}_4 )</td>
<td>0.356E-04</td>
<td>3.57</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>0.894E-03</strong></td>
<td><strong>89.41</strong></td>
</tr>
</tbody>
</table>

aqueous species accounting for 99% or more of \( \text{UO}_2^{2+} \)

<table>
<thead>
<tr>
<th>Species</th>
<th>Molal Conc</th>
<th>Per Cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{UO}_2(\text{CO}_3)^{2-} )</td>
<td>0.245E-04</td>
<td>61.46</td>
</tr>
<tr>
<td>( \text{UO}_2(\text{CO}_3)^{3-} )</td>
<td>0.123E-04</td>
<td>30.68</td>
</tr>
<tr>
<td>( \text{UO}_2(\text{OH})_2(\text{OH})_3 )</td>
<td>0.122E-05</td>
<td>6.15</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>0.245E-04</strong></td>
<td><strong>61.46</strong></td>
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</tbody>
</table>

----- Summary of aqueous redox reactions -----  

<table>
<thead>
<tr>
<th>Couple</th>
<th>Eh, volts</th>
<th>pO2</th>
<th>Log fo2</th>
<th>Eh, kcal</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Default</strong></td>
<td>0.786</td>
<td>0.132E+02</td>
<td>-0.700</td>
<td>18.132</td>
</tr>
<tr>
<td>Acetic a/( \text{HCO}_3^- )</td>
<td>0.786</td>
<td>0.132E+02</td>
<td>-0.700</td>
<td>18.132</td>
</tr>
<tr>
<td>Acetate(\text{HCO}_3^-)/( \text{CO}_2(\text{aq}) )</td>
<td>0.786</td>
<td>0.132E+02</td>
<td>-0.700</td>
<td>18.132</td>
</tr>
<tr>
<td>Cl(\text{aq})/Cl(\text{aq})</td>
<td>0.786</td>
<td>0.132E+02</td>
<td>-0.700</td>
<td>18.132</td>
</tr>
<tr>
<td>Ethano(a)/( \text{HCO}_3^- )</td>
<td>0.786</td>
<td>0.132E+02</td>
<td>-0.700</td>
<td>18.132</td>
</tr>
<tr>
<td>Fe(\text{aq})/Fe(\text{aq})</td>
<td>0.786</td>
<td>0.132E+02</td>
<td>-0.700</td>
<td>18.132</td>
</tr>
<tr>
<td>H(\text{aq})/H(\text{aq})</td>
<td>0.786</td>
<td>0.132E+02</td>
<td>-0.700</td>
<td>18.132</td>
</tr>
<tr>
<td>HN(\text{aq})/( \text{HCO}_3^- )</td>
<td>0.786</td>
<td>0.132E+02</td>
<td>-0.700</td>
<td>18.132</td>
</tr>
<tr>
<td>Methano(\text{HCO}_3^-)/( \text{CO}_2(\text{aq}) )</td>
<td>0.786</td>
<td>0.132E+02</td>
<td>-0.700</td>
<td>18.132</td>
</tr>
<tr>
<td>Methanolol(\text{HCO}_3^-)/( \text{CO}_2(\text{aq}) )</td>
<td>0.786</td>
<td>0.132E+02</td>
<td>-0.700</td>
<td>18.132</td>
</tr>
<tr>
<td>O(\text{aq})/( \text{HCO}_3^- )</td>
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<td>0.132E+02</td>
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<td>18.132</td>
</tr>
<tr>
<td>SO(\text{aq})/( \text{HCO}_3^- )</td>
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<td>0.132E+02</td>
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</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>0.786</strong></td>
<td><strong>0.132E+02</strong></td>
<td><strong>-0.700</strong></td>
<td><strong>18.132</strong></td>
</tr>
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</table>

----- Summary of aqueous non-equilibrium non-redox reactions -----  

<table>
<thead>
<tr>
<th>Couple</th>
<th>Affinity, kcal</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>None</strong></td>
<td></td>
</tr>
</tbody>
</table>

----- Summary of stoichiometric mineral saturation states -----  

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Log q/k</th>
<th>Aff, kcal</th>
<th>State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anhydrite</td>
<td>-1.900</td>
<td>-2.593</td>
<td></td>
</tr>
<tr>
<td>Bassanite</td>
<td>-2.545</td>
<td>-3.473</td>
<td></td>
</tr>
<tr>
<td>Caso4:0.5H2O(beta)</td>
<td>-2.714</td>
<td>-3.702</td>
<td></td>
</tr>
<tr>
<td>Fe(oh)3</td>
<td>-5.602</td>
<td>-7.942</td>
<td></td>
</tr>
<tr>
<td>Gypsum</td>
<td>-1.725</td>
<td>-2.351</td>
<td></td>
</tr>
<tr>
<td>Hematite</td>
<td>0.000</td>
<td>0.000</td>
<td>Ssatd</td>
</tr>
<tr>
<td>Mirabilite</td>
<td>-6.531</td>
<td>-8.911</td>
<td></td>
</tr>
<tr>
<td>Aragonite</td>
<td>-8.114</td>
<td>-0.197</td>
<td>Ssatd</td>
</tr>
<tr>
<td>Calcite</td>
<td>0.000</td>
<td>0.000</td>
<td>Ssatd</td>
</tr>
<tr>
<td>CaCO4</td>
<td>-0.499</td>
<td>-0.601</td>
<td></td>
</tr>
<tr>
<td>Glaubeite</td>
<td>-0.480</td>
<td>-0.655</td>
<td></td>
</tr>
<tr>
<td>Halite</td>
<td>-6.140</td>
<td>-6.306</td>
<td></td>
</tr>
<tr>
<td>Ice</td>
<td>-6.239</td>
<td>-6.389</td>
<td>Ssatd</td>
</tr>
<tr>
<td>Monoahydrocalcite</td>
<td>-6.034</td>
<td>-2.138</td>
<td></td>
</tr>
</tbody>
</table>
7.5. Calculating the Composition of a Custom pH Buffer: An Example

This short example illustrates the use of EQ3NR to calculate the composition of a custom pH buffer solution. Such buffers are highly useful in laboratory experiments, for example in determining the pH dependence of mineral dissolution kinetics (e.g., Knauss and Wolery, 1986). The model is defined by choosing the desired pH at the given temperature and the concentration of the buffering component. Electrical balancing is used to determine how much acid or base to include in the buffer recipe. The details are explained in the title on the input file, which is presented in both formats. This example was computed using the com data file. The activity coefficients were computed from the B-dot equation.

In this case, the buffer recipe is to consist of 0.05 molal boric and some unknown concentration of NaOH. The pH is to be 8.00 at 70°C. The desired concentration of NaOH is determined by
electrical balancing on the sodium ion. The calculated concentration of Na\(^+\) is 0.005691 molal. Hence the buffer should contain 0.005691 molal of NaOH.

By doing very similar calculations with electrical balancing on the hydrogen ion, it is possible to confirm consistency between code calculations and standard pH buffer recipes. The pH of such solutions at other temperatures can then be found simply by changing the temperature on the data file. Some examples of this are given by Knauss and Wolery (1986).

When doing calculations involving buffers intended for use in the laboratory, it is always wise to check the saturation index results to ensure that the desired buffer composition is not supersaturated with respect to some solid phase. If it is, the buffer solution may be impossible to make up, or if it can be made up, it may not be stable owing to eventual precipitation of the supersaturated phase. The buffer solution may also be hard to make up if the solid form of the buffer component (such as boric acid) is undersaturated, but fairly close to saturation.

The EQ3NR input file (custombuf.3i).custom pH buffer test case ("W" format):

```
EQ3NR input file name= custombuf.3i
DESCRIPTION= "Custom borate pH buffer, pH 8.00 at 70 C"
Version number= 3345 Stage number= 0
Created 06/08/90    Creator= T.J. Wolery
Revised 06/08/90   Revisor= T.J. Wolery

Compute the amount of NaOH required for the custom borate pH buffer solution:

pH 8.00 (at 70 C) buffer: 0.05 M H3BO3 + x M NaOH

This buffer is a spin-off of buffers used by Knauss and Wolery (1986) in mineral dissolution rate experiments. The H3BO3 concentration has been dropped by an order of magnitude to reduce interference with the analysis of alkali cations (such as K\(^+\)) in the leachate. The molality of Na\(^+\) is adjusted so as to find the molality of NaOH (x) required to obtain a buffer pH of 8.00 at 70 C, the intended temperature of the experiments. The adjusted molality is given as the "final" value in "moles/kg."

Purpose: to test electrical balancing on a solute other than H\(^+\) and to demonstrate the code's ability to calculate the composition of a custom pH buffer.

References
```
The EQ3NR input file (custombuf.3i) custom pH buffer test case ("D" format):

**EQ3NR input file name: custombuf.3i**

**Description:** Custom borate pH buffer, pH 8.00 at 70°C

**Version number:** 3245  **Stage number:** 01

**Created:** 06/08/90  **Creator:** T.J. Wolery

**Revised:** 06/08/90  **Revisor:** T.J. Wolery

---

Compute the amount of NaOH required for the custom borate pH buffer solution:

\[
\text{pH 8.00 (at 70°C) buffer: } 0.05 \times \text{H}_3\text{B}O_3 + x \times \text{NaOH}
\]

This buffer is a spin-off of buffers used by Knauss and Wolery (1986) in mineral dissolution rate experiments. The \(\text{H}_3\text{B}O_3\) concentration has been lowered by an order of magnitude to reduce interference with the analysis of alkali cations (such as \(\text{K}^+\)) in the leachate. The molality of \(\text{Na}^+\) is adjusted so as to find the molality of NaOH \((x)\) required to obtain a buffer pH of 8.00 at 70°C, the intended temperature of the experiments. The adjusted molality is given as the "final" value in "moles/kg."

**Purpose:** To test electrical balancing on a solute other than \(\text{H}^+\) and to demonstrate the code's ability to calculate the composition of a custom pH buffer.

**References**


---

**Temperature (C) |** 70.00  **Density (gm/cm³) |** 1.00000

**Total Dissolved Salts |** not used

**Electrical Balance on |** not performed

**SPECIES | BASIS SWITCH/CONSTRAINT | CONCENTRATION | UNITS ON TYPED**

<table>
<thead>
<tr>
<th>Species</th>
<th>Basis Switch/Constraint</th>
<th>Concentration</th>
<th>Units on Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>redox</td>
<td></td>
<td>-7.000</td>
<td>logfO2</td>
</tr>
<tr>
<td>h+</td>
<td></td>
<td>8.0000</td>
<td>pH</td>
</tr>
<tr>
<td>na+</td>
<td></td>
<td>0.40000E-02</td>
<td>molality</td>
</tr>
<tr>
<td>D(oh3)(aq)</td>
<td></td>
<td>0.50000E-01</td>
<td>molality</td>
</tr>
</tbody>
</table>

**Input Solid Solutions**

**Options**

- **SOLID SOLUTIONS**
  - ignore solid solutions
  - process hypothetical solid solutions
  - process input and hypothetical solid solutions
- **LOADING OF SPECIES INTO MEMORY**
  - does nothing
  - lists species loaded into memory
- **ECNO DATABASE INFORMATION**
  - does nothing
  - lists all reactions
  - lists reactions and log K values
  - lists reactions, log K values and polynomial coef.
- **LIST OF AQUEOUS SPECIES (ordering)**
  - in order of decreasing concentration
- **LIST OF AQUEOUS SPECIES (concentration limit)**
  - all species
  - only species > 10**-12 molal
  - not printed
- **LIST OF AQUEOUS SPECIES (by element)**
  - print major species
  - print all species
  - don't print
- **MINERAL SATURATION STATES**
  - print if affinity > -10 keals
  - print all
  - don't print
- **pH SCALE CONVERSION**
  - modified NBS
**Internal rational activity coefficient options**
- Davies' equation
- Pitzer's equations
- off

**Pitzer database information**
- print only warnings
- print species in model and number of Pitzer coefficients
- print species in model and names of Pitzer coefficients

**Auto basis switching**
- Off
- On

**Pitzer database information**
- print only warnings
- print species in model and number of Pitzer coefficients
- print species in model and names of Pitzer coefficients

**Pickup file**
- write pickup file
- don't write pickup file

**List mean ionic properties**
- print
- don't print

**Convergence criteria**
- test both residual functions and correction terms
- test only residual functions

**Debugging switches** (o-off, 1.2-on, default is off)
- generic debugging information
- print details of pre-Newton-Raphson iteration
- print details of Newton-Raphson iteration
- print details of stoichiometric factors calculation
- print details of stoichiometric factors calculation
- write reactions on RLIST
- list stoichiometric concentrations of master species
- request iteration variables to be killed

**Development options** (used for code development)
- none

**Tolerances** (desired values) (defaults)

<table>
<thead>
<tr>
<th>residual functions</th>
<th>correction terms</th>
<th>saturation state</th>
<th>number of N-R iterations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.e-10</td>
<td>1.e-10</td>
<td>0.5</td>
<td>30</td>
</tr>
</tbody>
</table>

The EQ3NR output file (custombuf3a), custom pH buffer test case (beginning with the message announcing the end of Newton-Raphson iteration):

```

(Material deleted)

Hybrid newton-raphson iteration converged in 5 steps.

----- Summary of the Aqueous Phase ----- 

----- Elemental composition of the aqueous phase ----- 

<table>
<thead>
<tr>
<th>element</th>
<th>mg/l</th>
<th>mg/kg</th>
<th>moles/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>0.89042E+06</td>
<td>0.89042E+06</td>
<td>0.556351558E+02</td>
</tr>
<tr>
<td>H</td>
<td>5.4525</td>
<td>5.4525</td>
<td>0.499999999E+01</td>
</tr>
<tr>
<td>H2O</td>
<td>0.11203E+06</td>
<td>0.11203E+06</td>
<td>0.111149963E+03</td>
</tr>
<tr>
<td>Na</td>
<td>230.83</td>
<td>230.83</td>
<td>0.556957940E+02</td>
</tr>
</tbody>
</table>

----- elemental composition as strict basis species ----- 

<table>
<thead>
<tr>
<th>species</th>
<th>mg/l</th>
<th>mg/kg</th>
<th>moles/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>h2o</td>
<td>0.10026E+07</td>
<td>0.10026E+07</td>
<td>0.556351558E+02</td>
</tr>
<tr>
<td>h(co3;2+:aq)</td>
<td>3093.7</td>
<td>3093.7</td>
<td>0.499999999E+01</td>
</tr>
<tr>
<td>h+</td>
<td>0.11203E+06</td>
<td>0.11203E+06</td>
<td>0.111149963E+03</td>
</tr>
</tbody>
</table>

- 121 -
```
--- equivalent composition of the aqueous phase (cto balances) ---

**original basis**

<table>
<thead>
<tr>
<th>species</th>
<th>moles/kg H2O</th>
<th>species</th>
<th>moles/kg H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O</td>
<td>0.5565315583E+02</td>
<td>H2O</td>
<td>0.5565315583E+02</td>
</tr>
<tr>
<td>B(OH)3(aq)</td>
<td>0.4999999993E-01</td>
<td>B(OH)3(aq)</td>
<td>0.4999999993E-01</td>
</tr>
<tr>
<td>H+</td>
<td>0.1111499637E+03</td>
<td>H+</td>
<td>0.1111499637E+03</td>
</tr>
<tr>
<td>Na+</td>
<td>0.5690279408E-02</td>
<td>Na+</td>
<td>0.5690279408E-02</td>
</tr>
</tbody>
</table>

**existing basis**

<table>
<thead>
<tr>
<th>species</th>
<th>moles/kg H2O</th>
<th>species</th>
<th>moles/kg H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O</td>
<td>0.5565315583E+02</td>
<td>H2O</td>
<td>0.5565315583E+02</td>
</tr>
<tr>
<td>B(OH)3(aq)</td>
<td>0.4999999993E-01</td>
<td>B(OH)3(aq)</td>
<td>0.4999999993E-01</td>
</tr>
<tr>
<td>H+</td>
<td>0.1111499637E+03</td>
<td>H+</td>
<td>0.1111499637E+03</td>
</tr>
<tr>
<td>Na+</td>
<td>0.5690279408E-02</td>
<td>Na+</td>
<td>0.5690279408E-02</td>
</tr>
</tbody>
</table>

Single ion activities and activity coefficients are here defined with respect to the modified NBS pH scale.

<table>
<thead>
<tr>
<th>ph</th>
<th>ch</th>
<th>pe</th>
</tr>
</thead>
<tbody>
<tr>
<td>modified NBS pH scale</td>
<td>8.0000</td>
<td>0.6660</td>
</tr>
<tr>
<td>rational pH scale</td>
<td>7.9869</td>
<td>0.6684</td>
</tr>
</tbody>
</table>

**activity of water** = 0.99900

**log activity of water** = -0.00043

**true osmotic coefficient** = 0.99439

**stoichiometric osmotic coefficient** = 0.95396

**sum of true molalities** = 0.05568475100840

**sum of stoichiometric molalities** = 0.0556718616625

**true ionic strength** = 0.0056661824285

**stoichiometric ionic strength** = 0.0028537623461

----- electrical balance totals -----

**equiv/kg**

| sigma(mz) cations | 0.56661824285E-02 |
| sigma(mz) anions  | -0.5666182358E-02 |
| total charge      | 0.1111226479E+01  |
| mean charge       | 0.5666182393E-02  |
| charge imbalance  | 0.7043946671E-10  |

**total charge = sigma(mz) cations + abs (sigma(mz) anions)**

**mean charge = 1/2 total charge**

The electrical imbalance is

0.622E-05 per cent of the total charge
0.124E-05 per cent of the mean charge
0.124E-05 per cent of sigma(mz) cations
0.124E-05 per cent of abs (sigma(mz) anions)

----- electrical balancing on Na+ -----

<table>
<thead>
<tr>
<th>mg/l</th>
<th>mg/kg</th>
<th>moles/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>input</td>
<td>91.959</td>
<td>91.959</td>
</tr>
<tr>
<td>final</td>
<td>130.83</td>
<td>130.83</td>
</tr>
<tr>
<td>adj</td>
<td>38.866</td>
<td>38.866</td>
</tr>
</tbody>
</table>

----- activity ratios of ions -----

log (act(B(OH)3(aq)) / act(H+)) = -1.3533
log (act(Na+) / act(H+)) = 5.7143
log (act(H2O) / act(H+)) = -37.7891
log (act(OH-) / act(H+)) = -3.7843
log (act(OH-) / act(H+)) = -12.0090

----- distribution of aqueous species -----
### Summary of Aqueous Species

#### Major Aqueous Species Contributing to Mass Balances

<table>
<thead>
<tr>
<th>Species</th>
<th>Molal Conc</th>
<th>Per Cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b(oh)_3(aq)$</td>
<td>0.4433E-01</td>
<td>88.65</td>
</tr>
<tr>
<td>$bo_2^-$</td>
<td>0.5619E-02</td>
<td>11.30</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>99.95</strong></td>
</tr>
</tbody>
</table>

#### Aqueous Species Accounting for 99% or More of $b(oh)_3(aq)$

<table>
<thead>
<tr>
<th>Species</th>
<th>Molal Conc</th>
<th>Per Cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b(oh)_3(aq)$</td>
<td>0.4433E-01</td>
<td>88.65</td>
</tr>
<tr>
<td>$bo_2^-$</td>
<td>0.5619E-02</td>
<td>11.30</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>99.95</strong></td>
</tr>
</tbody>
</table>

#### Aqueous Species Accounting for 99% or More of $na^+$

<table>
<thead>
<tr>
<th>Species</th>
<th>Molal Conc</th>
<th>Per Cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>$na^+$</td>
<td>0.5666E-02</td>
<td>99.57</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>99.57</strong></td>
</tr>
</tbody>
</table>

### Summary of Aqueous Redox Reactions

<table>
<thead>
<tr>
<th>Couple</th>
<th>Reduction Volts</th>
<th>$f_{o_2}$ Log</th>
<th>$h_{a}$ kcal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Default</td>
<td>0.666</td>
<td>-0.700</td>
<td>15.359</td>
</tr>
<tr>
<td>$h_2(aq)/h_2o$</td>
<td>0.666</td>
<td>-0.700</td>
<td>15.359</td>
</tr>
<tr>
<td>$o_2(aq)/h_2o$</td>
<td>0.666</td>
<td>-0.700</td>
<td>15.359</td>
</tr>
</tbody>
</table>

### Summary of Aqueous Non-Equilibrium Non-Redox Reactions

None

### Summary of Stoichiometric Mineral Saturation States

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Log $q/k$</th>
<th>Aff, kcal</th>
<th>State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boric Acid</td>
<td>-1.644</td>
<td>-2.582</td>
<td></td>
</tr>
<tr>
<td>Ice</td>
<td>-0.330</td>
<td>-0.519</td>
<td></td>
</tr>
</tbody>
</table>

0 approx. saturated pure minerals
0 approx. saturated end-members of specified solid solutions
0 saturated end-members of hypothetical solid solutions
0 supersaturated pure minerals
0 supersaturated end-members of specified solid solution phases
0 supersaturated hypothetical solid solution phases

### Summary of Gases

<table>
<thead>
<tr>
<th>Gas</th>
<th>Fugacity</th>
<th>Log Fugacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b(g)$</td>
<td>0.217492E-171</td>
<td>-171.66256</td>
</tr>
<tr>
<td>$h_2(g)$</td>
<td>0.221420E-34</td>
<td>-34.65478</td>
</tr>
<tr>
<td>$h_2o(g)$</td>
<td>0.233598E-00</td>
<td>-0.59244</td>
</tr>
<tr>
<td>$na(g)$</td>
<td>0.942317E-61</td>
<td>-63.02580</td>
</tr>
<tr>
<td>$o_2(g)$</td>
<td>0.199526E+00</td>
<td>-0.70000</td>
</tr>
</tbody>
</table>

#### End of Output

---

--- Pickup file has been successfully written ---
--- Reading the input file ---
--- No further input found ---

**Start time**: 09:25 **Hec'91**
**End time**: 09:25 **Hec'91**
**User time**: 3.430
**CPU time**: 0.870

Normal exit
7.6. Computing Oxygen Fugacity from Mineral Equilibria: An Example

In this example, the oxygen fugacity of a hydrothermal solution at 250°C is estimated by assuming equilibrium between the aqueous solution, hematite, and magnetite. Note the use of the option \texttt{iopt1} = -3, which opens up a species input block for \(O_2(g)\). Note that equilibrium with magnetite is the constraint assigned to \(Fe^{2+}\). Equilibrium with hematite is assigned to \(O_2(g)\). This problem also determines the concentration of dissolved iron. This test case was adapted from one given by Henley et al. (1984), which also involves equilibrium with quartz, albite, K-feldspar, and muscovite, and electrical balancing to determine the \(pH\). The results shown here were obtained using the \texttt{com} data file. The activity coefficients were computed from the B-dot equation. The input file is presented in both formats. The output file is presented beginning with the message announcing the end of Newton-Raphson iteration.

Equilibrium between hematite \((Fe_2O_3(c))\) and magnetite \((Fe_3O_4(c))\) fixes the oxygen fugacity because the reaction between the two can be written as:

\[
6Fe_2O_3(c) = 4Fe_3O_4(c) + O_2(g)
\]

(223)

Because the thermodynamic activities of the two minerals are each unity, the corresponding mass action equation reduces to:

\[
\log f_{O_2} = \log K
\]

(224)

where \(K\) is the equilibrium constant for the stated reaction.

Note that on the output file that the calculated saturation indices for hematite and magnetite are indeed zero. The \(pH\) is \(-7.1045\), the log oxygen fugacity is \(-35.301\), and the concentration of dissolved iron is a very low \(0.624 \times 10^{-9}\) molal.

The EQ3NR input file (fo2mineq.3i), the oxygen fugacity from mineral equilibria test case ("W" format):

EQ3NR input file name= fo2mineq.3i
Description= "Compute \(fO_2\) from hematite-magnetite equilibria"
Version number= 3245 Stage number= 01
Created 06/08/90 Creator= T.J. Kolery
Revised 06/08/90 Revisor= T.J. Kolery

Compute the oxygen fugacity assuming equilibrium with hematite and magnetite. This is an extension of the problem in henleyph.3i, taken from Henley et al. (1984, p. 96-97). In the original problem, the \(pH\) was to be calculated from electrical balancing. The initial value was 6.0, the adjusted value about 7.1. An initial value of 7.1 is used here.

Purpose: to test the computation of \(fO_2\) from specified mineral equilibria.

References:
The EQ3NR input file (fo2mineq.3i), the oxygen fugacity from mineral equilibria test case ("D" format):

```
EQR3 input file name: fo2mineq.3i
Description: "Compute fO2 from hematite-magnetite equilibria"
Version number: 3245 Stage number: 01
Created 06/08/90 Creator: T.J. Kolery
Revised 06/08/90 Revised by: T.J. Kolery

Compute the oxygen fugacity assuming equilibrium with hematite
and magnetite. This is an extension of the problem in
henleyJ.3i, taken from Henley et al. (1984, p. 96-97). In the original problem,
the pH was to be calculated from electrical balancing. The initial
value was 6.0, the adjusted value about 7.1. An initial value
of 7.1 is used here.

Reference:
Henley, R. W., Truesdell, A. H., Barton, P. R., Jr., and Whitney,
Reviews in Economic Geology, v. 1. Society of Economic Geologists,
```

---

The EQ3NR input file (fo2mineq.3i) includes the following details:

- **Temperature (°C):** 250.00
- **Density (g/cm³):** 1.00000

The input file contains a list of species and their properties, including:

- **Albite**
- **Muscovite**
- **SiO₂(aq)**
- **K-feldspar**
- **H₂O**

Each species is associated with specific concentrations and units.

---

The EQ3NR input file (fo2mineq.3i) is designed to compute the oxygen fugacity from mineral equilibria, specifically using hematite and magnetite as reference minerals. The input data includes various species and their concentrations, reflecting the equilibrium conditions in hydrothermal systems.
<table>
<thead>
<tr>
<th>SOLID SOLUTIONS</th>
<th>OUTPUT SOLID SOLUTIONS</th>
<th>TOLERANCES (desired values)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SUPPRESSED SPECIES</td>
<td>OPTIONS</td>
<td>DEVELOPMENT OPTIONS</td>
</tr>
<tr>
<td>O2(g)</td>
<td>hematite</td>
<td>0.10</td>
</tr>
<tr>
<td>mineral</td>
<td>0.5</td>
<td>30</td>
</tr>
</tbody>
</table>

### OPTIONS

- **SOLID SOLUTIONS**
  - *ignore solid solutions*
  - process hypothetical solid solutions
  - process input and hypothetical solid solutions

- **LOADING OF SPECIES INTO MEMORY**
  - does nothing
  - lists species loaded into memory

- **ECO DATABASE INFORMATION**
  - does nothing
  - lists all reactions
  - lists reactions and log K values
  - lists reactions, log K values and polynomial coeff.

- **LIST OF AQUEOUS SPECIES (ordering)**
  - in order of decreasing concentration
  - in same order as input file

- **LIST OF AQUEOUS SPECIES (concentration limit)**
  - all species
  - only species > 10^-20 molal
  - only species > 10^-12 molal
  - not printed

- **LIST OF AQUEOUS SPECIES (by element)**
  - print major species
  - print all species
  - don't print

- **MINERAL SATURATION STATES**
  - print if affinity > -10 kcals
  - print all
  - don't print

- **pH SCALE CONVENTION**
  - modified NUS
  - internal
  - rational

- **ACTIVITY COEFFICIENT OPTIONS**
  - use U-dot equation
  - Davich's equation
  - Pitzer's equations

- **AUTO BASIS SWITCHING**
  - off
  - on

- **PITZER DATABASE INFORMATION**
  - print only warnings
  - print species in model and number of Pitzer coefficients
  - print species in model and names of Pitzer coefficients

- **PICKUP FILE**
  - write pickup file
  - don't write pickup file

- **LIST MEAN IONIC PROPERTIES**
  - print all
  - don't print

- **LIST AQUEOUS SPECIES, ION SIZES, AND HYDRATION NUMBERS**
  - print all
  - don't print

- **CONVERGENCE CRITERIA**
  - test both residual functions and correction terms
  - test only residual functions

- **DEBUGGING SWITCHES**
  - 1.2-on, default is off

- **DEVELOPMENT OPTIONS** (used for code development)
  - none
The EQ3NR output file (fo2mineq.3p), the oxygen fugacity from mineral equilibria test case (beginning with the message announcing the end of Newton-Raphson iteration):

- Hybird newton-raphson iteration converged in 4 steps.

----- Summary of the Aqueous Phase -----

--- Elemental composition of the aqueous phase ---

<table>
<thead>
<tr>
<th>Element</th>
<th>mg/l</th>
<th>mg/kg</th>
<th>moles/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>3.55E+06</td>
<td>5.55E+06</td>
<td>5.55E-02</td>
</tr>
<tr>
<td>( \text{Al}^{+++} )</td>
<td>2.15E+06</td>
<td>2.15E+06</td>
<td>2.15E-02</td>
</tr>
<tr>
<td>( \text{Cl}^{-} )</td>
<td>3.54E+03</td>
<td>3.54E+03</td>
<td>3.54E-01</td>
</tr>
<tr>
<td>( \text{Fe}^{+++} )</td>
<td>3.64E+02</td>
<td>3.64E+02</td>
<td>3.64E-01</td>
</tr>
<tr>
<td>( \text{K}^{+} )</td>
<td>2.68E+02</td>
<td>2.68E+02</td>
<td>2.68E-01</td>
</tr>
<tr>
<td>( \text{Na}^{+} )</td>
<td>2.20E+02</td>
<td>2.20E+02</td>
<td>2.20E-01</td>
</tr>
<tr>
<td>( \text{Si}^{4+} )</td>
<td>1.77E+02</td>
<td>1.77E+02</td>
<td>1.77E-01</td>
</tr>
</tbody>
</table>

--- Elemental composition as strict basis species ---

<table>
<thead>
<tr>
<th>Species</th>
<th>moles/kg ( \text{H}_2\text{O} )</th>
<th>moles/kg ( \text{H}_2\text{O} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>5.55E-02</td>
<td>5.55E-02</td>
</tr>
<tr>
<td>( \text{Al}^{+++} )</td>
<td>2.15E-04</td>
<td>2.15E-04</td>
</tr>
<tr>
<td>( \text{Cl}^{-} )</td>
<td>1.00E-01</td>
<td>1.00E-01</td>
</tr>
<tr>
<td>( \text{Fe}^{+++} )</td>
<td>6.52E-08</td>
<td>6.52E-08</td>
</tr>
<tr>
<td>( \text{K}^{+} )</td>
<td>6.87E-03</td>
<td>6.87E-03</td>
</tr>
<tr>
<td>( \text{Na}^{+} )</td>
<td>9.59E-02</td>
<td>9.59E-02</td>
</tr>
<tr>
<td>( \text{SiO}_2(aq) )</td>
<td>6.33E-02</td>
<td>6.33E-02</td>
</tr>
</tbody>
</table>

--- Equivalent composition of the aqueous phase (cte balances) ---

<table>
<thead>
<tr>
<th>Species</th>
<th>moles/kg ( \text{H}_2\text{O} )</th>
<th>moles/kg ( \text{H}_2\text{O} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>5.55E-02</td>
<td>5.55E-02</td>
</tr>
<tr>
<td>( \text{Al}^{+++} )</td>
<td>2.15E-04</td>
<td>2.15E-04</td>
</tr>
<tr>
<td>( \text{Cl}^{-} )</td>
<td>1.00E-01</td>
<td>1.00E-01</td>
</tr>
<tr>
<td>( \text{Fe}^{+++} )</td>
<td>6.52E-08</td>
<td>6.52E-08</td>
</tr>
<tr>
<td>( \text{K}^{+} )</td>
<td>6.87E-03</td>
<td>6.87E-03</td>
</tr>
<tr>
<td>( \text{Na}^{+} )</td>
<td>9.59E-02</td>
<td>9.59E-02</td>
</tr>
<tr>
<td>( \text{SiO}_2(aq) )</td>
<td>6.33E-02</td>
<td>6.33E-02</td>
</tr>
</tbody>
</table>

Single ion activities and activity coefficients are here defined with respect to the modified NBS pH scale:

\[
\begin{align*}
\text{pH} & = 7.1043 \\
\text{pE} & = -0.4409 \\
\text{pH} & = 7.0303 \\
\text{pE} & = -0.4333
\end{align*}
\]

Activity of water = 0.9995
Log activity of water = -0.0002

True osmotic coefficient = 0.95501
Stoichiometric osmotic coefficient = 0.94765
Sum of true molalities = 0.26601162250
Sum of stoichiometric molalities = 0.26601162250
True ionic strength = 0.01079926658
Stoichiometric ionic strength = 0.01054464292

----- Electrical balance totals -----
equiv/kg

\[
\text{total charge} = \text{sigma(mz) cations} + \text{mean charge} + \text{abs (sigma(mz) anions)}
\]

the electrical imbalance is

\[
0.691E-09 \text{ per cent of the total charge}
\]

\[
0.136E-08 \text{ per cent of the mean charge}
\]

\[
0.136E-08 \text{ per cent of abs (sigma(mz) anions)}
\]

... electrical balancing on H^+

---

log activity

input -7.1000
final -7.1043
ad) -0.4264E-01

----- activity ratios of ions -----

log (act(ei+)) / act(h^+xx1) = -1.0029
log (act(ei++)) / act(h^+xx1) = -3.6367
log (act(h2aq)) / act(h^+xx1) = -3.8448
log (act(h2aq)) / act(h^+xx1) = -4.9916
log (act(h2aq)) / act(h^+xx1) = -2.2057
log (act(h2aq)) / act(h^+xx1) = -97.9170
log (act(h2aq)) / act(h^+xx1) = -3.4517
log (act(h2aq)) / act(h^+xx1) = -5.3500
log (act(h2aq)) / act(h^+xx1) = -37.9494
log (act(h2aq)) / act(h^+xx1) = -13.1677

----- distribution of aqueous species -----
----- major aqueous species contributing to mass balances ----- 

aqueous species accounting for 99% or more of Al+++ 

<table>
<thead>
<tr>
<th>species</th>
<th>molal conc</th>
<th>per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(OH)4^-</td>
<td>0.991E-04</td>
<td>99.18</td>
</tr>
<tr>
<td>total</td>
<td></td>
<td>99.18</td>
</tr>
</tbody>
</table>

aqueous species accounting for 99% or more of Cl- 

<table>
<thead>
<tr>
<th>species</th>
<th>molal conc</th>
<th>per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl^-</td>
<td>0.980E-02</td>
<td>99.06</td>
</tr>
<tr>
<td>NaCl(aq)</td>
<td>0.187E-03</td>
<td>1.87</td>
</tr>
<tr>
<td>total</td>
<td></td>
<td>99.93</td>
</tr>
</tbody>
</table>

aqueous species accounting for 99% or more of Fe** 

<table>
<thead>
<tr>
<th>species</th>
<th>molal conc</th>
<th>per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(OH)2(aq)</td>
<td>0.644E-08</td>
<td>98.78</td>
</tr>
<tr>
<td>Fe++</td>
<td>0.640E-10</td>
<td>0.98</td>
</tr>
<tr>
<td>total</td>
<td></td>
<td>99.77</td>
</tr>
</tbody>
</table>

aqueous species accounting for 99% or more of K+ 

<table>
<thead>
<tr>
<th>species</th>
<th>molal conc</th>
<th>per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>K+</td>
<td>0.680E-03</td>
<td>99.98</td>
</tr>
<tr>
<td>NaCl(aq)</td>
<td>0.704E-03</td>
<td>1.05</td>
</tr>
<tr>
<td>total</td>
<td></td>
<td>100.00</td>
</tr>
</tbody>
</table>

aqueous species accounting for 99% or more of Na+ 

<table>
<thead>
<tr>
<th>species</th>
<th>molal conc</th>
<th>per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na+</td>
<td>0.940E-02</td>
<td>99.93</td>
</tr>
<tr>
<td>NaCl(aq)</td>
<td>0.187E-03</td>
<td>1.95</td>
</tr>
<tr>
<td>total</td>
<td></td>
<td>99.87</td>
</tr>
</tbody>
</table>

aqueous species accounting for 99% or more of SiO2(aq) 

<table>
<thead>
<tr>
<th>species</th>
<th>molal conc</th>
<th>per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2(aq)</td>
<td>0.622E-02</td>
<td>98.38</td>
</tr>
<tr>
<td>H2SiO3^-</td>
<td>0.985E-04</td>
<td>1.43</td>
</tr>
<tr>
<td>total</td>
<td></td>
<td>99.81</td>
</tr>
</tbody>
</table>

----- summary of aqueous redox reactions ----- 

<table>
<thead>
<tr>
<th>couple</th>
<th>Eh, volts</th>
<th>pE</th>
<th>log fO2</th>
<th>Eh, kcal</th>
</tr>
</thead>
<tbody>
<tr>
<td>default</td>
<td>-0.441</td>
<td>-0.424E+01</td>
<td>-35.301</td>
<td>-10.169</td>
</tr>
<tr>
<td>clo4^- /cl-</td>
<td>-0.441</td>
<td>-0.424E+01</td>
<td>-35.301</td>
<td>-10.169</td>
</tr>
<tr>
<td>Fe+++ /Fe++</td>
<td>-0.441</td>
<td>-0.424E+01</td>
<td>-35.301</td>
<td>-10.169</td>
</tr>
<tr>
<td>H2(aq) /H20</td>
<td>-0.441</td>
<td>-0.424E+01</td>
<td>-35.301</td>
<td>-10.169</td>
</tr>
<tr>
<td>O2(aq) /H20</td>
<td>-0.441</td>
<td>-0.424E+01</td>
<td>-35.301</td>
<td>-10.169</td>
</tr>
</tbody>
</table>

----- summary of aqueous non-equilibrium non-redox reactions ----- 

<table>
<thead>
<tr>
<th>couple</th>
<th>affinity, kcal</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td></td>
</tr>
</tbody>
</table>

----- summary of stoichiometric mineral saturation states ----- 

(minerals with affinities |≤10 kcal are not listed) 

<table>
<thead>
<tr>
<th>mineral</th>
<th>log q/k</th>
<th>aff. kcal state</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albite</td>
<td>0.000</td>
<td>0.000 satd</td>
</tr>
<tr>
<td>Albite low</td>
<td>0.000</td>
<td>0.001 satd</td>
</tr>
<tr>
<td>Analcime-deby</td>
<td>1.475</td>
<td>0.318 andalusite</td>
</tr>
<tr>
<td>Analcime</td>
<td>0.767</td>
<td>-1.637 beidellite-h</td>
</tr>
<tr>
<td>Beidellite-h</td>
<td>1.272</td>
<td>-0.056 beidellite-na</td>
</tr>
</tbody>
</table>
## 7.7. Computing Eh from a Redox Couple: An Example

This test case illustrates the computation of Eh (or \( \rho E \), oxygen fugacity, or \( Ah \)) from data for both members of a redox couple. The fluid is an acid (\( pH = 1.1 \)) mine water whose composition is taken from Nordstrom, Jenne, and Ball (1979). The redox state is calculated for the \( Fe^{2+} - Fe^{3+} \) couple. This is possible because the concentration of each form of dissolved iron is sufficiently high to be measured. The objective is to compare the \( Eh \) calculated for this couple with the measured \( Eh \) of +622 mV. This problem was run using the \texttt{com} data file, and the activity coefficients are calculated from the B-dot equation. The input file in both formats is given below, followed by the output file, beginning with the message announcing the completion of Newton-Raphson iteration.

### Input File (Example)

```plaintext
boehmite -1.095 -2.621
chamosite-7a -2.151 -5.143
coesite -0.489 -1.170
cristobalite -0.266 -0.636
cristobalite-b -0.441 -1.056
daphnite-14a -1.927 -4.614
fayalite -1.606 -3.845
frech -1.738 -4.160
gibbsite -1.501 -3.594
greenalite -2.242 -5.367
hercynite -1.541 -3.689
jaluite -1.643 -3.934
kaolinite -1.730 -4.141
kyanite -2.243 -3.330
neptialina -1.655 -4.033
paragonite -0.641 -1.535
quartz 0.000 0.000
tridymite -0.371 -0.889

9 approx. saturated pure minerals
0 approx. saturated end-members of specified solid solutions
0 saturated end-members of hypothetical solid solutions
0 supersaturated pure minerals
0 supersatd. end-members of specified solid solutions
0 supersatd. hypothetical solid solution phases
```

### Output File

```
...... summary : cases ......

**gas**  **fugacity**  **key fugacity**

\( \text{H}_2\text{O}(g) \)
  0.116238E-76  -76.93465

\( \text{CO}_2(g) \)
  0.194732E-34  -34.70600

\( \text{H}_2\text{O}(g) \)
  0.264546E-22  -22.57350

\( \text{H}_2\text{O}(g) \)
  0.295222E-02  -0.14900

\( \text{NaCl} \)
  0.739658E-09  -9.05950

\( \text{H}_2\text{O}(g) \)
  0.821243E-12  -12.50565

\( \text{O}_2(g) \)
  0.104033E-30  -30.38065

```

- **end of output**

- **pickup file has been successfully written**

- **reading the input file**

- **no further input found**

- **start time = 09:25  3Dec91**
  
  **end time = 09:25  3Dec91**

  **user time = 4.080**
  
  **cpu time = 0.890**

  - **normal exit**

A detailed explanation of the data and calculations can be found in the input file, followed by the output file, which includes the summary of cases and the fugacity and key fugacity values for the gas phase.

---

7.7. Computing Eh from a Redox Couple: An Example

This test case illustrates the computation of Eh (or \( \rho E \), oxygen fugacity, or \( Ah \)) from data for both members of a redox couple. The fluid is an acid (\( pH = 1.1 \)) mine water whose composition is taken from Nordstrom, Jenne, and Ball (1979). The redox state is calculated for the \( Fe^{2+} - Fe^{3+} \) couple. This is possible because the concentration of each form of dissolved iron is sufficiently high to be measured. The objective is to compare the \( Eh \) calculated for this couple with the measured \( Eh \) of +622 mV. This problem was run using the \texttt{com} data file, and the activity coefficients are calculated from the B-dot equation. The input file in both formats is given below, followed by the output file, beginning with the message announcing the completion of Newton-Raphson iteration.
In this particular case, the measured \( Eh \) of +622 mV was used as the default redox parameter. This was accomplished by setting \( \text{ioptl} = -1 \) and \( \text{fep} = 0.622 \). This was used to constrain all the redox couples in the solution, except that for \( Fe^{2+} - Fe^{3+} \). For the latter couple, a separate analytical concentration was entered for each member, and the corresponding redox state then calculated. Of particular interest is the following table:

--- summary of aqueous redox reactions ---

<table>
<thead>
<tr>
<th>couple</th>
<th>( Eh, \text{volts} )</th>
<th>( \text{pE}^+ )</th>
<th>( \log \text{fo}_2 )</th>
<th>( ah, \text{kcal} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>default</td>
<td>0.622</td>
<td>0.1050E+02</td>
<td>-36.590</td>
<td>14.345</td>
</tr>
<tr>
<td>( Fe^{3+} / Fe^{2+} )</td>
<td>0.718</td>
<td>0.1312E+02</td>
<td>-30.315</td>
<td>16.557</td>
</tr>
<tr>
<td>( h_2 / h_2O )</td>
<td>0.622</td>
<td>0.1050E+02</td>
<td>-36.590</td>
<td>14.345</td>
</tr>
<tr>
<td>( hs^- / so_4^{2-} )</td>
<td>0.622</td>
<td>0.1050E+02</td>
<td>-36.590</td>
<td>14.345</td>
</tr>
<tr>
<td>( o_2 / h_2O )</td>
<td>0.622</td>
<td>0.1050E+02</td>
<td>-36.590</td>
<td>14.345</td>
</tr>
</tbody>
</table>

Here we see that the redox state of the ferrous-ferric couple expressed as \( Eh \) is +718 mV, higher than the measured value of +622 mV. The \( Eh \) of all other redox couples matches the default value. If we had set \( \text{ioptl} = 1 \) and \( \text{uredox} = 'Fe^{+++}' \), the default redox state would have been determined by that for the ferrous-ferric couple instead.

Is the difference between the computed \( Eh \) for the ferrous-ferric couple and the measured \( Eh \) significant? This is not immediately obvious. To pursue this question, one might like to know the likely error in the measured \( Eh \). One might also like to estimate the uncertainty in the calculated \( Eh \) of the ferrous-ferric couple due to the analytical uncertainties in the measurement of the concentration of the two forms of dissolved iron. One might also like to estimate the component of uncertainty in this quantity arising from uncertainty in the measurement of the \( pH \). Recall that the reported \( pH \) value was 1.1. Calibration buffers are generally available for \( pH \) values of about 4.0, 7.0, and 10.0. Thus it is likely that the measurement involved considerable extrapolation, and the true uncertainty is probably at least a few tenths of a \( pH \) unit. Note also that the calculated charge imbalance for the total water analysis on the high side (-16% of the total ionic charge). In addition to those considerations, uncertainty in the calculated \( Eh \) also arises from uncertainties in the thermodynamic data and the activity coefficients. Nordstrom, Jenne, and Ball (1979) were partly able to get around such problems by plotting the ferrous-ferric \( Eh \) versus the measured \( Eh \) for a suite of such waters.

Although this example involves the additional data required to evaluate the redox state of only one couple, data may be specified to allow the determination of the redox states of any number of redox couples. Generally speaking, two analytical data inputs are required per couple. However, if water is one of the members of a couple, only an analytical data input for the other member is required.

The EQ3NR input file (acidmwb.3i), the redox couple test case (“W” format):
Purpose: to test the code in the case of an acid mine water.

References


Temperature (°C) | 25.50 | Density (g/cm³) | 1.00000
---|---|---|---
Total Dissolved Salts | | mg/kg | mg/l | not used
<table>
<thead>
<tr>
<th>SPECIES</th>
<th>CONCENTRATION</th>
<th>UNITS OR TYPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>h</td>
<td>0.2220</td>
<td>eH</td>
</tr>
<tr>
<td>Ca++</td>
<td>1.1000</td>
<td>pH</td>
</tr>
<tr>
<td>Mg++</td>
<td>173.00</td>
<td>mg/L</td>
</tr>
<tr>
<td>Na+</td>
<td>92.50</td>
<td>mg/L</td>
</tr>
<tr>
<td>K+</td>
<td>128.00</td>
<td>mg/L</td>
</tr>
<tr>
<td>Fe++</td>
<td>9050.0</td>
<td>mg/L</td>
</tr>
<tr>
<td>Fe+++</td>
<td>2650.0</td>
<td>mg/L</td>
</tr>
<tr>
<td>Al+++</td>
<td>1400.0</td>
<td>mg/L</td>
</tr>
<tr>
<td>SiO2</td>
<td>130.00</td>
<td>mg/L</td>
</tr>
<tr>
<td>SO4++</td>
<td>60000.0</td>
<td>mg/L</td>
</tr>
</tbody>
</table>

Input Solid Solutions:
- none

Suppressed Species (suppress, replace, augmentk, augmentg) Value:
- none

Options:
- Solid Solutions:
  - Ignore solid solutions
  - Process hypothetical solid solutions
  - Process input and hypothetical solid solutions
- Loading of Species Into Memory:
  - Does nothing
  - Lists species loaded into memory
- Echo Database Information:
  - Does nothing
  - Lists all reactions
  - Lists reactions and log K values
  - Lists reactions, log K values and polynomial coeff.
- List of Aqueous Species (Ordering):
  - In order of decreasing concentration
  - In same order as input file
- List of Aqueous Species (Concentration Limit):
  - All species
  - Only species > 10**-20 molal
  - Only species > 10**-12 molal
  - Not printed
- List of Aqueous Species (By Element):
  - Print major species
  - Print all species
  - Don't print
- Mineral Saturation States:
  - Print if affinity > -10 kcaL
  - Print all
  - Don't print
- pH Scale Convention:
  - Modified NBS
  - Internal
  - Rational
- Activity Coefficient Options:
  - Use D-dot equation
  - Davies' equation
  - Pitzer's equations
- Auto Basis Switching:
  - Off
  - On
- Pitzer Database Information:
  - Print only warnings
  - Print species in model and number of Pitzer coefficients
  - Print species in model and names of Pitzer coefficients
- Pickup File:
  - Write pickup file
  - Don't write pickup file
- List Mean Ionic Properties:
  - Don't print
- Print
- List Aqueous Species, Ion Sizes, and Hydration Numbers:
  - Don't print
  - Print
- Convergence Criteria:
  - Test both residual functions and correction terms
  - Test only residual functions
- Debugging Switches (o-off, 1,2-on, default is off)
  - Generic debugging information
  - Print details of pre-Newton-Naphson iteration
  - Print details of Newton-Naphson iteration
  - Print details of stoichiometric factors
  - Print details of stoichiometric factors calculation
  - Write reactions on RLIST
  - List stoichiometric concentrations of master species
  - Request iteration variables to be killed
The EQ3NR output file (acidmwb.3o) the redox couple test case (beginning with the message announcing the end of Newton-Raphson iteration):

```
Hybrid newton-raphson iteration converged in 7 steps.

Summary of the Aqueous phase

Elemental composition of the aqueous phase

<table>
<thead>
<tr>
<th>Element</th>
<th>mg/l</th>
<th>mg/kg</th>
<th>moles/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>0.92814E+06</td>
<td>0.92814E+06</td>
<td>0.1113224E+02</td>
</tr>
<tr>
<td>Al</td>
<td>1400.0</td>
<td>1400.0</td>
<td>0.588734687E-01</td>
</tr>
<tr>
<td>Ca</td>
<td>173.00</td>
<td>173.00</td>
<td>0.46583154E-02</td>
</tr>
<tr>
<td>Fe</td>
<td>11700.0</td>
<td>11700.0</td>
<td>0.25096830E+00</td>
</tr>
<tr>
<td>H</td>
<td>0.11228E+06</td>
<td>0.11228E+06</td>
<td>0.113975425E+03</td>
</tr>
<tr>
<td>K</td>
<td>128.00</td>
<td>128.00</td>
<td>0.327397975E-02</td>
</tr>
<tr>
<td>Mg</td>
<td>685.00</td>
<td>685.00</td>
<td>0.2818350558E-01</td>
</tr>
<tr>
<td>Na</td>
<td>92.500</td>
<td>92.500</td>
<td>0.4023520925E-02</td>
</tr>
<tr>
<td>Si</td>
<td>60.767</td>
<td>60.767</td>
<td>0.283626771E-02</td>
</tr>
<tr>
<td>S</td>
<td>20028.</td>
<td>20028.</td>
<td>0.615863179E+00</td>
</tr>
</tbody>
</table>
```

Elemental composition as strict basis species

```
<table>
<thead>
<tr>
<th>Species</th>
<th>mg/l</th>
<th>mg/kg</th>
<th>moles/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O</td>
<td>1.03452E-07</td>
<td>0.10451E-07</td>
<td>0.5801113224E+02</td>
</tr>
<tr>
<td>Al+++</td>
<td>1400.0</td>
<td>1400.0</td>
<td>0.588734687E-01</td>
</tr>
<tr>
<td>Ca+++</td>
<td>173.00</td>
<td>173.00</td>
<td>0.46583154E-02</td>
</tr>
<tr>
<td>Fe+++</td>
<td>11700.0</td>
<td>11700.0</td>
<td>0.25096830E+00</td>
</tr>
<tr>
<td>H+++</td>
<td>0.11228E+06</td>
<td>0.11228E+06</td>
<td>0.113975425E+03</td>
</tr>
<tr>
<td>K+++</td>
<td>128.00</td>
<td>128.00</td>
<td>0.327397975E-02</td>
</tr>
<tr>
<td>Mg+++</td>
<td>685.00</td>
<td>685.00</td>
<td>0.2818350558E-01</td>
</tr>
<tr>
<td>Na+++</td>
<td>92.500</td>
<td>92.500</td>
<td>0.4023520925E-02</td>
</tr>
<tr>
<td>SiO2(aq)</td>
<td>130.00</td>
<td>130.00</td>
<td>0.283626771E-02</td>
</tr>
<tr>
<td>SO4---</td>
<td>60000.</td>
<td>60000.</td>
<td>0.615863179E+00</td>
</tr>
</tbody>
</table>
```

--- Equivalent composition of the aqueous phase (cfe balances) ---

<table>
<thead>
<tr>
<th>Species</th>
<th>moles/kg H2O</th>
<th>moles/kg H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O</td>
<td>0.5801113224E+02</td>
<td>0.5801113224E+02</td>
</tr>
<tr>
<td>Al+++</td>
<td>0.5188734687E-01</td>
<td>0.5188734687E-01</td>
</tr>
<tr>
<td>Ca+++</td>
<td>0.4316583154E-02</td>
<td>0.4316583154E-02</td>
</tr>
<tr>
<td>Fe+++</td>
<td>0.1620490906E-06</td>
<td>0.1620490906E-06</td>
</tr>
<tr>
<td>H+++</td>
<td>0.113975425E+03</td>
<td>0.113975425E+03</td>
</tr>
<tr>
<td>K+++</td>
<td>0.327397975E-02</td>
<td>0.327397975E-02</td>
</tr>
<tr>
<td>Mg+++</td>
<td>0.2818350558E-01</td>
<td>0.2818350558E-01</td>
</tr>
<tr>
<td>Na+++</td>
<td>0.4023520925E-02</td>
<td>0.4023520925E-02</td>
</tr>
<tr>
<td>SO4---</td>
<td>0.283626771E-02</td>
<td>0.283626771E-02</td>
</tr>
</tbody>
</table>

Single ion activities and activity coefficients are here defined with respect to the modified nbs ph scale.

---
activity of water = 0.98059
log activity of water = -0.00569

true osmotic coefficient = 0.86473

stoichiometric osmotic coefficient = 0.52784

sum of true molalities = 0.84190395829

sum of stoichiometric molalities = 1.3779110304192

true ionic strength = 0.9234813242653

stoichiometric ionic strength = 2.3659275751569

----- electrical balance totals -----

equiv/kg

\[ \text{total charge} = \sum \text{(molal cations) cations} + \sum \text{(molal anions) anions} \]

\[ \text{mean charge} = \frac{1}{2} \text{total charge} \]

the electrical imbalance is

-16.0 per cent of the total charge
-32.1 per cent of the mean charge
-32.2 per cent of \( \sum \text{(molal cations) cations} \)
-27.7 per cent of \( \sum \text{(molal anions) anions} \)

----- activity ratios of ions ----- 

\[ \frac{\log \text{activity of } (\text{ion}^{n+})}{\log \text{activity of } (\text{ion}^{m+})} = -0.0061 \]

\[ \frac{\log \text{activity of } (\text{ion}^{n-})}{\log \text{activity of } (\text{ion}^{m-})} = 0.4761 \]

\[ \frac{\log \text{activity of } (\text{ion}^{m+})}{\log \text{activity of } (\text{ion}^{n+})} = -0.3497 \]

\[ \frac{\log \text{activity of } (\text{ion}^{m-})}{\log \text{activity of } (\text{ion}^{n-})} = 1.5500 \]

\[ \frac{\log \text{activity of } (\text{ion}^{+})}{\log \text{activity of } (\text{ion}^{2+})} = -2.6448 \]

\[ \frac{\log \text{activity of } (\text{ion}^{2+})}{\log \text{activity of } (\text{ion}^{+})} = -3.8058 \]

\[ \frac{\log \text{activity of } (\text{ion}^{m+})}{\log \text{activity of } (\text{ion}^{n+})} = 0.6877 \]

\[ \frac{\log \text{activity of } (\text{ion}^{n+})}{\log \text{activity of } (\text{ion}^{m+})} = -2.2036 \]

\[ \frac{\log \text{activity of } (\text{ion}^{m+})}{\log \text{activity of } (\text{ion}^{2+})} = -39.4856 \]

\[ \frac{\log \text{activity of } (\text{ion}^{2+})}{\log \text{activity of } (\text{ion}^{m+})} = -30.6086 \]

----- distribution of aqueous species ----- 

<table>
<thead>
<tr>
<th>species</th>
<th>molal conc</th>
<th>log conc</th>
<th>log q</th>
<th>activity</th>
<th>log act</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSO₄⁻</td>
<td>0.2789E+00</td>
<td>-0.3546</td>
<td>-0.1662</td>
<td>0.1002E+00</td>
<td>-0.7208</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.1592E+00</td>
<td>-0.0088</td>
<td>-0.8060</td>
<td>0.2475E+00</td>
<td>-1.6058</td>
</tr>
<tr>
<td>H⁺</td>
<td>0.3006E+00</td>
<td>-0.0972</td>
<td>-1.0385</td>
<td>0.7643E+00</td>
<td>-1.1000</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>0.8774E+01</td>
<td>-1.0500</td>
<td>-0.6671</td>
<td>0.1888E+01</td>
<td>-1.7239</td>
</tr>
<tr>
<td>H₂SO₄(aq)</td>
<td>0.7433E-01</td>
<td>-1.1290</td>
<td>0.0000</td>
<td>0.7433E-01</td>
<td>-1.1290</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>0.3466E+01</td>
<td>-1.4601</td>
<td>-1.1522</td>
<td>0.2442E+02</td>
<td>-2.6123</td>
</tr>
<tr>
<td>Al(SO₄)²⁻</td>
<td>0.2970E+01</td>
<td>-2.5273</td>
<td>0.1662</td>
<td>0.2025E+01</td>
<td>-1.6953</td>
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<tr>
<td>Mg²⁺</td>
<td>0.9002E+02</td>
<td>-2.0043</td>
<td>-0.5454</td>
<td>0.2620E+02</td>
<td>-2.5497</td>
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<tr>
<td>FeSO₄(aq)</td>
<td>0.8118E-02</td>
<td>-2.0905</td>
<td>-0.1921</td>
<td>0.5216E+02</td>
<td>-2.2826</td>
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<tr>
<td>Al³⁺</td>
<td>0.5836E+02</td>
<td>-2.2339</td>
<td>-1.1522</td>
<td>0.4118E+03</td>
<td>-3.3861</td>
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<tr>
<td>Fe⁴⁺</td>
<td>0.3098E+02</td>
<td>-2.4440</td>
<td>-3.1662</td>
<td>0.2452E+02</td>
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<tr>
<td>Ca²⁺</td>
<td>0.3484E+02</td>
<td>-2.4579</td>
<td>-0.1921</td>
<td>0.2239E+02</td>
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<tr>
<td>Na⁺</td>
<td>0.2705E-02</td>
<td>-3.5516</td>
<td>-0.2273</td>
<td>0.1656E+02</td>
<td>-2.7809</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.5036E+02</td>
<td>-2.5911</td>
<td>0.6671</td>
<td>0.7403E+02</td>
<td>-1.2602</td>
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<tr>
<td>SiO₂(aq)</td>
<td>0.2164E-02</td>
<td>-2.6040</td>
<td>0.0000</td>
<td>0.2164E-02</td>
<td>-2.6648</td>
</tr>
<tr>
<td>CaSO₄(aq)</td>
<td>0.1748E+02</td>
<td>-3.7534</td>
<td>0.0000</td>
<td>0.1764E+02</td>
<td>-2.7534</td>
</tr>
<tr>
<td>FeOH⁺</td>
<td>0.3072E+02</td>
<td>-2.9781</td>
<td>0.8000</td>
<td>0.1567E+03</td>
<td>-3.7781</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>0.5392E-03</td>
<td>-3.2583</td>
<td>0.1662</td>
<td>0.3677E+03</td>
<td>-3.4345</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.5549E+03</td>
<td>-3.7101</td>
<td>-0.1662</td>
<td>0.3155E+03</td>
<td>-3.5064</td>
</tr>
<tr>
<td>CaSO₄(aq)</td>
<td>0.3545E+02</td>
<td>-4.6645</td>
<td>0.0000</td>
<td>0.2162E-02</td>
<td>-4.6645</td>
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<tr>
<td>Fe₂(OH)₄⁺</td>
<td>0.1494E+04</td>
<td>-4.8250</td>
<td>0.5000</td>
<td>0.1494E+04</td>
<td>-4.8250</td>
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<tr>
<td>FeOH⁺</td>
<td>0.8156E+05</td>
<td>-5.0746</td>
<td>0.3300</td>
<td>0.1209E+05</td>
<td>-5.8865</td>
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<tr>
<td>Fe(OH)⁺</td>
<td>0.3305E+05</td>
<td>-5.1743</td>
<td>0.3300</td>
<td>0.1209E+05</td>
<td>-5.8865</td>
</tr>
<tr>
<td>Fe(OH)²⁻</td>
<td>0.3131E+05</td>
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<tr>
<td>SiOH⁻</td>
<td>0.3252E+05</td>
<td>-6.4878</td>
<td>-0.3050</td>
<td>0.5184E+07</td>
<td>-7.2878</td>
</tr>
<tr>
<td>Fe²(OH)²⁻</td>
<td>0.3657E+07</td>
<td>-7.4138</td>
<td>-2.9876</td>
<td>0.4905E+10</td>
<td>-10.3014</td>
</tr>
<tr>
<td>Species</td>
<td>Molal Concentration</td>
<td>Percentage</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------------------------</td>
<td>---------------------</td>
<td>------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al$_2$(OH)$_2$</td>
<td>0.4334E-09</td>
<td>-8.88E-07</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Al(OH)$_2$</td>
<td>0.183E-11</td>
<td>5.37E-07</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>H$_3$SiO$_4$</td>
<td>0.457E-11</td>
<td>6.66E-07</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(OH)$_3$</td>
<td>0.314E-11</td>
<td>1.74E-07</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaOH</td>
<td>0.564E-12</td>
<td>2.00E-07</td>
<td></td>
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</tr>
<tr>
<td>CaO</td>
<td>0.156E-12</td>
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<tr>
<td>Al$_3$(OH)$_4$</td>
<td>0.475E-15</td>
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<tr>
<td>Na$_2$CO$_3$</td>
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<td>2.00E-07</td>
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<tr>
<td>MgO</td>
<td>0.539E-12</td>
<td>1.66E-07</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.301E-12</td>
<td>1.00E-07</td>
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<td>OH$^-$</td>
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</tr>
<tr>
<td>Na$_2$SiO$_4$</td>
<td>0.314E-11</td>
<td>1.74E-07</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg$_2$SiO$_4$</td>
<td>0.314E-11</td>
<td>1.74E-07</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca$_2$SiO$_4$</td>
<td>0.314E-11</td>
<td>1.74E-07</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$SiO$_4$</td>
<td>0.314E-11</td>
<td>1.74E-07</td>
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<tr>
<td>H$_2$SO$_4$</td>
<td>0.314E-11</td>
<td>1.74E-07</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>0.314E-11</td>
<td>1.74E-07</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O$_3$</td>
<td>0.314E-11</td>
<td>1.74E-07</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O$_4$</td>
<td>0.314E-11</td>
<td>1.74E-07</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

--- major aqueous species contributing to mass balances ---

**aqueous species accounting for 99% or more of Al**

<table>
<thead>
<tr>
<th>Species</th>
<th>Molal Concentration</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$(SO$_4$)$_3$</td>
<td>0.297E-01</td>
<td>57.23</td>
</tr>
<tr>
<td>Al$_3$O$_4$</td>
<td>0.163E-01</td>
<td>31.22</td>
</tr>
<tr>
<td>Al$^3+$</td>
<td>0.583E-02</td>
<td>11.25</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100.00</strong></td>
<td></td>
</tr>
</tbody>
</table>

**aqueous species accounting for 99% or more of Ca**

<table>
<thead>
<tr>
<th>Species</th>
<th>Molal Concentration</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$^{2+}$</td>
<td>0.255E-02</td>
<td>59.32</td>
</tr>
<tr>
<td>CaO</td>
<td>0.476E-02</td>
<td>40.68</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100.00</strong></td>
<td></td>
</tr>
</tbody>
</table>

**aqueous species accounting for 99% or more of Fe**

<table>
<thead>
<tr>
<th>Species</th>
<th>Molal Concentration</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^{3+}$</td>
<td>0.321E-01</td>
<td>58.14</td>
</tr>
<tr>
<td>Fe$_2$O$_3$(aq)</td>
<td>0.743E-01</td>
<td>41.86</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100.00</strong></td>
<td></td>
</tr>
</tbody>
</table>

**aqueous species accounting for 99% or more of K**

<table>
<thead>
<tr>
<th>Species</th>
<th>Molal Concentration</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$^+$</td>
<td>0.279E-02</td>
<td>85.38</td>
</tr>
<tr>
<td>K$_2$O$^-$</td>
<td>0.456E-02</td>
<td>13.62</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100.00</strong></td>
<td></td>
</tr>
</tbody>
</table>
### Aqueous Species Accounting for 99% or More of Mg²⁺

<table>
<thead>
<tr>
<th>Species</th>
<th>Molal Conc</th>
<th>Per Cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>mgso₄(aq)</td>
<td>0.123E+01</td>
<td>64.65</td>
</tr>
<tr>
<td>mg²⁺</td>
<td>0.900E-02</td>
<td>35.13</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td>100.00</td>
</tr>
</tbody>
</table>

### Aqueous Species Accounting for 99% or More of Na⁺

<table>
<thead>
<tr>
<th>Species</th>
<th>Molal Conc</th>
<th>Per Cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>na⁺</td>
<td>0.340E+01</td>
<td>86.60</td>
</tr>
<tr>
<td>nasa₄-</td>
<td>0.539E+01</td>
<td>13.40</td>
</tr>
<tr>
<td><strong>Total</strong></td>
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<td>100.00</td>
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</tbody>
</table>

### Aqueous Species Accounting for 99% or More of SiO₂(aq)

<table>
<thead>
<tr>
<th>Species</th>
<th>Molal Conc</th>
<th>Per Cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>si₉₂(aq)</td>
<td>0.216E+01</td>
<td>100.00</td>
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<td><strong>Total</strong></td>
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<td>100.00</td>
</tr>
</tbody>
</table>

### Aqueous Species Accounting for 99% or More of SO₄²⁻

<table>
<thead>
<tr>
<th>Species</th>
<th>Molal Conc</th>
<th>Per Cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>hsso₄⁻</td>
<td>0.278E+00</td>
<td>44.65</td>
</tr>
<tr>
<td>so₄²⁻</td>
<td>0.158E+00</td>
<td>25.33</td>
</tr>
<tr>
<td>feso₄(aq)</td>
<td>0.741E-01</td>
<td>11.90</td>
</tr>
<tr>
<td>h₂so₄(aq)</td>
<td>0.273E-01</td>
<td>9.51</td>
</tr>
<tr>
<td>mgo₄(aq)</td>
<td>0.102E-01</td>
<td>2.93</td>
</tr>
<tr>
<td>also₄⁻</td>
<td>0.163E-01</td>
<td>2.62</td>
</tr>
<tr>
<td>feso₄⁺</td>
<td>0.811E-02</td>
<td>1.30</td>
</tr>
<tr>
<td>fe(so₄)²⁻</td>
<td>0.359E-02</td>
<td>1.15</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td>99.96</td>
</tr>
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</table>

### Aqueous Species Accounting for 99% or More of Fe³⁺

<table>
<thead>
<tr>
<th>Species</th>
<th>Molal Conc</th>
<th>Per Cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>fe³⁺</td>
<td>0.346E+01</td>
<td>73.05</td>
</tr>
<tr>
<td>feso₄⁻</td>
<td>0.811E-02</td>
<td>17.11</td>
</tr>
<tr>
<td>fe(so₄)²⁻</td>
<td>0.359E-02</td>
<td>7.58</td>
</tr>
<tr>
<td>fe³⁺so₄⁺⁺</td>
<td>0.105E+02</td>
<td>2.22</td>
</tr>
<tr>
<td><strong>Total</strong></td>
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<td>99.96</td>
</tr>
</tbody>
</table>

#### Summary of Aqueous Redox Reactions

<table>
<thead>
<tr>
<th>Couple</th>
<th>Eh, Volts</th>
<th>Pe⁻</th>
<th>Log fo₂</th>
<th>Ah, kcal</th>
</tr>
</thead>
<tbody>
<tr>
<td>default</td>
<td>0.622</td>
<td>0.105E+02</td>
<td>-36.584</td>
<td>14.345</td>
</tr>
<tr>
<td>Fe³⁺ /fe⁻</td>
<td>0.718</td>
<td>0.121E+02</td>
<td>-30.109</td>
<td>16.557</td>
</tr>
<tr>
<td>H₂(aq) /H₂O</td>
<td>0.622</td>
<td>0.105E+02</td>
<td>-36.584</td>
<td>14.345</td>
</tr>
<tr>
<td>H⁺ /H₂O</td>
<td>0.622</td>
<td>0.105E+02</td>
<td>-36.584</td>
<td>14.345</td>
</tr>
<tr>
<td>O₂(aq) /O₂⁻</td>
<td>0.622</td>
<td>0.105E+02</td>
<td>-36.584</td>
<td>14.345</td>
</tr>
<tr>
<td>SO₃²⁻ /SO₄²⁻</td>
<td>0.622</td>
<td>0.105E+02</td>
<td>-36.584</td>
<td>14.345</td>
</tr>
</tbody>
</table>

#### Summary of Aqueous Non-Equilibrium Non-Redox Reactions

<table>
<thead>
<tr>
<th>Couple</th>
<th>Affinity, kcal</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td></td>
</tr>
</tbody>
</table>

#### Summary of Speciometric Mineral Saturation States

**Minerals with affinities \( \pm 10 \text{ kcal} \) are not listed:**

<table>
<thead>
<tr>
<th>Mineral</th>
<th>log q/k</th>
<th>Aff, kcal</th>
<th>State</th>
<th>Mineral</th>
<th>log q/k</th>
<th>Aff, kcal</th>
<th>State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alum-k</td>
<td>-3.712</td>
<td>-5.672</td>
<td></td>
<td>Alunite</td>
<td>-6.615</td>
<td>+9.040</td>
<td></td>
</tr>
<tr>
<td>Anhydrite</td>
<td>-0.524</td>
<td>-0.756</td>
<td></td>
<td>Arcanite</td>
<td>-5.374</td>
<td>-7.344</td>
<td></td>
</tr>
<tr>
<td>Bassanite</td>
<td>-1.202</td>
<td>-1.643</td>
<td></td>
<td>Caso₄:0.5h₂o(beta)</td>
<td>-1.369</td>
<td>-1.071</td>
<td></td>
</tr>
<tr>
<td>Chalcedony</td>
<td>1.094</td>
<td>1.440</td>
<td>ssatd</td>
<td>Coesite</td>
<td>0.516</td>
<td>0.705</td>
<td>ssatd</td>
</tr>
<tr>
<td>Cristobalite</td>
<td>0.775</td>
<td>1.059</td>
<td>ssatd</td>
<td>Cristobalite-a</td>
<td>0.775</td>
<td>1.059</td>
<td>ssatd</td>
</tr>
</tbody>
</table>

- 137 -
7.8. The Dead Sea Brine Test Case

Marcus (1977) attempted to calculate the activity of water and the mean activity of potassium chloride in Dead Sea brine. He was forced to use less accurate means than are presently available. Here, we repeat his work using Pitzer’s equations and the hmw data file (based on Harvie, Möller, and Weare, 1984). As no meaningful pH measurement can be made for such a concentrated solution, we have here attempted to obtain an estimate of the pH and the pHCl function proposed by Knauss, Jackson, and Wolery (1990) by constraining the hydrogen ion to satisfy equilibrium with carbon dioxide in the atmosphere (log fugacity of CO$_2$ = -3.5). The dissolution reaction for CO$_2$ gas can be written as:

$$CO_2(g) + H_2O(l) = H^+ + HCO_3^-$$  \hspace{1cm} (225)
### Aqueous Species Accounting for 99% or More

#### Mg++

<table>
<thead>
<tr>
<th>Species</th>
<th>Molal Conc</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgSO₄(aq)</td>
<td>0.1828E-01</td>
<td>64.87</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.9902E-02</td>
<td>35.13</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100.00</td>
</tr>
</tbody>
</table>

#### Na+

<table>
<thead>
<tr>
<th>Species</th>
<th>Molal Conc</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>0.3464E-02</td>
<td>86.60</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>0.5392E-03</td>
<td>13.40</td>
</tr>
<tr>
<td>Total</td>
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<td>100.00</td>
</tr>
</tbody>
</table>

#### SiO₂(aq)

<table>
<thead>
<tr>
<th>Species</th>
<th>Molal Conc</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂(aq)</td>
<td>0.2164E-02</td>
<td>100.00</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100.00</td>
</tr>
</tbody>
</table>

#### SO₄²⁻

<table>
<thead>
<tr>
<th>Species</th>
<th>Molal Conc</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSO₄⁻</td>
<td>0.2789E+00</td>
<td>44.65</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.1582E+00</td>
<td>25.33</td>
</tr>
<tr>
<td>Fe₂(SO₄)₃⁻</td>
<td>0.7431E-01</td>
<td>11.90</td>
</tr>
<tr>
<td>MgSO₄(aq)</td>
<td>0.2970E-01</td>
<td>9.51</td>
</tr>
<tr>
<td>Al₂(SO₄)₃⁻</td>
<td>0.1038E-01</td>
<td>2.93</td>
</tr>
<tr>
<td>Total</td>
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<td>99.38</td>
</tr>
</tbody>
</table>

#### Fe³⁺

<table>
<thead>
<tr>
<th>Species</th>
<th>Molal Conc</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe³⁺</td>
<td>0.3466E-01</td>
<td>73.05</td>
</tr>
<tr>
<td>Fe₂(SO₄)₃⁻</td>
<td>0.8118E-02</td>
<td>17.11</td>
</tr>
<tr>
<td>Fe₂(SO₄)₃⁻</td>
<td>0.1038E-02</td>
<td>7.58</td>
</tr>
<tr>
<td>Fe₃(SO₄)₂⁻</td>
<td>0.1038E-02</td>
<td>2.22</td>
</tr>
<tr>
<td>Total</td>
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<td>99.96</td>
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#### Summary of Aqueous Redox Reactions

<table>
<thead>
<tr>
<th>Couple</th>
<th>Oxidation State</th>
<th>Reduction State</th>
<th>Eₜ, Volts</th>
<th>pe⁻</th>
<th>log fO₂</th>
<th>aH, kcal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Default</td>
<td></td>
<td></td>
<td>0.622</td>
<td>0.1050E+02</td>
<td>-36.594</td>
<td>14.345</td>
</tr>
<tr>
<td>Fe⁺⁺ / Fe⁺⁺</td>
<td></td>
<td></td>
<td>0.710</td>
<td>0.1212E+02</td>
<td>-36.109</td>
<td>16.557</td>
</tr>
<tr>
<td>H₂O / H₂O</td>
<td></td>
<td></td>
<td>0.622</td>
<td>0.1050E+02</td>
<td>-36.594</td>
<td>14.345</td>
</tr>
<tr>
<td>H₂O / H₂O</td>
<td></td>
<td></td>
<td>0.622</td>
<td>0.1050E+02</td>
<td>-36.594</td>
<td>14.345</td>
</tr>
<tr>
<td>SO₃⁻ / SO₄⁻</td>
<td></td>
<td></td>
<td>0.622</td>
<td>0.1050E+02</td>
<td>-36.594</td>
<td>14.345</td>
</tr>
</tbody>
</table>

#### Summary of Aqueous Non-Equilibrium Non-Redox Reactions

None

#### Summary of Stoichiometric Mineral Saturation States

(Minerals with affinities ≤ 10 kcal are not listed)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>log q/k</th>
<th>Aff, kcal</th>
<th>State</th>
<th>Mineral</th>
<th>log q/k</th>
<th>Aff, kcal</th>
<th>State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alum-k</td>
<td>-3.712</td>
<td>-5.073</td>
<td>ssatd</td>
<td>Alunite</td>
<td>-6.615</td>
<td>-9.040</td>
<td>ssatd</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>-0.554</td>
<td>-0.758</td>
<td>ssatd</td>
<td>Arcanite</td>
<td>-5.374</td>
<td>-7.344</td>
<td>ssatd</td>
</tr>
<tr>
<td>Bassanite</td>
<td>-1.102</td>
<td>-1.643</td>
<td>ssatd</td>
<td>Caso₄·0.5H₂O(beta)</td>
<td>-1.369</td>
<td>-1.871</td>
<td>ssatd</td>
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<tr>
<td>Halocarbon</td>
<td>1.054</td>
<td>1.484</td>
<td>ssatd</td>
<td>Comsite</td>
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<td>0.705</td>
<td>ssatd</td>
</tr>
<tr>
<td>Cristobalite</td>
<td>0.775</td>
<td>1.059</td>
<td>ssatd</td>
<td>Cristobalite-a</td>
<td>0.775</td>
<td>1.059</td>
<td>ssatd</td>
</tr>
<tr>
<td>Mineral</td>
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<td>End Members (y)</td>
<td>Satd (x)</td>
<td>End Members (y)</td>
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<td>-3.012</td>
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<tr>
<td>Fe(OH)3</td>
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<td>-5.965</td>
<td>-8.151</td>
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<tr>
<td>Gibbsite</td>
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<td>-9.392</td>
<td>-6.303</td>
<td>-8.613</td>
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<tr>
<td>Goethite</td>
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<td>0.219</td>
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<td>Hematite</td>
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<td>-3.166</td>
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<td>Ice</td>
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<tr>
<td>Jarosite</td>
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<td>-3.302</td>
<td>-3.094</td>
<td>-5.322</td>
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<td>Limonite</td>
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<td>Marcasite</td>
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<td>-5.846</td>
<td>-7.989</td>
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</tr>
<tr>
<td>Nontronite</td>
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<td>4.456</td>
<td>4.369</td>
<td>5.971</td>
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<td></td>
</tr>
<tr>
<td>Nontronite-ca</td>
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<td>3.395</td>
<td>4.639</td>
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</tr>
<tr>
<td>Nontronite-ka</td>
<td>2.844</td>
<td>3.887</td>
<td>-2.797</td>
<td>-3.822</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td>1.324</td>
<td>1.610</td>
<td>0.044</td>
<td>0.050</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Starkeyite</td>
<td>-3.178</td>
<td>-4.343</td>
<td>-4.439</td>
<td>-6.866</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thenardite</td>
<td>-5.596</td>
<td>-9.014</td>
<td>1.153</td>
<td>1.576</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4 approx. saturated pure minerals
0 approx. saturated end-members of specified solid solutions
0 saturated end-members of hypothetical solid solutions

1) supersaturated pure minerals
0 supersatd. end-members of specified solid solutions
0 supersatd. hypothetical solid solution phases

7.8. The Dead Sea Brine Test Case

Marcus (1977) attempted to calculate the activity of water and the mean activity of potassium chloride in Dead Sea brine. He was forced to use less accurate means than are presently available. Here, we repeat his work using Pitzer's equations and the hwm data file (based on Harvie, Möller, and Weare, 1984). As no meaningful pH measurement can be made for such a concentrated solution, we have here attempted to obtain an estimate of the pH and the pHCl function proposed by Knauss, Jackson, and Wolery (1990) by constraining the hydrogen ion to satisfy equilibrium with carbon dioxide in the atmosphere (log fugacity of CO₂ = -3.5). The dissolution reaction for CO₂ gas can be written as:

\[
CO₂(g) + H₂O(l) = H⁺ + HCO₃⁻
\]  
(225)
The analytical data include a measurement of bicarbonate, which frees this reaction to be used as a constraint on the hydrogen ion. The input file is presented in both formats, and the output file is given starting with the message announcing the end of Newton-Raphson iteration.

Marcus (1977) concluded that the activity of water in Dead Sea brine was 0.754±0.004. The EQ3NR calculation gives a value of 0.750, in good agreement. Marcus also concluded that the mean ionic activity of KCl was in the range 0.876-1.199. The value calculated by EQ3NR is somewhat lower, 0.827. This is taken from the table of mean ionic properties, which was written on the output file because the option switch iopr6 was set to 1 on the input file. The pH calculated by EQ3NR is 7.43 on the NBS scale and 8.50 on the scale on which \( \log \gamma_{H^+} = 0 \). The pHCl is 6.94. Although the pH of Dead Sea brine can not be measured in the usual way, it should be possible to measure the pHCl using the method proposed by Knauss, Jackson, and Wolery (1990).

Ben-Yaakov and Sass (1977) attempted to measure the pH of artificial Dead Sea brine using a procedure that was conceptually very similar to the recommended pHCl method. Their artificial brine is very similar to that of Marcus (1977), but not identical. Using an electrochemical cell that in theory should respond linearly to pHCl, they took emf measurements on the artificial brine and three HCl solutions. In order to obtain the pH from their results, they had to estimate the activity coefficient of the chloride ion. They did this by first calculating the mean activity coefficient of potassium chloride in the brine using the Harned rule (Harned and Owen, 1958). This is an older approach to estimating activity coefficients in electrolyte mixtures which does not possess the accuracy of Pitzer's equations. They then estimated the activity coefficient of the chloride ion using the Maclnnes (1919) convention:

\[
\gamma_{Cl^-} = \gamma_{K^+} = \gamma_{+, KCl}
\]  

(226)

Using this approach, they determined that the pH of the artificial brine was 5.86. They compared this to the result of a conventional pH measurement, which gave a value of 6.22. Their value of 5.86 certainly differs from the value of 7.43 that we obtained by assuming equilibrium with atmospheric carbon dioxide. What does this mean?

Ben-Yaakov and Sass (1977) obtained a value of 0.757 for the mean activity coefficient of KCl. The value obtained in our test (see the output file) is 0.823. The corresponding values for the logarithm of this quantity are -0.1209 and -0.0846, respectively. This means that their estimate of pH should be lower than ours by only 0.036 unit. A more significant problem is that Ben-Yaakov and Sass' use of the Maclnnes convention has put their result on a "Maclnnes" pH scale. On the NBS scale used in our example, we obtained the following results:

<table>
<thead>
<tr>
<th>Species</th>
<th>( \log \gamma_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K^+ )</td>
<td>0.1055</td>
</tr>
<tr>
<td>( Cl^- )</td>
<td>-0.2750</td>
</tr>
<tr>
<td>( Cl^- ) (on the &quot;Maclnnes&quot; scale)</td>
<td>-0.0846</td>
</tr>
<tr>
<td>( Cl^- ) (Ben-Yaakov and Sass, 1977)</td>
<td>-0.1209</td>
</tr>
</tbody>
</table>
If we were to correct our result to the "MacInnes" scale, we would have to add 0.190 pH unit to our result, which would give us a pH of 7.62. This moves us even farther away from agreement with Ben-Yaakov and Sass.

It seems most likely that the pH of Dead Sea water must be closer to the value estimated by Ben-Yaakov and Sass (1977). Therefore, the equilibrium fugacity of carbon dioxide must be higher than the atmospheric value used in our test case. Without conducting new measurements, the best approach to estimating the pH of Dead Sea brine is probably to update Ben-Yaakov and Sass' calculation using Pitzer's equations and expressing the results on the NBS scale. This can be done by finding the pHCl corresponding to Ben-Yaakov and Sass' emf measurements and using this as an input to EQ3NR (how to use pHCl as an input is demonstrated in the following example in this chapter). In order to find this pHCl, one could use EQ3NR to calculate the pHCl of the three HCl solutions that Ben-Yaakov and Sass used as standards. One could then plot their measured emf results against these pHCl values. This plot could then be used as a calibration plot to determine the pHCl of the artificial brine from Ben-Yaakov and Sass' emf measurement. The resulting calculation would give the equilibrium fugacity of carbon dioxide, which could be compared against the atmospheric value. This would be a good exercise for the user who is particularly interested in brine chemistry.

The EQ3NR input file (deadseabr.3i), the Dead Sea brine test case ("W" format):

```
EQU3R input file name= deadseabr.3i
Description= "Dead Sea brine"
Version number= 1.2.51 Stage number= 01
Created 10/29/90  Creator= T. J. Wolory
Revised 10/29/90  Reviser= T. J. Wolory

Dead Sea brine, after Marcus (1977). Because no pH data are available, the pH is calculated from the assumption that the brine is in equilibrium with CO2 in the atmosphere (log PCsO2 = -3.5). According to Marcus, the activity of water in this brine should be 0.754 +/- 0.004, and the mean ionic activity of KCl should be in the range 0.876 - 1.199.

Purpose: to test the code on a small problem involving a very concentrated brine, using Pitzer's equations to calculate the activity coefficients of the aqueous species.

This problem is best addressed using the thermodynamic data base of Harvie, Moller, and Weare (1984).

The print option switch icop is set to 1 to direct the code to print a table of mean ionic properties.

Because Br- is not part of the Harvie-Moller-Weare model, the reported 0.0602 m Br- is ignored on this input file.

References


```

The EQ3NR input file (deadseabr3j), the Dead Sea brine test case ("D" format):

```
uebal= none
nxmlns= 0

data file master species= na+
  switch with species=
  jflag= 0  esp= 1.7519

data file master species= k+
  switch with species=
  jflag= 0  esp= 0.1739

data file master species= mg++
  switch with species=
  jflag= 0  esp= 0.4274

data file master species= ca++
  switch with species=
  jflag= 0  esp= 1.5552

data file master species= cl-
  switch with species=
  jflag= 0  cep= 5.8098

data file master species= hco3-
  switch with species=
  jflag= 0  esp= 0.00392

data file master species= so4--
  switch with species=
  jflag= 0  csp= 0.0063

data file master species= tit-
  switch with species=
  jflag= 21  esp= -3.5

endit.
```

EQ3NR input file name= deadseabr.3j
Description= "Dead Sea brine"
Version number= 1245  Stage number= 01
Created 10/29/90  Creator= T.J. Wolery
Revised 10/29/90  Revisor= T.J. Wolery

Dead Sea brine, after Marcus (1977). Because no pH data are available, the pH is calculated from the assumption that the brine is in equilibrium with CO2 in the atmosphere (log P CO2 = -3.5). According to Marcus, the activity of water in this brine should be 0.754 +/- 0.004, and the mean ionic activity of KCl should be in the range 0.976 - 1.399.

Purpose: to test the code on a small problem involving a very concentrated brine, using Pitzer's equations to calculate the activity coefficients of the aqueous species.

This problem is best addressed using the thermodynamic data base of Harvie, Moller, and Weare (1984).

The print option switch iop6 is set to 1 to direct the code to print a table of mean ionic properties.

Because Br- is not part of the Harvie-Moller-Weare model, the reported 0.0602 m Br- is ignored on this input file.

References
Harvie, C. E., Moller, N., and Weare, J. H., 1984, The prediction of mineral solubilities in natural waters: The Na-K-Hg-Ca-Mg-C1-SO4-
OH-HCO3-CO3-CO2-H2O system to high ionic strengths at 25 C:


<table>
<thead>
<tr>
<th>Temperature (C)</th>
<th>25.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm3)</td>
<td>1.20700</td>
</tr>
</tbody>
</table>

Total dissolved salts | mg/kg | mg/l | not used

Electrical balancing on | code selects | not performed

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>BASIS SWITCH/CONSTRAINT</th>
<th>CONCENTRATION</th>
<th>UNITS OR TYPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>na+</td>
<td>1.7519 molality</td>
<td></td>
<td></td>
</tr>
<tr>
<td>h+</td>
<td>0.1739 molality</td>
<td></td>
<td></td>
</tr>
<tr>
<td>mg++</td>
<td>0.4274 molality</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ca++</td>
<td>1.5552 molality</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cl-</td>
<td>5.8098 molality</td>
<td></td>
<td></td>
</tr>
<tr>
<td>hco3-</td>
<td>0.00392 molality</td>
<td></td>
<td></td>
</tr>
<tr>
<td>so4--</td>
<td>0.0063 molality</td>
<td></td>
<td></td>
</tr>
<tr>
<td>tit-</td>
<td>-3.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---
Input Solid Solutions

**SUPPRESSED SPECIES** (suppress, replace, augments)

OPTIONS

- **SOLID SOLUTIONS**
  - * ignore solid solutions
  - process hypothetical solid solutions
- **LOADING OF SPECIES INTO MEMORY**
  - * does nothing
  - lists species loaded into memory
- **ECHO DATABASE INFORMATION**
  - * does nothing
  - lists all reactions
  - lists reactions and log K values
  - lists reactions, log K value, and polynomial coefficients
- **LIST OF AQUEOUS SPECIES (ordering)**
  - * in order of decreasing concentration
  - in same order as input file
- **LIST OF MINERAL SPECIES (concentration limit)**
  - * all species
  - only species > 10^-12 molar
  - not printed
- **LIST OF AQUEOUS SPECIES (by element)**
  - * print major species
  - print all species
  - don't print
- **MINERAL SATURATION STATES**
  - * print if affinity > 10 kcal
  - print all
  - don't print
- **pH SCALE CONVERSION**
  - * modified NBS
  - internal
- **ACTIVITY COEFFICIENT OPTIONS**
  - * use R-dot equation
  - Davies' equation
  - Pitzer's equations
- **AUTO BASIS SWITCHING**
  - * off
  - on
- **PITZER DATABASE INFORMATION**
  - * print only warnings
  - print species in model and number of Pitzer coefficients
  - print species in model and names of Pitzer coefficients
- **PICKUP FILE**
  - * write pickup file
  - don't write pickup file
- **LIST OF AQUEOUS SPECIES, ION SIZES, AND HYDRATION NUMBERS**
  - * print
  - don't print
- **CONVERGENCE CRITERIA**
  - * test both residual functions and correction terms
  - test only residual functions

DEVELOPMENT OPTIONS (used for code development)

<table>
<thead>
<tr>
<th>TOLERANCES</th>
<th>(desired values)</th>
<th>(defaults)</th>
</tr>
</thead>
<tbody>
<tr>
<td>residual functions</td>
<td>1.0e-10</td>
<td>1.0e-10</td>
</tr>
<tr>
<td>correction terms</td>
<td>1.0e-10</td>
<td>1.0e-10</td>
</tr>
<tr>
<td>saturation state</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>number of N+M iterations</td>
<td>30</td>
<td>30</td>
</tr>
</tbody>
</table>
The EQ3NR output file for the Dead Sea brine test case (beginning with the message announcing the end of Newton-Raphson iteration):

Hybrid newton-raphson iteration converged in 4 steps.

----- Summary of the Aqueous Phase -----

Elemental composition of the aqueous phase

<table>
<thead>
<tr>
<th>element</th>
<th>mg/l</th>
<th>mg/kg</th>
<th>moles/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>o</td>
<td>0.10771E+07</td>
<td>0.88879E+06</td>
<td>0.5554602070E+02</td>
</tr>
<tr>
<td>ca</td>
<td>20675.</td>
<td>17129.</td>
<td>0.4274000000E+00</td>
</tr>
<tr>
<td>cl</td>
<td>2.49561E+06</td>
<td>2.05972E+06</td>
<td>0.5009800000E+01</td>
</tr>
<tr>
<td>h</td>
<td>0.12096E+06</td>
<td>0.11706E+06</td>
<td>0.3110000000E+03</td>
</tr>
<tr>
<td>k</td>
<td>56.029</td>
<td>47.503</td>
<td>0.5920000000E+01</td>
</tr>
<tr>
<td>mg</td>
<td>0.2066.</td>
<td>0.1799.</td>
<td>0.1739000000E+00</td>
</tr>
<tr>
<td>na</td>
<td>40613.</td>
<td>40276.</td>
<td>0.1751900000E+01</td>
</tr>
<tr>
<td>s</td>
<td>243.83</td>
<td>202.02</td>
<td>0.6300000000E+02</td>
</tr>
</tbody>
</table>

Elemental composition as strict basis species

<table>
<thead>
<tr>
<th>species</th>
<th>mg/l</th>
<th>mg/kg</th>
<th>moles/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>h2o</td>
<td>0.12070E+07</td>
<td>0.10007E+07</td>
<td>0.5554602070E+02</td>
</tr>
<tr>
<td>ca++</td>
<td>20675.</td>
<td>17129.</td>
<td>0.4274000000E+00</td>
</tr>
<tr>
<td>cl-</td>
<td>2.49561E+06</td>
<td>2.05972E+06</td>
<td>0.5009800000E+01</td>
</tr>
<tr>
<td>h+</td>
<td>0.12096E+06</td>
<td>0.11706E+06</td>
<td>0.3110000000E+03</td>
</tr>
<tr>
<td>k+</td>
<td>56.029</td>
<td>47.503</td>
<td>0.5920000000E+01</td>
</tr>
<tr>
<td>mg++</td>
<td>0.2066.</td>
<td>0.1799.</td>
<td>0.1739000000E+00</td>
</tr>
<tr>
<td>na+</td>
<td>40613.</td>
<td>40276.</td>
<td>0.1751900000E+01</td>
</tr>
<tr>
<td>so4++</td>
<td>730.84</td>
<td>405.20</td>
<td>0.6300000000E+02</td>
</tr>
</tbody>
</table>

Equivalent composition of the aqueous phase (cpe balances)

<table>
<thead>
<tr>
<th>species</th>
<th>moles/kg h2o</th>
<th>species</th>
<th>moles/kg h2o</th>
</tr>
</thead>
<tbody>
<tr>
<td>h2o</td>
<td>0.5554602070E+02</td>
<td>h2o</td>
<td>0.5554602070E+02</td>
</tr>
<tr>
<td>ca++</td>
<td>0.4274000000E+00</td>
<td>ca++</td>
<td>0.4274000000E+00</td>
</tr>
<tr>
<td>cl-</td>
<td>0.5009800000E+01</td>
<td>cl-</td>
<td>0.5009800000E+01</td>
</tr>
<tr>
<td>h+</td>
<td>0.3110000000E+03</td>
<td>h+</td>
<td>0.3110000000E+03</td>
</tr>
<tr>
<td>k+</td>
<td>0.1739000000E+00</td>
<td>k+</td>
<td>0.1739000000E+00</td>
</tr>
<tr>
<td>mg++</td>
<td>0.1555200000E+01</td>
<td>mg++</td>
<td>0.1555200000E+01</td>
</tr>
<tr>
<td>na+</td>
<td>0.1751900000E+01</td>
<td>na+</td>
<td>0.1751900000E+01</td>
</tr>
<tr>
<td>so4++</td>
<td>0.6300000000E+02</td>
<td>so4++</td>
<td>0.6300000000E+02</td>
</tr>
</tbody>
</table>

Single ion activities and activity coefficients are here defined with respect to the modified NBS pH scale

<table>
<thead>
<tr>
<th>pH</th>
<th>7.4270</th>
<th>0.7830</th>
<th>1.3237E+01</th>
</tr>
</thead>
<tbody>
<tr>
<td>eH</td>
<td>0.5048</td>
<td>0.7193</td>
<td>1.2159E+01</td>
</tr>
<tr>
<td>Pe</td>
<td>-143</td>
<td>-143</td>
<td>-143</td>
</tr>
</tbody>
</table>

Activity of water = 0.75020
Log activity of water = -0.12402
Stoichiometric osmotic coefficient = 1.64613
Sum of true molalities = 9.7255522592305
Sum of stoichiometric molalities = 9.726964445673
True ionic strength = 7.8402407646366
stoichiometric ionic strength = 7.8486287476994

----- electrical balance totals -----

equiv/kg

\[
\begin{align*}
\text{Sigma(mz) cations} & = 0.5884630387 \times 10^{11} \\
\text{Sigma(mz) anions} & = -0.5823980803 \times 10^{11} \\
\text{Total charge} & = 0.1370061119 \times 10^{12} \\
\text{Mean charge} & = 0.5854305595 \times 10^{11} \\
\text{Charge imbalance} & = 0.6064905353 \times 10^{-1} \\
\end{align*}
\]

the electrical imbalance is

\[
\begin{align*}
\text{0.516 per cent of the total charge} \\
\text{1.04 per cent of the mean charge} \\
\text{1.03 per cent of sigma(mz) cations} \\
\text{1.04 per cent of abs ( sigma(mz) anions )} \\
\end{align*}
\]

----- activity ratios of ions -----

\[
\begin{align*}
\log \left( \frac{\text{act}(ca^{2+})}{\text{act}(h^{+}) \times 2} \right) & = 15.3905 \\
\log \left( \frac{\text{act}(cl^{-})}{\text{act}(h^{+}) \times 2} \right) & = 6.9376 \\
\log \left( \frac{\text{act}(so_{4}^{2-})}{\text{act}(h^{+}) \times 2} \right) & = 16.2165 \\
\log \left( \frac{\text{act}(co_{3}^{2-})}{\text{act}(h^{+}) \times 2} \right) & = 15.7229 \\
\log \left( \frac{\text{act}(co_{2}^{-})}{\text{act}(h^{+}) \times 2} \right) & = 4.9816 \\
\log \left( \frac{\text{act}(h^{+})^{2}}{\text{act}(so_{4}^{2-})} \right) & = 21.7633 \\
\log \left( \frac{\text{act}(so_{4}^{2-})}{\text{act}(h^{+}) \times 2} \right) & = 14.1215 \\
\end{align*}
\]

----- distribution of aqueous species ----- 

\[
\begin{align*}
\text{Species} & & \text{Molar conc} & \text{Log conc} & \text{Log g} & \text{Activity} & \text{Log act} \\
\text{cl}^{-} & & 0.5010E+01 & 0.7642 & -2.2756 & 0.3084E+01 & 0.4892 \\
\text{na}^{+} & & 0.1752E+01 & 0.2435 & 0.4858 & 0.3262E+01 & 0.7293 \\
\text{mg}^{2+} & & 0.1552E+01 & 0.1910 & 1.1716 & 0.2304E+02 & 1.3625 \\
\text{ca}^{2+} & & 0.4269E+00 & -0.3697 & 0.9063 & 0.3440E+01 & 0.5366 \\
\text{k}^{+} & & 0.1739E+00 & -1.9797 & 1.0155 & 0.2217E+00 & -0.6542 \\
\text{so}_{4}^{2-} & & 0.6300E-02 & -2.2067 & -2.6683 & 0.1352E+00 & -4.8690 \\
\text{caco}_{3}(aq) & & 0.2299E-02 & -6.3308 & 0.0606 & 0.2299E+00 & -2.6384 \\
\text{mgch}^{+} & & 0.6244E-03 & -3.8044 & 0.0399 & 0.7196E-03 & -3.1443 \\
\text{caco}_{3}(aq) & & 0.5735E-03 & -3.2415 & 0.0000 & 0.5735E-03 & -3.2415 \\
\text{co}_{3}^{2-} & & 0.5223E-03 & -3.2739 & 1.3157E-06 & 0.2304E+02 & -9.2924 \\
\text{hco}_{3}^{-} & & 0.5115E-03 & -2.3291 & -1.1716 & 0.2304E+01 & 1.3625 \\
\text{so}_{4}^{2-} & & 0.6383E-02 & -2.49917 & 3.168E-03 & 1.871E-01 & 1.692E-01 \\
\text{co}_{3}^{2-} & & 0.5735E-03 & -3.2415 & 4.221E-02 & 1.871E-01 & 1.692E-01 \\
\text{oh}^{-} & & 0.5115E-03 & -2.3291 & -1.1716 & 0.2304E+01 & 1.3625 \\
\text{co}_{2}(aq) & & 0.5223E-03 & -3.2739 & 4.221E-02 & 1.871E-01 & 1.692E-01 \\
\text{h}^{+} & & 0.5223E-03 & -3.2739 & 4.221E-02 & 1.871E-01 & 1.692E-01 \\
\text{hso}_{4}^{-} & & 0.5223E-03 & -3.2739 & 4.221E-02 & 1.871E-01 & 1.692E-01 \\
\end{align*}
\]

mean ionic properties

\[
\begin{align*}
\text{Species} & & \text{Log a (+/-)} & \text{a (+/-)} & \text{m (+/-)} & \text{g (+/-)} & \text{Log act} \\
\text{cl}^{-} & & 0.5005E+00 & 3.7499E+00 & 2.433E+00 & 1.315E+00 & 2.434E+00 \\
\text{na}^{+} & & 0.7642 & 3.199E+00 & 2.433E+00 & 1.315E+00 & 2.434E+00 \\
\text{mg}^{2+} & & 0.8050E+00 & 4.092E+00 & 2.433E+00 & 1.315E+00 & 2.434E+00 \\
\text{ca}^{2+} & & 0.7642 & 3.199E+00 & 2.433E+00 & 1.315E+00 & 2.434E+00 \\
\text{k}^{+} & & 0.8050E+00 & 4.092E+00 & 2.433E+00 & 1.315E+00 & 2.434E+00 \\
\text{so}_{4}^{2-} & & 0.7642 & 3.199E+00 & 2.433E+00 & 1.315E+00 & 2.434E+00 \\
\text{co}_{3}^{2-} & & 0.8050E+00 & 4.092E+00 & 2.433E+00 & 1.315E+00 & 2.434E+00 \\
\text{oh}^{-} & & 0.7642 & 3.199E+00 & 2.433E+00 & 1.315E+00 & 2.434E+00 \\
\text{co}_{2}(aq) & & 0.8050E+00 & 4.092E+00 & 2.433E+00 & 1.315E+00 & 2.434E+00 \\
\text{h}^{+} & & 0.8050E+00 & 4.092E+00 & 2.433E+00 & 1.315E+00 & 2.434E+00 \\
\text{hso}_{4}^{-} & & 0.8050E+00 & 4.092E+00 & 2.433E+00 & 1.315E+00 & 2.434E+00 \\
\end{align*}
\]

(a) true quantities consistent with the speciation model

(b) stoichiometric quantities consistent with the cto max

-144-
balance lumpings, except that
1. effective cte(h+) = cte(h+) - conc(h2o)
2. effective cte(ch+) = cte(h2o) - conc(h2o)

----- major aqueous species contributing to mass balances ----- 

aqueous species accounting for 99% or more of ca++
species     molal conc     per cent
ca++        0.4266E+00       99.87
             -             -             -
total       99.87

aqueous species accounting for 99% or more of cl-
species     molal conc     per cent
cl-         0.5810E+01       100.00
             -             -             -
total       100.00

aqueous species accounting for 99% or more of hco3-
species     molal conc     per cent
mgco3(aq)   0.2299E-02       58.65
caco3(aq)   0.5715E-03       14.63
c03--       0.5322E-03       13.55
hco3-       0.5115E-03       13.05
             -             -             -
total       99.91

aqueous species accounting for 99% or more of k+
species     molal conc     per cent
k+          0.1739E+00       100.00
             -             -             -
total       100.00

aqueous species accounting for 99% or more of mg++
species     molal conc     per cent
mg++        0.1552E+01       99.81
             -             -             -
total       99.81

aqueous species accounting for 99% or more of na+
species     molal conc     per cent
na+         0.1752E+01       100.00
             -             -             -
total       100.00

aqueous species accounting for 99% or more of so4--
species     molal conc     per cent
so4--       0.6300E-02       100.00
             -             -             -
total       100.00

----- summary of aqueous redox reactions ----- 
couple     eh, volts     pe-     log fo2     ah, kcal
default    0.783        0.1324E+02    -0.700     18.059

----- summary of aqueous non-equilibrium non-redox reactions ----- 
couple     affinity, kcal
none

----- summary of stoichiometric mineral saturation states ----- 
(minerals with affinities >lt. -10 kcal are not listed)
### Summary of Gases

<table>
<thead>
<tr>
<th>Gas</th>
<th>Log Fugacity</th>
<th>Log Fugacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO2(g)</td>
<td>0.310228E-03</td>
<td>3.500000</td>
</tr>
<tr>
<td>N2(g)</td>
<td>0.437613E+11</td>
<td>41.32092</td>
</tr>
<tr>
<td>O2(g)</td>
<td>0.199526E+00</td>
<td>0.700000</td>
</tr>
</tbody>
</table>

---

### 7.9. Using pHCl as an Input: An Example

In the earlier example treating sea water with Pitzer's equations, we found that the pHCl was computed to be 8.6722. The pH value that was used as an input in this example was 8.22 on the NBS scale. The purpose of the present example is to show how pHCl can be used in place of pH. Here we partially invert the earlier problem by entering the pHCl. We should then get back the original pH. Other results (i.e., the calculated electrical imbalance, values of the mineral saturation indices) should also match the results from the previous example. This problem was run using the same hmw data file. The input file is presented in both formats. The output file is given starting with the message announcing the end of Newton-Raphson iteration.

The computed pH on the NBS scale is printed on the output file as “8.2200.” The correctness of the inversion is therefore verified. One may compare other computed results to verify that the computed model is otherwise identical to that obtained previously.
The EQ3NR input file (swphcl.3i), the pHCl test case ("W" format):

```
EQ3NR input file name = swphcl.3i
Description = "Sea water, using pHCl as input in place of pH"
Version number = 3245 Stage number = 01
Created 10/07/90 Creator = T.J. Wolery
Revised 10/07/90 Revisor = T.J. Wolery

Sea water, including only the major ions. This is a considerably pared-down version of swtst.3i, which contains the full benchmark sea water test case of Nordstrom et al. (1979, Table III). This input file is a variant of swmajp.inp, which uses Pitzer's equations. Here the input for pH (0.22) has been replaced by one for pHCl (0.6717), the value obtained as output from running swmajp.3i and using the thermodynamic data base of Harvie, Moller, and Woare (1984). The output of running the present input file should include a pH of 0.22.

Purpose: to test the pHCl-type (log activity combination) input option.

References
```

The EQ3NR input file (swphcl.3i), the pHCl test case ("W" format):

```
EQ3NR input file name = swphcl.3i
Description = "Sea water, using pHCl as input in place of pH"
Version number = 3245 Stage number = 01
Created 10/07/90 Creator = T.J. Wolery
Revised 10/07/90 Revisor = T.J. Wolery
```

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Sea water, including only the major ions. This is a considerably pared-down version of swtst.3i, which contains the full benchmark sea water test case of Nordstrom et al. (1979, Table III). This input file is a variant of swajp.inp, which uses Pitzer's equations. Here the input for pH (8.22) has been replaced by one for pHCl (8.6717), the value obtained as output from running swajp.3i and using the thermodynamic database of Harvie, Holler, and Keare (1984). The output of running the present input file should include a pH of 8.22.

Purpose: to test the pHCl-type (log activity combination) input option.

References

OH-HCO3-CO2-H2O system to high ionic strengths at 25 C:

Nordstrom, D. K., et al., 1979, A comparison of computerized chemical models for equilibrium calculations in aqueous systems, in Jenne,
E. A., editor, Chemical Modeling in Aqueous Systems, ACS Symposium Series, v. 93, American Chemical Society, Washington, D.C.,
p. 851-892.

---

Temperature (C) | 25.00
Total Dissolved Salts | mg/kg
Electrical Balancing On

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>BASIS SWITCH/CONSTRAINT</th>
<th>CONCENTRATION UNITS OR TYPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na+</td>
<td>0.5000</td>
<td>e-1</td>
</tr>
<tr>
<td>K+</td>
<td>1.0166</td>
<td>mg/kg</td>
</tr>
<tr>
<td>Ca++</td>
<td>399.10</td>
<td>mg/kg</td>
</tr>
<tr>
<td>Mg++</td>
<td>412.30</td>
<td>mg/kg</td>
</tr>
<tr>
<td>H+</td>
<td>1291.8</td>
<td>mg/kg</td>
</tr>
<tr>
<td>HCO3-</td>
<td>-8.6722</td>
<td>log activity combo</td>
</tr>
<tr>
<td>Cl-</td>
<td>0.2022E+02</td>
<td>molality</td>
</tr>
<tr>
<td>SO4-</td>
<td>19353.</td>
<td>mg/kg</td>
</tr>
</tbody>
</table>

Input Solid Solutions

none

SUPPRESSED SPECIES (suppress,replace,augment*,augmentg) value

none

OPTIONS

- SOLID SOLUTIONS
  * ignore solid solutions
  * process hypothetical solid solutions
  * process input and hypothetical solid solutions
- LOADING OF SPECIES INTO MEMORY
  * does nothing
  * lists species loaded into memory
- ECHO DATABASE INFORMATION
  * does nothing
  * lists all reactions
  * lists reactions and log K values
  * lists reactions, log K values and polynomial coeff.
- LIST OF AQUEOUS SPECIES (ordering)
  * in order of decreasing concentration
  * in same order as input file
- LIST OF AQUEOUS SPECIES (concentration limit)
  * all species
  * only species > 10**-20 molal
  * only species > 10**-12 molal
  * not printed
- LIST OF AQUEOUS SPECIES (by element)
  * print major species
  * print all species
  * don't print
- MINERAL SATURATION STATES
  * print all
  * print at salinity > 30 keals
  * don't print
- pH SCALE CONVENTION
  * modified NUN
  * internal
  * rational
- ACTIVITY COEFFICIENT OPTIONS
  * use N-U-T equation
  * Nernst equation
  * Pitzer's equations
- AUTO BASIS SWITCHING

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The EQ3NR output file (swphcl3o), the pHCl test case (beginning with the message announcing the end of Newton-Raphson iteration):

----- Summary of the Aqueous Phase ----- 

----- Elemental composition of the aqueous phase ----- 

<table>
<thead>
<tr>
<th>element</th>
<th>mg/l</th>
<th>mg/kg</th>
<th>moles/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>o</td>
<td>0.91080E+06</td>
<td>0.89001E+06</td>
<td>0.5562742040E+02</td>
</tr>
<tr>
<td>ca</td>
<td>421.93</td>
<td>412.30</td>
<td>0.1028743969E+01</td>
</tr>
<tr>
<td>cl</td>
<td>19805.00</td>
<td>19353.00</td>
<td>0.2558022600E+02</td>
</tr>
<tr>
<td>h</td>
<td>0.11451E+06</td>
<td>0.11190E+06</td>
<td>0.1110186597E+03</td>
</tr>
<tr>
<td>c</td>
<td>24.854</td>
<td>24.286</td>
<td>0.1022008000E-02</td>
</tr>
<tr>
<td>mg</td>
<td>132.20</td>
<td>129.10</td>
<td>0.1040760493E-01</td>
</tr>
<tr>
<td>na</td>
<td>11020.00</td>
<td>10768.00</td>
<td>0.5903922413E+00</td>
</tr>
<tr>
<td>s</td>
<td>926.41</td>
<td>905.26</td>
<td>0.2923129777E+01</td>
</tr>
</tbody>
</table>

----- Elemental composition as strict basis species ----- 

<table>
<thead>
<tr>
<th>species</th>
<th>mg/l</th>
<th>mg/kg</th>
<th>moles/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>h2o</td>
<td>0.10250E+07</td>
<td>0.10021E+07</td>
<td>0.5562742040E+02</td>
</tr>
<tr>
<td>ca++</td>
<td>421.93</td>
<td>412.30</td>
<td>0.1028743969E+01</td>
</tr>
<tr>
<td>cl-</td>
<td>19805.00</td>
<td>19353.00</td>
<td>0.2558022600E+02</td>
</tr>
<tr>
<td>h+</td>
<td>0.11451E+06</td>
<td>0.11190E+06</td>
<td>0.1110186597E+03</td>
</tr>
<tr>
<td>hco3-</td>
<td>126.26</td>
<td>123.30</td>
<td>0.2022008000E-02</td>
</tr>
</tbody>
</table>
--- equivalent composition of the aqueous phase (cte balances) ---

<table>
<thead>
<tr>
<th>species</th>
<th>moles/kg H2O</th>
<th>species</th>
<th>moles/kg H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O</td>
<td>0.5562742040E+02</td>
<td>H2O</td>
<td>0.5562742040E+02</td>
</tr>
<tr>
<td>Ca++</td>
<td>0.1028743949E+01</td>
<td>Ca++</td>
<td>0.1028743949E+01</td>
</tr>
<tr>
<td>Cl^-</td>
<td>0.5458226000E+00</td>
<td>Cl^-</td>
<td>0.5458226000E+00</td>
</tr>
<tr>
<td>H+</td>
<td>0.1110186924E+03</td>
<td>H+</td>
<td>0.1110186924E+03</td>
</tr>
<tr>
<td>HCO3^-</td>
<td>0.2022000000E+02</td>
<td>HCO3^-</td>
<td>0.2022000000E+02</td>
</tr>
<tr>
<td>Mg++</td>
<td>0.5149557700E+01</td>
<td>Mg++</td>
<td>0.5149557700E+01</td>
</tr>
<tr>
<td>Na+</td>
<td>0.4683022413E+00</td>
<td>Na+</td>
<td>0.4683022413E+00</td>
</tr>
<tr>
<td>SO4--</td>
<td>0.2823129677E+01</td>
<td>SO4--</td>
<td>0.2823129677E+01</td>
</tr>
</tbody>
</table>

single ion activities and activity coefficients are hereby defined with respect to the modified nbs ph scale

<table>
<thead>
<tr>
<th>ph</th>
<th>dn</th>
<th>dp</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.2508</td>
<td>0.5000</td>
<td>8.4522E+00</td>
</tr>
<tr>
<td>0.1132</td>
<td>0.5063</td>
<td>8.5590E+00</td>
</tr>
</tbody>
</table>

activity of water = 0.98198
log activity of water = -0.00790
true osmotic coefficient= 0.90273
stoichiometric osmotic coefficient= 0.90255
sum of true molalities= 1.11057944932
sum of stoichiometric molalities= 1.110573364436
true ionic strength= 0.6966434861048
stoichiometric ionic strength= 0.69664105473

----- electrical balance totals ----- |

equiv/kg
sigma(mz) cations = 0.6052455103E+00
sigma(mz) anions = -0.6052455103E+00
mean charge = 0.6052455103E+00
charge imbalance = 0.9083519534E-03

total charge = sigma(mz) cations + abs ( sigma(mz) anions )
mean charge = 1/2 total charge
the electrical imbalance is

0.751E-01 per cent of the total charge
0.150 per cent of the mean charge
0.150 per cent of abs ( sigma(mz) cations )
0.150 per cent of abs ( sigma(mz) anions )

----- activity ratios of ions ----- |

log (act(Ca++)) / act(H+)xx 2 = 13.7045
log (act(Cl^-)) x act(H+)xx 1 = -8.6722
log (act(HCO3^-)) / act(H+)xx 1 = -11.2062
log (act(Mg++)) / act(H+)xx 1 = 6.0593
log (act(Mg++)) / act(H+)xx 2 = 14.5358
log (act(Na+)) / act(H+)xx 1 = 7.7243
log (act(SO4--)) / act(H+)xx 2 = -19.0097
log (act(H2O)) / act(H+)xx 3 = -4.8609
log (act(H2O)) / act(H+)xx 2 = -21.5435
log (act(H2O)) / act(H+)xx 1 = -14.0046

----- distribution of aqueous species ----- |

<table>
<thead>
<tr>
<th>species</th>
<th>molal conc</th>
<th>log conc</th>
<th>log g</th>
<th>activity</th>
<th>log act</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl^-</td>
<td>0.5459E+00</td>
<td>-0.2629</td>
<td>0.1803</td>
<td>0.3530E+00</td>
<td>-0.4522</td>
</tr>
<tr>
<td>Na+</td>
<td>0.4683E+00</td>
<td>-0.3294</td>
<td>-0.1663</td>
<td>0.3194E+00</td>
<td>-0.4957</td>
</tr>
<tr>
<td>Mg++</td>
<td>0.5366E+01</td>
<td>-1.2752</td>
<td>-0.6251</td>
<td>0.1247E+01</td>
<td>-1.9043</td>
</tr>
<tr>
<td>SO4--</td>
<td>0.2833E+01</td>
<td>-1.5493</td>
<td>1.0204</td>
<td>0.2094E+02</td>
<td>-2.5659</td>
</tr>
</tbody>
</table>

-150-
--- major aqueous species contributing to mass balances ---

<table>
<thead>
<tr>
<th>Species</th>
<th>molal conc</th>
<th>per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>ca++</td>
<td>0.1026E-01</td>
<td>99.76</td>
</tr>
<tr>
<td>total</td>
<td>99.76</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Species</th>
<th>molal conc</th>
<th>per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>cl-</td>
<td>0.5459E+00</td>
<td>100.00</td>
</tr>
<tr>
<td>total</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Species</th>
<th>molal conc</th>
<th>per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>hco3-</td>
<td>0.1836E-02</td>
<td>2.20</td>
</tr>
<tr>
<td>co3-</td>
<td>0.3038E-02</td>
<td>0.60</td>
</tr>
<tr>
<td>mgco3(aq)</td>
<td>0.6292E-04</td>
<td>0.00</td>
</tr>
<tr>
<td>cac03(aq)</td>
<td>0.2456E-04</td>
<td>0.00</td>
</tr>
<tr>
<td>mgoh+</td>
<td>0.1224E-04</td>
<td>0.00</td>
</tr>
<tr>
<td>oh-</td>
<td>0.3038E-03</td>
<td>0.00</td>
</tr>
<tr>
<td>h+</td>
<td>0.7706E-08</td>
<td>0.00</td>
</tr>
<tr>
<td>hso4-</td>
<td>0.2332E-08</td>
<td>0.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Species</th>
<th>molal conc</th>
<th>per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>hco3-</td>
<td>0.1836E-02</td>
<td>6.56</td>
</tr>
<tr>
<td>co3-</td>
<td>0.1224E-04</td>
<td>0.00</td>
</tr>
<tr>
<td>mgco3(aq)</td>
<td>0.6292E-04</td>
<td>0.00</td>
</tr>
<tr>
<td>cac03(aq)</td>
<td>0.2456E-04</td>
<td>0.00</td>
</tr>
<tr>
<td>mgoh+</td>
<td>0.1224E-04</td>
<td>0.00</td>
</tr>
<tr>
<td>oh-</td>
<td>0.3038E-03</td>
<td>0.00</td>
</tr>
<tr>
<td>h+</td>
<td>0.7706E-08</td>
<td>0.00</td>
</tr>
<tr>
<td>hso4-</td>
<td>0.2332E-08</td>
<td>0.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Species</th>
<th>molal conc</th>
<th>per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg++</td>
<td>0.5306E-01</td>
<td>99.94</td>
</tr>
<tr>
<td>total</td>
<td>99.94</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Species</th>
<th>molal conc</th>
<th>per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>na+</td>
<td>0.4684E-00</td>
<td>100.00</td>
</tr>
<tr>
<td>total</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Species</th>
<th>molal conc</th>
<th>per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>so4--</td>
<td>0.2823E-01</td>
<td>100.00</td>
</tr>
<tr>
<td>total</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>

--- summary of aqueous redox reactions ---

couple  ch, volts  pe  log f02  ah, kcal

| default  | 0.500 | 0.8452E+01 | -16.432 | 11.531 |

--- summary of aqueous non-equilibrium non-redox reactions ---

couple  affinity, kcal
### Summary of Stoichiometric Mineral Saturation States

(minerals with affinities < -10 kcal are not listed)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>log q/k</th>
<th>aff, kcal</th>
<th>State</th>
<th>Mineral</th>
<th>log q/k</th>
<th>aff, kcal</th>
<th>State</th>
</tr>
</thead>
<tbody>
<tr>
<td>anhydrite</td>
<td>-0.063</td>
<td>-1.177</td>
<td>ssatd</td>
<td>aragonite</td>
<td>0.459</td>
<td>0.626</td>
<td>ssatd</td>
</tr>
<tr>
<td>arcanite</td>
<td>-5.175</td>
<td>-7.000</td>
<td>ssatd</td>
<td>bischofite</td>
<td>-7.321</td>
<td>-9.975</td>
<td>ssatd</td>
</tr>
<tr>
<td>bloedite</td>
<td>-5.720</td>
<td>-7.803</td>
<td>ssatd</td>
<td>brucite</td>
<td>-2.509</td>
<td>-3.532</td>
<td>ssatd</td>
</tr>
<tr>
<td>calcite</td>
<td>0.649</td>
<td>0.080</td>
<td>ssatd</td>
<td>dolomite</td>
<td>2.312</td>
<td>3.154</td>
<td>ssatd</td>
</tr>
<tr>
<td>epsomite</td>
<td>-1.640</td>
<td>-1.613</td>
<td>ssatd</td>
<td>gypsum</td>
<td>-4.476</td>
<td>6.107</td>
<td>ssatd</td>
</tr>
<tr>
<td>glauconite</td>
<td>-3.542</td>
<td>-4.032</td>
<td>ssatd</td>
<td>haloite</td>
<td>-0.660</td>
<td>-0.901</td>
<td>ssatd</td>
</tr>
<tr>
<td>halite</td>
<td>-0.518</td>
<td>-3.436</td>
<td>ssatd</td>
<td>kieserite</td>
<td>0.824</td>
<td>1.124</td>
<td>ssatd</td>
</tr>
<tr>
<td>kainite</td>
<td>-6.946</td>
<td>-9.479</td>
<td>ssatd</td>
<td>kieserite</td>
<td>-5.659</td>
<td>-7.947</td>
<td>ssatd</td>
</tr>
<tr>
<td>kieserite</td>
<td>-4.335</td>
<td>-5.547</td>
<td>ssatd</td>
<td>kieserite</td>
<td>-5.457</td>
<td>7.447</td>
<td>ssatd</td>
</tr>
<tr>
<td>nacaca(sio3)3:2h2o</td>
<td>-6.691</td>
<td>-9.128</td>
<td>ssatd</td>
<td>natron</td>
<td>3.079</td>
<td>4.200</td>
<td>ssatd</td>
</tr>
<tr>
<td>natron</td>
<td>-3.351</td>
<td>-7.360</td>
<td>ssatd</td>
<td>oxychloride-mg</td>
<td>-1.066</td>
<td>-2.346</td>
<td>ssatd</td>
</tr>
<tr>
<td>oxychloride-mg</td>
<td>-5.886</td>
<td>-7.757</td>
<td>ssatd</td>
<td>picromerite</td>
<td>-3.343</td>
<td>4.034</td>
<td>ssatd</td>
</tr>
<tr>
<td>plshydrate</td>
<td>-4.630</td>
<td>-6.317</td>
<td>ssatd</td>
<td>plshydrate</td>
<td>-3.274</td>
<td>4.466</td>
<td>ssatd</td>
</tr>
<tr>
<td>thermotrite</td>
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<td>-8.986</td>
<td>ssatd</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

0 approx. saturated pure minerals
0 approx. saturated end-members of specified solid solutions
0 saturated end-members of hypothetical solid solutions
4 supersaturated pure minerals
0 supersatd. end-members of specified solid solutions
0 supersatd. hypothetical solid solution phases

### Summary of Gases

<table>
<thead>
<tr>
<th>Gas</th>
<th>Fugacity log fugacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>co2(g)</td>
<td>0.3398</td>
</tr>
<tr>
<td>h2(g)</td>
<td>-3.3790</td>
</tr>
<tr>
<td>o2(g)</td>
<td>0.41375</td>
</tr>
</tbody>
</table>

### End of Output

--- pickup file has been successfully written ---

--- reading the input file ---

--- End of Output ---

--- no further input found ---

**Start time** = 11:11  17Dec91
**End time** = 11:12  17Dec91
**User time** = 1.380
**Cpu time** = 1.380
**Normal exit**

--- End of Output ---

--- no further input found ---

**Start time** = 11:11  17Dec91
**End time** = 11:12  17Dec91
**User time** = 1.380
**Cpu time** = 1.380
**Normal exit**

--- End of Output ---

--- no further input found ---
8. The EQ3NR to EQ6 Connection: The Pickup File

EQ3NR creates a model of an aqueous solution. The EQ6 code may then be used to calculate models of geochemical processes in which this solution is an initial component. The two codes are constructed so that the initial model constraints on the aqueous solution are input only to EQ3NR. The user does not repeat this information in the user-created portion of the EQ6 input file. Instead, EQ3NR writes the necessary data on a small file called pickup.

EQ6 normally reads the information from the EQ3NR pickup file as the bottom part of the EQ6 input file. It can also read it directly under an option that can be specified on the EQ6 input file. The contents of the EQ3NR pickup file will be discussed in more detail in the EQ6 Theoretical Manual and User’s Guide (Wolery and Daveler, 1992b). EQ3NR automatically writes a pickup file unless the user specifies otherwise (by setting iopt3 = -1).

The example given in this chapter is the pickup file written for the sea water example presented in Chapter 7. This is given in both “W” and “D” formats; the code writes the pickup file in the format corresponding to the input file used. Discussion here will focus primarily on the example in “W” format.

The following discussion assumes that the reader is familiar with the parameters that appear on the EQ3NR input file (Chapter 6). The pickup file begins with a repetition of the original title (util1). This is useful because it carries any documentation identifying the particular aqueous solution model.

The following line contains the temperature (°C) of the EQ3NR run, which is specified in the variable tempci. The EQ6 run that uses this input may actually start at a different temperature. If so, there is said to be a temperature jump. The tempci input allows EQ6 to recognize when this is the case and to issue a warning to the user.

The alter/suppress options follow in the same format as on the EQ3NR input file. In this example, no such options are specified, hence nxmod = 0. If any had been specified, two lines would have followed for each option, one for the uxmod parameter and another for the jxmod, kxmod, and xlkmod parameters.

The next five inputs (kct, kmt, kxt, kdim, and kprs) are key parameters in the scheme by which EQ6 organizes important variables. Here kct is the number of chemical elements in the system. The variable kdim is the number of total master species, which in EQ6 includes not only the aqueous master species discussed in this report, but also any mineral species in equilibrium with the aqueous solution. The variables kmt and kxt mark, respectively, the last pure mineral and last solid-solution end-member that are in the master species set. These species must have corresponding masses present in the geochemical model. This is never the case in EQ3NR, and consequently no such species can appear among the master species written on an EQ3NR pickup file. This condition is marked by kmt and kxt having values equal to that of kdim. The variable kprs is the number of pure mineral and solid-solution end-member species in the “physically removed system,” a concept relating only to the flow-through open system model in EQ6. Hence, kprs must always be zero on the EQ3NR pickup file.
Following the parameters discussed above are the symbols of the kct chemical elements in the system and their masses in moles relative to one kilogram of solvent (mte). The calculated electrical imbalance (electr) is given in the same format.

The last part of the EQ3NR pickup file gives the names of the “run” master iteration variables (the “run” basis species), the corresponding “data file” basis species, and the values of the corresponding variables. These are the base ten logarithms of the molal concentrations of the “run” basis species. If a “run” basis species is not the same as the corresponding “data file” master species, it marks the pair of species for a basis switch.

Example of an EQ3NR pickup file in “W” format:

```
* pickup file written by eq3nr.3245R124x
* supported by eqlib.324SR153
EQ3NR input file name=swmaj.3i
Description= "Sea water, major ions only"
Version number= 3245 Stage number= 01
Created 06/08/90 Creator= T.J. Wolery
Revised 06/08/90 Revisor= T.J. Wolery

Sea water, including only the major ions. This is a considerably pared-down version of swat.3i, which contains the full benchmark sea water test case of Nordstrom et al. (1979, Table III).

Purpose: to test the code on a small problem involving a moderately concentrated solution. The activity coefficients of the aqueous species are calculated from the η-dot equation and related equations.

References
```

```
iopgl= 0 iopg2= 0 iopgl= 0
iopg7= 0 iopg9= 0
iopgl0= 0

kef 9 ksq= 10
kxf 10 kdira= 10

ca 0.1874395785819E+00
cl 0.54588226055639E-01
h 0.11101873344624E+03
k 0.10207604947242E-01
mg 0.53149553490461E-01
na 0.48838224218575E+00
s 0.28231297915883E-01
electr 0.95407965800320E-03
```

```
Ca++ 0.17443589835269E+01
Cl- -0.20330152386677E+01
H+ -0.28924363492939E+01
HCO3- -0.20008825704104E+01
K+ -0.13901735132372E+01
Na+ -0.35176277088127E+00
SO4- -0.16788094095832E+01
```

```
C2(g) -0.18788099409583E+01
```
Example of an EQ3NR pickup file in “D” format:

- 155 -
9. Solving the Governing Equations

9.1. Introduction

The governing equations that apply to speciation-solubility modeling were introduced in Chapters 2, 3, and 4. The purpose of this chapter is to derive the mathematics necessary to solve them. The approach is to set up the problem in terms of \( n \) equations in \( n \) unknowns (or "iteration variables") and solve them. Technically, there are a large number of equations and corresponding unknowns to deal with. The unknowns include the concentrations of all the species appearing in the model and their thermodynamic activity coefficients. The corresponding equations are algebraic, and these must be solved using appropriate methods.

In EQ3NR, the set of unknowns is first reduced to a relatively small set of unknowns, from which the remaining unknowns can be calculated. These are the primary iteration variables. They are defined in this code as the log concentrations of the species in the active basis set. The algebraic equations are solved by a combination of two iterative methods which are applied in sequence. The first method, called pre-Newton-Raphson optimization, has the characteristic of rapid convergence far from the solution, and slow (limiting first order) convergence near the solution. It is used primarily to get all of the primary iteration variables within an order of magnitude of the solution. The second method, a hybrid Newton-Raphson method, has the characteristic of poor convergence behavior far from the solution, and very fast (limiting second order) convergence near the solution. These methods thus complement one another. We will discuss these, as well as supplementary methods designed to aid convergence. Lastly, we will briefly discuss the subject of crash diagnostics.

9.2. The Set of Master Iteration Variables

In the EQ3NR code, the number of equations and unknowns is reduced by substituting all governing aqueous mass action equations into the mass balance and electrical balance equations. The remaining aqueous species giving rise to unknowns then comprise the relatively small active basis set. These master iteration variables reside in the vector \( z \), which has the following structure:

\[
z = \begin{bmatrix}
\log x_w \\
\vdots \\
\log m_{s', s = 1, s_B - 1, s \neq w} \\
\vdots \\
\log f_{O_2} \\
\vdots \\
\log m_{s', s = s_B + 1, s_Q}
\end{bmatrix}
\]  

(227)
The first part of this vector contains entries for the $s_B$ strict basis species appearing in a given problem. The second part contains any auxiliary basis variables which appear in the problem and for which $jflag \neq 30$ (those with $jflag = 30$ are treated as non-basis species). The structure is further simplified if $s_Q = s_B$ (no active auxiliary basis set). For a problem in which this is the case, it is implied that the aqueous solution is in a state of complete internal (homogeneous) equilibrium. If $s_Q = s_B + 1$, complete internal equilibrium is also implied if the $s_Q$-th species is part of a redox couple used to define the redox state of the fluid (the $iopt1 = 1$ option). In all other cases, partial internal disequilibrium is implied.

We will first look at the aqueous mass action equations that are to be eliminated. Here $s''$ denotes a non-basis species and $r$ denotes the corresponding reaction. As index labels, these are related according to:

$$ r = s'' - s_B $$

(228)

This reflects the fact that strict basis species appear first in the list of all aqueous species and that they have no associated reactions. A mass action equations takes the following logarithmic form:

$$ logK_r = b_{w_r} (log x_w + log \lambda_w) + b_{s_B} log f_o + b_{s''_r} (log m_{s''} + log \gamma_{s''}) $$

$$ + \sum_{s' = 1}^{s_Q} b_{s'_r} (log m_{s'} + log \gamma_{s'}) $$

(229)

where $K_r$ is the thermodynamic equilibrium constant for the reaction, $b_{s_r}$ is the reaction coefficient for the $s$-th species, $\lambda_w$ is the activity coefficient of water, and $\gamma_s (s \neq w)$ is the molal activity coefficient of the $s$-th species. Note that $s'$ implies a basis species, and that $s''$ denotes the only non-basis species appearing in the reaction. This equation can be rearranged to give:

$$ log m_{s''} = \frac{log K_r}{b_{s''_r}} - log \gamma_{s''} - \frac{b_{w_r}}{b_{s''_r}} (log x_w + log \lambda_w) - \frac{b_{s_B}}{b_{s''_r}} log f_o $$

$$ - \sum_{s' = 1}^{s_Q} \frac{b_{s'_r}}{b_{s''_r}} (log m_{s'} + log \gamma_{s'}) $$

(230)

Recall the relation:

$$ \frac{dx}{d \log x} = 2.303x $$

(231)

It follows that:
\[ \frac{dm_{s^n}}{dx} = 2.303 m_{s^n} \frac{d\log m_{s^n}}{dx} \]  
(232)

Treating the activity coefficients as constants, this can be used to show that:

\[ \frac{\partial m_{s^n}}{\partial \log x_w} = -2.303 m_{s^n} \frac{b_{s^n r}}{b_{s^n r}} \]  
(233)

\[ \frac{\partial m_{s^n}}{\partial \log \rho_{O_2}} = -2.303 m_{s^n} \frac{b_{s^n r}}{b_{s^n r}} \]  
(234)

\[ \frac{\partial m_{s^n}}{\partial \log z_{s'}} = -2.303 m_{s^n} \frac{b_{s^n r}}{b_{s^n r}}, \quad s' = 1, s_Q, \quad s' \neq w, \quad s_B \]  
(235)

These relations will be used later in this chapter in deriving the Jacobian matrix elements corresponding to the mass and charge balance residual functions. This matrix is used in Newton-Raphson iteration.

Certain factors will appear repeatedly in some of the derivations below and will be given special symbols. In the EQ3NR code, these parameters are themselves evaluated before the calculation of the Jacobian matrix elements in which they appear. This is done to avoid repetitive arithmetic in the code. These are defined as follows:

\[ H_{s'r} = \frac{m_{s^n} z_{s^n}}{b_{s^n r}}, \quad s' = 1, s_Q, \quad s' \neq w \]  
(236)

\[ H_{z'r} = \frac{m_{s^n} z_{s^n}}{b_{s^n r}} \]  
(237)

All of the so-called alternative constraints involve equations which are written only in terms of the concentrations (or activities) of species in the active basis set. Therefore, it is not necessary to make any substitutions of the sort noted above in dealing with the mass balance equations and the charge balance equation.

9.3. Expanding the System from the Set of Master Iteration Variables

If one knows the vector \( z \), one may "expand the system" by computing the concentrations of all non-basis species (all species not in the active basis set; this includes any auxiliary basis species with \texttt{jflag} values of 30) and the activity coefficients of all species in solution. The \( z \) vector uniquely defines all system properties. However, the process of expanding the system is not exactly straightforward. In order to calculate the concentrations of the non-basis species, one must evaluate the corresponding mass action equations. The activity coefficients appear in these equations. Hence, the activity coefficients must be evaluated first. However, the activity coefficients depend in general on the concentrations of all solute species, both basis and non-basis. So to deal with these, one must compute the concentrations of the non-basis species first.
This creates a problem analogous to the old puzzle, "Which came first, the chicken or the egg?" In previous versions of EQ3/6 (e.g., Wolery, 1983), this problem was overcome by treating the ionic strength as a master iteration variable. The equation defining the ionic strength has the same form as a mass balance equation, and this equation was treated in like form. However, this only works if the activity coefficient model depends only on the ionic strength, not the specific composition of the solution. Thus, this approach works for the Davies equation and the B-dot equation, but not for Pitzer's equations or any other set of equations likely to be valid in concentrated solutions.

The concentrations of non-basis species may vary over many orders of magnitude. The activity coefficients of aqueous species generally vary over about two orders of magnitude or less. The approach taken in EQ3/6 is to start by computing a set of reasonable values for the activity coefficients, then hold these constant until the concentrations of the non-basis species become reasonably stable. The activity coefficients are then updated. In the pre-Newton-Raphson optimization algorithm, the computed concentrations of the basis and non-basis species are typically adjusted 3-7 times before the activity coefficients are recalculated. In the hybrid Newton-Raphson method, they are recalculated between each Newton-Raphson step (it is because of this treatment that we refer to our usage of the Newton-Raphson method as a hybrid). In either case, the system is expanded by first calculating the new concentrations of the non-basis species, using the existing values of the activity coefficients. The activity coefficients are then recalculated. An exception to this order occurs when starting values are constructed (see below).

One could view the expansion itself as an iterative process. One could recalculate the concentrations of the non-basis species, recalculate the activity coefficients, and then repeat the process one or more times. In the context of the pre-Newton-Raphson optimization method, this makes little sense because this method is only used to get in the neighborhood of the solution. The merits of a single update, a double update, and a multiple update (repeating the process until a convergence tolerance is satisfied) were examined in the context of the hybrid Newton-Raphson method. Significant differences in performance were only observed in the case of highly concentrated electrolyte solutions. Thus, in the case of less concentrated solutions, the single update method was best because it gave the same performance for the lowest cost. In the case of the more concentrated solutions, it was found that the single update also gave the best performance, followed by the multiple update method. In such solutions, the double update method often led to failure to converge. The method which has been adopted, therefore, is the single update method.

9.4. Beginning the Process: Computing Starting Values

The whole process must begin by assigning starting values. This is done in module arrset.f. Initially, this is done as follows. For every basis species with a jflag value of less than 15, either the total or free molality is known. The concentration of each such individual basis species is assigned this corresponding value. This value is an upper bound if the corresponding concentration is the total molality, and the actual value if it is a free molality. For species having a jflag value of 16, the log activity is known. The concentration of each such species is assigned a value equal to the thermodynamic activity, thus assuming that the activity coefficient has unit value. All other basis species are initially assigned a value of $1 \times 10^{-7}$ molal. All non-basis species at this point have assigned concentrations of zero.
The charge imbalance is computed. The functions $\Sigma m$ and the ionic strength are then estimated. The estimate of the ionic strength at this point includes a term in which the computed charge imbalance is treated as though it were due to an unmeasured monovalent ion. The mole fraction of water is computed from the value of $\Sigma m$. Then the activity coefficients are computed. The concentrations of non-basis species are taken as zero until the code enters the pre-Newton-Raphson optimization stage.

Assuming that the concentration of a basis species is equal to its total concentration may or may not be a good approximation. If it turns out to be a very poor approximation, then the first estimate of the concentration of at least one non-basis species will have to be large, typically a few to a few tens of orders of magnitude greater than the limit on its actual concentration imposed by the corresponding mass balance constraint. This first estimate is very often quite large in an absolute as well as a relative sense, often on the order of $10^{-10}$ to $10^{-60}$ molal. It is critical not to compute functions such $\Sigma m$, the ionic strength, and the activity coefficients until the concentrations for such species have been brought down to physically realistic values.

9.5. Methods to Aid Convergence

Several techniques are used in EQ3NR to aid convergence, both in pre-Newton-Raphson optimization and hybrid Newton-Raphson iteration. These are:

- Use of logarithmic iteration variables.
- Under-relaxation techniques.
- Automatic and user-specified basis switching.

We have not found it necessary to employ other methods, such as the “curve-crawler” technique discussed by Crerar (1975).

The physical quantities that correspond to the iteration variables are intrinsically positive. Use of logarithmic iteration variables restricts the generated values to the physically reasonable range. Also, logarithmic corrections are effectively relative corrections to the corresponding physical quantities. Recall that $d \log x/dx = 1/(2.303 x)$. It follows that:

$$\Delta \log x \approx \frac{\Delta x}{2.303 x}$$

(238)

Because of this, effective under-relaxation techniques are especially easy to implement when using logarithmic iteration variables.

Under-relaxation is the technique of judiciously reducing the magnitude of the computed correction terms. Assume that the unmodified method involves adding a correction term vector ($\delta_k$), where $k$ is the iteration number. This is typical in Newton-Raphson iteration. The new vector of master iteration variables is obtained thusly:

$$z_{k+1} = z_k + \delta_k$$

(239)
If the new vector of master iteration variables is obtained instead by evaluating some set of corresponding equations not in this format, one can still utilize under-relaxation by defining a correction term vector as follows:

$$\delta_k = z_{k+1} - z_k \quad (240)$$

Global under-relaxation is effected by replacing the correction equation given above by:

$$z_{i+1} = z_i + \kappa \delta_i \quad (241)$$

where $\kappa$ is a positive number less than one. Non-global under-relaxation is also possible. This does not involve the use of an under-relaxation factor. Rather it involves truncating the magnitudes of individual correction terms to satisfy specified limits, which may be different depending on the species involved and on the direction of change.

There are several methods of applying global under-relaxation. EQ3NR uses two relatively simple ones in making Newton-Raphson steps. The first of these places a limit on the element of the correction term vector having the largest magnitude:

$$\kappa = \frac{\delta'}{\delta_{max}} \quad (242)$$

where $\delta'$ is the imposed limit and $\delta_{max}$ is the max norm of $\delta$. In a Newton-Raphson iteration step (which occurs in the EQLIB module nrstep.f), this imposed limit is represented by the variable screwd. In EQ3NR, this is set in the main program (module eq3nr.f) at a value of 2.0. Besides aiding convergence, this method causes divergence, when it does occur, to occur more slowly. In such cases, it helps to yield useful information about the cause of divergence.

The other global under-relaxation method is applied for only the first 8 iterations. The under-relaxation factor is cut in half if the residual vector max norm $\beta_{max}$ exceeds the value of the variable screwn. Initially, $\kappa$ is set to a value of unity; when the current method of under-relaxation is applied, this factor may have been reduced as a result of applying the method described above. In EQ3NR, screwn is set to 0.5 in the main program (module eq3nr.f).

Some degree of non-global under-relaxation is also employed in pre-Newton-Raphson optimization. This optimization function takes place in EQ3NR in module arrset.f. Here under-relaxation is effected by imposing truncation limits on changes for individual master variables. The master variables for species constrained by mass balance equations are not permitted to decrease by more than 20.0 log units in a given step. A master variable constrained by the charge balance equation may not change by more than 2.0 log units.

Some truncation limits also apply to the activity coefficients and the functions $\Sigma m$ and the ionic strength. These limits are applied during both pre-Newton-Raphson optimization and hybrid Newton-Raphson iteration. These limits are defined in the variable chgfac, which is in the calling sequence of the EQLIB module ngadv.f. The value of this variable is set in the calling modules, and is usually scaled inversely with the value of $\Sigma m$. Values range from 1.3 to 100.
If automatic basis switching is turned on (iopt2 = 1), EQ3NR (in the module arrset.f) will attempt to improve the starting values by means of basis switching. The methodology here is quite simple. Consider the case of dissolved aluminum. The data file basis species is Al$^{3+}$. At low temperature, typically low values of dissolved aluminum, and moderate to high pH, the mass balance is typically very strongly dominated by the species Al(OH)$_4^{-}$. The concentration of Al$^{3+}$ is many orders of magnitude below the concentration of this species. If one assumes that the concentration of this species is instead essentially equal to the total concentration, the computed concentration of Al(OH)$_4^{-}$ may be something on the order of 10$^{-20}$-10$^{-40}$ molal. The value of the corresponding residual function will be similarly extremely large. On the other hand, when Al(OH)$_4^{-}$ is in the basis set, the initial assumption is that its concentration is equal to the total concentration, and the computed concentration of Al$^{3+}$ is an appropriately much smaller number.

In the present version of EQ3NR, the total concentration quantity associated with a mass balance is redefined in terms of the new basis species. Assuming this quantity is expressed as molality, this change has no numerical significance in the above example. However, if a species to be switched into the basis set contributes to the original total concentration by a factor different from that of the original basis species, the difference is quite significant. For example, if Al$_{13}$O$_4$(OH)$_{24}^{7+}$ is switched into the basis set in place of Al$^{3+}$, then the associated total concentration must be redefined as:

$$m_{T,Al_{13}O_4(OH)_{24}^{7+}} = \frac{m_{T,Al^{3+}}}{13}\quad(243)$$

Automatic basis switching is accomplished in a loop structure. More than one switch may be done each time through the loop. After this, the activity coefficients are recomputed (again assuming that the concentrations of non-basis species are zero), the residual functions are recomputed and more switches may be made. In the process, some switches may be undone by later ones. For example, Al$_{13}$O$_4$(OH)$_{24}^{7+}$ may first be switched into the basis set in place of Al$^{3+}$, and then Al(OH)$_4^{-}$ in place of, Al$_{13}$O$_4$(OH)$_{24}^{7+}$. When one switch replaces another, the original switch is first undone. In this example, Al$^{3+}$ is switched back into the basis set in place of Al$_{13}$O$_4$(OH)$_{24}^{7+}$; Al(OH)$_4^{-}$ is then switched into the basis set in place of Al$^{3+}$. This loop continues until there are no candidates for basis switching or the loop has been passed through nlopmx times. This variable is currently set to 12 in a data statement in arrset.f.

To be a candidate for automatic basis switching, a species must have a computed concentration ten times that of the corresponding basis species. Furthermore, it cannot already be in the basis set. A data file basis species which has been switched out of the basis set can only be brought back into the basis set by undoing an earlier switch. The involvement of a basis species in the input constraint associated with another basis species may prevent switching it out of the basis set. For example, if the input constraint for H$^+$ is a value for the pHCl function, then Cl$^-$ is locked into the basis set. Conflicts may arise in candidate basis switches. For example, the same species
could dominate more than one mass balance. It is then switched into the basis so as to reduce the affected mass balance residual which has the highest value.

The user may specify certain basis switches on the input file (see Chapter 5). These switches are executed prior to entry to module arrset.f and the construction of the initial starting estimates. If certain switches really need to be made, it is more efficient to make them in this manner. If the software is run on a machine with a small floating point exponent range, such as a VAX system lacking the G_FLOATTING option, the code may stop execution because of a floating point overflow (in the computation of one of the elements of the residual function vector \( \beta \)) unless such switches are directed on the input file. In such a situation, one may have to guess which switches are necessary to avoid such overflow.

If automatic basis switching is turned off (\( \text{iopt2} = 0 \)), the code will proceed directly from having made the initial starting estimates into pre-Newton-Raphson optimization. If it is turned on and the user has directed certain switches to be made on the input file, it may undo one or more of those switches, as well as make additional switches.

### 9.6. The Pre-Newton-Raphson Optimization Algorithm

After any automatic basis switching is completed, arrset.f uses an optimization algorithm. This process occurs in a loop structure, the times through which are known as passes. At the end of a pass, the activity coefficients are recomputed. If the concentration of an ion is to be adjusted to satisfy electrical balance, this adjustment is also recomputed at this point. Within each pass is another loop structure, the times through which are called cycles. Here, adjustments are made to the concentrations of the basis species (other than one which is constrained to satisfy electrical balance). A pass is completed after some number of cycles. The cycles within a pass terminate if some rather rough convergence criteria are satisfied, or if the maximum number of cycles in a pass have been completed. This is determined by the variable \( \text{ncl ylim} \), which is currently set to 15 in a data statement in arrset.f. The passes terminate if rough convergence criteria applying to both the cycles and passes are satisfied, or if the maximum number of passes has been completed. This is determined by the variable \( \text{npllim} \), which is currently set to 7 in a data statement in arrset.f.

The cycle algorithm is applied only to basis species which are constrained by mass balances. It is an example of what is sometimes called a "continued fraction" method. A variation on this approach (Wolery and Walters, 1975) was in fact the principal method used to solve speciation-solubility problems in an early version of what is now EQ3NR. The derivation to be given here is different than that previously given elsewhere, and includes an important modification that has apparently not been previously noted.

Consider the case of dissolved aluminum. The total dissolved aluminum is expressed as total \( Al^{3+} \). The normalized mass balance residual is:

\[
\beta_{Al^{3+}} = \frac{m_{T, calc, Al^{3+}} - m_{T, Al^{3+}}}{m_{T, Al^{3+}}} \tag{244}
\]
where: $m_{T,\text{calc},Al^{3+}}$ is the total concentration of $Al^{3+}$ as calculated from a mass balance expression, using the current estimated values of the concentrations of the basis species and estimates of the concentrations of non-basis species as calculated from the associated mass action equations, using in these the current estimated values of the concentrations of the basis species. In contrast, $m_{T,Al^{3+}}$ is one of the model constraints.

We will assume, for the moment, that $Al^{3+}$ dominates this calculated mass balance. We may express this by writing:

$$m_{Al^{3+}} \approx m_{T,\text{calc},Al^{3+}} \quad (245)$$

We may then write:

$$\beta_{Al^{3+}} = \frac{m_{Al^{3+}} - m_{T,Al^{3+}}}{m_{T,Al^{3+}}} \quad (246)$$

We can rearrange this to:

$$\frac{m_{Al^{3+}}}{\beta_{Al^{3+}} + 1} = m_{T,Al^{3+}} \quad (247)$$

We take the current iteration in the cycle to be the $k$-th. Applying the above equation to this iteration, we may write:

$$\frac{m_{Al^{3+},k}}{\beta_{Al^{3+},k} + 1} \approx m_{T,Al^{3+}} \quad (248)$$

Similar, applying it to the next iteration (the $k+1$-th) gives:

$$\frac{m_{Al^{3+},k+1}}{\beta_{Al^{3+},k+1} + 1} \approx m_{T,Al^{3+}} \quad (249)$$

Combining these equations then gives:

$$m_{Al^{3+},k+1} \approx \frac{m_{Al^{3+},k} \left(\beta_{Al^{3+},k+1} + 1\right)}{\beta_{Al^{3+},k} + 1} \quad (250)$$

We would like the residual function to approach zero quickly. This desire can be written as:
Substitution of this into the above equation gives the following the iteration equation:

\[ m_{Al^{3+}, k+1} = \frac{m_{Al^{3+}, k}}{\beta_{Al^{3+}, k+1}} \]  

(252)

In a dilute, acid solution, the species \( Al^{3+} \) will indeed dominate its own mass balance. The starting assumption based on this should be a good one. Also, this species should dominate the calculated mass balances during the iteration process. We would expect the above iteration equation to work well. However, in solutions of moderate to high pH, the species \( Al(OH)_4^- \) dominates the mass balance of \( Al^{3+} \). What happens then? Note that we could do a basis switch, replacing \( Al^{3+} \) with \( Al(OH)_4^- \). The above equations would then apply to \( Al(OH)_4^- \) and all should again work well.

If we do not make this basis switch, we would still assume \( Al(OH)_4^- \) dominates the calculated mass balances. Following the previous approach, we are led to an equation of the form:

\[ m_{Al(OH)_4^-, k+1} = \frac{m_{Al(OH)_4^-, k}}{\beta_{Al^{3+}, k+1}} \]  

(253)

This is almost what we would have if we had made the basis switch. However, in this case, the normalized residual is still defined in terms of \( Al^{3+} \), not \( Al(OH)_4^- \). However, we can not directly use this equation, because it is written in terms of molalities of \( Al(OH)_4^- \), not \( Al^{3+} \). However, we can convert it into a form in terms of molalities of \( Al^{3+} \). The two species are related by the reaction:

\[ Al(OH)_4^- + 4H^+ = Al^{3+} + 4H_2O \]  

(254)

The corresponding mass action equation is:

\[ K_{Al(OH)_4^-} = \frac{m_{Al^{3+}, \gamma_{Al^{3+}, w}^4 \lambda_{w}^4}}{m_{Al(OH)_4^-} \gamma_{Al(OH)_4^-} m_{H^+}^4 \gamma_{H^+}^4} \]  

(755)

Let us consider all activity coefficients to be fixed, as well as the concentrations of other basis species appearing in this relation. Then the concentrations of the two aluminum species of interest satisfy the following proportionality:

\[ m_{Al^{3+}} \propto m_{Al(OH)_4^-} \]  

(256)
Presuming that the proportionality constant does not change significantly allows us to use this relation to obtain the same iteration equation that we had before:

\[ m_{Al^{3+}, k + 1} = \frac{m_{Al^{3+}, k}}{\beta_{Al^{3+}, k} + 1} \]  

The only significant difference in the iteration process in this case (versus either that in which \( Al^{3+} \) is dominant or that in which \( Al(OH)^{4-} \) is dominant but switched into the basis set) is that the starting estimate is not so good. In fact, it might be very bad, off by many orders of magnitude. However, it turns out that this algorithm is very good for quickly getting to about the right order of magnitude, even if the starting estimate is off (high) by several tens of orders of magnitude. On the other hand, it is not so efficient in a close neighborhood of the solution. This makes it a good complement to Newton-Raphson iteration, which is very efficient near the solution, but which often fails to converge at all if the starting estimates are far from the solution.

Now suppose the complex \( Al_{13}O_4(OH)_{24}^{7+} \) dominates the calculated mass balance of \( Al^{3+} \). Again, we do not make a basis switch. This then leads us to a result of the form:

\[ m_{Al_{13}O_4(OH)_{24}^{7+}, k + 1} = \frac{13 m_{Al_{13}O_4(OH)_{24}^{7+}, k}}{\beta_{Al^{3+}, k} + 1} \]  

The species \( Al_{13}O_4(OH)_{24}^{7+} \) and \( Al^{3+} \) are related by the reaction:

\[ Al_{13}O_4(OH)_{24}^{7+} + 32H^+ = 13Al^{3+} + 28H_2O(l) \]  

The corresponding mass action equation is:

\[ K_{Al_{13}O_4(OH)_{24}^{7+}} = \frac{m_{Al_{13}O_4(OH)_{24}^{7+}}^{13} m_{Al_{13}O_4(OH)_{24}^{7+}}^{32}}{m_{Al_{13}O_4(OH)_{24}^{7+}}^{28} m_{Al_{13}O_4(OH)_{24}^{7+}}^{28}} \]  

Using the same assumptions as before leads to the following proportionality:

\[ m_{Al^{3+}}^{13} \propto m_{Al_{13}O_4(OH)_{24}^{7+}} \]  

Using this as before leads to the following iteration equation:

\[ m_{Al^{3+}, k + 1} = \frac{1}{13} \frac{m_{Al^{3+}, k}}{(\beta_{Al^{3+}, k} + 1)^{13}} \]
This differs from the previous results in two ways. First, an exponent now appears on the \((p + 1)\) term. This exponent is the factor expressing the stoichiometric equivalence of the basis species corresponding to a mass balance expression to the species which dominates the calculated mass balance. Also, a factor appears in the numerator on the right hand side which is the inverse of the same exponent with a matching exponent. This is the general case. These "new" elements of the equation did not explicitly appear in the previous results because the stoichiometric equivalence happened to be unity.

The exponent on the \((p + 1)\) term is critical to the success of this method. This is because it has a large effect on the exponent of the resultant calculated concentration of the basis species. When one starts the iteration process, the value of \(p\) may initially be something like \(10^{+60}\). Use of the iteration equation ignoring this exponent would result in the calculated concentration of the basis species being lowered by 60 orders of magnitude. The effect of the exponent on the \((p + 1)\) is to cause it to be lowered only about 4.6 orders of magnitude. The effect of ignoring this exponent on the remainder of the calculation would be wild oscillation.

The effect of the factor in the numerator is less extreme. It does not affect the resulting order of magnitude. For example, \(3^1 = 1\), \(2^2 = 1.41\), \(3^3 = 1.44\), \(4^1 = 1.41\), and \(5^5 = 1.38\). In the case shown above, \(13^{13} = 1.22\). The absence of this factor doesn't have much effect if all one is trying to do is get within an order of magnitude of the solution before switching to another algorithm. However, it would cause convergence to fail in a close neighborhood of the solution if one attempted to use this algorithm to obtain a final solution.

Not all basis species are constrained by mass balance relations. If a species is constrained by a value for its log activity, the concentration is simply estimated from this value using the current value for the corresponding activity coefficient:

\[
log m_{i,k+1} = log a_i - log \gamma_i
\]

The concentration of such a species can not change during a pass, because activity coefficients are only recalculated as the end of a pass.

A basis species whose concentration is to be adjusted to satisfy electrical balance has its concentration recalculated in a cycle after the concentrations of all other basis species have been recalculated. This will be discussed below.

The concentrations of basis species which are constrained by any other types of constraints are calculated simultaneously by solving a matrix equation. This is the case for \(O_{2(g)}\) when an \(Eh\) or \(pe\) value is input, for cases in which heterogeneous or homogeneous equilibria must be satisfied, and cases in which a combination activity function such as \(pHCl\) is utilized. It is not always strictly necessary to make these calculations simultaneously, but it is more convenient to always do it this way than to deal otherwise with those cases which would allow complete or partial solution by a sequence of individual calculations (whose order would have to be determined in each individual case).
For example, suppose dissolved calcium is constrained to satisfy equilibrium with calcite and bicarbonate is constrained to satisfy a specified fugacity of carbon dioxide. We will assume that chloride is constrained by a total concentration and that the hydrogen is constrained by an input value of pH. The respective relevant governing equations for $Ca^{2+}$ and $H^+$ are:

$$\log K_{calcite} = \log m_{Ca^{2+}} + \log \gamma_{Ca^{2+}} + \log m_{HCO_3^-} + \log \gamma_{HCO_3^-} - \log m_{H^+} - \log \gamma_{H^+}$$

(264)

$$\log K_{CO_2(g)} = \log m_{HCO_3^-} + \log \gamma_{HCO_3^-} + \log m_{H^+} + \log \gamma_{H^+} - \log f_{CO_2} - \log x_w - \log \lambda_w$$

(265)

These may be rearranged to give:

$$\log m_{Ca^{2+}} + \log m_{HCO_3^-} = \log K_{calcite} - \log \gamma_{Ca^{2+}} - \log \gamma_{HCO_3^-} + \log m_{H^+} + \log \gamma_{H^+}$$

(266)

$$\log m_{HCO_3^-} - \log x_w = \log K_{CO_2(g)} - \log \gamma_{HCO_3^-} - \log m_{H^+} - \log \gamma_{H^+} + \log f_{CO_2} + \log \lambda_w$$

(267)

where the variables treated as the unknowns are on the left hand sides. As all these concentration values pertain to the $k + 1$-th iteration, they could be so marked in the rearranged equations (but we leave them out for clarity). The mole fraction of water may also be adjusted as part of the process, using the approximate relation:

$$\log x_{w, k+1} = \log x_{w, k} + \sum_{s' \in S} \frac{\partial \log x_{w}}{\partial \log m_{s'}} (\log m_{s'}, k + 1 - \log m_{s'}, k)$$

(268)

where $S$ is the set of solute basis species whose concentrations must be solved for in this manner. This is a Taylor’s series truncated to first order. For notational convenience, we make the following definition:

$$W_{s', s} = \frac{\partial \log x_{w}}{\partial \log m_{s'}} , \quad s' \neq w, s_B$$

(269)

Then the equation in the present example may be written as:

$$\log x_w - W_{Ca^{2+}} \log m_{Ca^{2+}} - W_{HCO_3^-} \log m_{HCO_3^-} = \log x_{w, k} - W_{Ca^{2+}} \log m_{Ca^{2+}, k} - W_{HCO_3^-} \log m_{HCO_3^-, k}$$

(270)

where again all the variables treated as unknowns are on the left hand side. For notational consistency, we have dropped the “$k + 1$” subscripts.

We now evaluate the necessary partial derivatives. The mole fraction of water must be expressed as a function of the concentrations of the basis species other than water. We first write this in the form:
\[
\log x_w = \log \left( \frac{\Omega}{\sum_{s' = 1}^{s_Q} m_{s'} + \sum_{r = 1}^{r_T} m_{s''}} \right)
\]

where \(s''\) denotes the non-basis species associated with the \(r\)-th aqueous reaction. Partial differentiation leads to the following intermediate result:

\[
W_{s'} = -\frac{x_w}{\Omega} \left( m_{s'} - \sum_{r}^{r_T} \frac{b_{s' r} m_{s''}}{b_{s'' r}} \right)
\]

where \(s'\) is a basis species other than water. Rearranging then gives the final result:

\[
W_{s'} = -\frac{x_w}{\Omega} \left( m_{s'} - \sum_{r}^{r_T} \frac{b_{s' r} m_{s''}}{b_{s'' r}} \right)
\]

Technically, these partial derivatives should be evaluated using data corresponding to the \(k\)-th iteration. However, as the method is not exact anyway and the mole fraction of water does not really vary much in the process, this is not critical.

In the above example, we have three equations in three unknowns. These equations are linear in the four log concentration variables; hence, they can be solved simultaneously by solving a corresponding matrix equation. This takes the form:

\[
\begin{bmatrix}
1 & 1 & 0 \\
0 & 1 & -1 \\
-W_{Ca^{2+}} & -W_{HCO_3^-} & 1
\end{bmatrix}
\begin{bmatrix}
\log m_{Ca^{2+}} \\
\log m_{HCO_3^-} \\
\log x_w
\end{bmatrix}
= \begin{bmatrix}
R_{Ca^{2+}} \\
R_{HCO_3^-} \\
R_w
\end{bmatrix}
\]

where the elements in the right hand side vector are equal to the expressions on the right hand side of eqs (266), (267), and (270). Matrix equations of this form are evaluated after new values have been calculated for the concentrations of the other basis species.

At the end of a cycle, a full set of residual functions is computed. This includes the \(\beta\) array and its max norm, \(\beta_{max}\). The only non-zero elements of \(\beta\) at the end of a cycle are those which pertain to mass and charge balance constraints. The elements of this vector corresponding to the former have been previously introduced. In the case of the latter, the relevant equation is:
\[ \beta_{s_z} = \frac{\alpha_{s_z}}{\sum_c z_cm_c + \sum_a z_am_a} \]  

(275)

where \( s_z \) is the basis species so constrained, \( c \) denotes cations and \( a \) anions, and:

\[ \alpha_{s_z} = \sum_c z_cm_c + \sum_a z_am_a \]  

(276)

The concentration of this species is then adjusted so as to make these residuals zero:

\[ m_{s_z,k+1} = m_{s_z,k} - \frac{\alpha_{s_z,k}}{|z_{s_z}|} \]  

(277)

A pass ends when one of the following occurs:

- The non-zero (mass balance) elements of \( \beta \) satisfy a loose convergence test (all fall in the range -10% to +50%).
- The maximum number of cycles per pass have been completed.
- A convergence function \( \beta_{func} \) (betfunc) indicates that iteration in the present cycle is diverging. This convergence function will be discussed later in this chapter.

At the end of a pass, the \( \Sigma m \) function and the ionic strength are recalculated, the mole fraction of water is recalculated, and the activity coefficients are recalculated. The code defines residual functions based on the magnitude of the changes in \( \Sigma m \), the ionic strength, and the activity coefficients from the values pertaining to the previous pass. The sequence of passes is stops when one of the following occurs:

- The residuals defined for \( \Sigma m \), the ionic strength, and the activity coefficients satisfy a loose convergence test (all less than or equal to 0.1).
- The maximum number of passes have been completed.

The optimization is deemed successful if both sets of loose convergence tolerances are satisfied. The code will then execute hybrid Newton-Raphson iteration. If optimization is not successful, the code checks to see if any equilibrium constraints appear to imply unrealistically high solute concentrations. If this is the case, the code will not attempt hybrid Newton-Raphson iteration and a message to this effect is written to the screen and output files. Otherwise, the code will execute hybrid Newton-Raphson iteration, which often succeeds even when the optimization step fails to satisfy its own convergence tolerances.

The cycle algorithm discussed in this section is an example of a first order method. This means that in a close neighborhood of the solution, one has that:
\[ \delta_{i,k+1} = \sum_{j=1}^{n} p_{ij} \delta_{jk} \] (278)

where \( n \) is the number of iteration variables and the \( p_{ij} \) are constants.

9.7. The Newton-Raphson Method

The Newton-Raphson method is a well-known iterative technique for solving non-linear systems of algebraic equations (see for example Van Zeggeren and Storey, 1970; Carnahan, Luther, and Wilkes, 1969; or any introductory text on numerical methods). We will not discuss the derivation of the method here, only its application. Given a set \( n \) governing equations and \( n \) unknowns (represented by a vector \( z \) of iteration variables), one may construct a set of residual functions (represented by the vector \( \alpha \)), each member of which has a value of zero when the \( n \) equations are satisfied. Both \( z \) and \( \alpha \) are of length \( n \).

A simple example will illustrate this. Suppose we wish to solve the general quadratic equation:

\[ ax^2 + bx + c = 0 \] (279)

This is a case in which \( n = 1 \). Here \( a \), \( b \), and \( c \) are given coefficients, and \( x \) is the only unknown. The residual function can be defined as:

\[ \alpha = ax^2 + bx + c \] (280)

Other definitions are possible, however. The only requirement is that they take on a value of zero when the governing equation is satisfied. We note here that the choice of definition may affect the convergence behavior.

Let \( k \) be the number of iterations, such that \( z_k \) and \( \alpha_k \) are the iteration variable and residual function vectors on the \( k \)-th iteration. Let \( z_0 \) represent the set of starting estimates. An iteration step is made by calculating \( z_{k+1} \) from \( z_k \). The Newton-Raphson method does this by computing a vector of correction terms, \( \delta \), by solving the matrix equation:

\[ J\delta = -\alpha \] (281)

Here \( J \) is the Jacobian matrix, defined by:

\[ J = \begin{bmatrix} \frac{\partial \alpha_i}{\partial z_j} \end{bmatrix} \] (282)

where \( i \) and \( j \) are the matrix coordinates. In our example, this becomes:

\[ J = 2ax + b \] (283)

The correction term is then applied:

\[ z_k + 1 = z_k + \delta \] (284)
If the iteration converges, all elements of both $\alpha$ and $\delta$ approach zero. It is useful to define another residual function vector $\beta$ which is identical to $\alpha$, except that some elements may be normalized to provide a better measure of convergence. It is then convenient to define $\beta_{\text{max}}$ and $\delta_{\text{max}}$ as the largest absolute values of the elements of $\beta$ and $\delta$, respectively. Both $\beta_{\text{max}}$ and $\delta_{\text{max}}$ may then be used in tests to determine if the iteration has converged satisfactorily.

A useful measure of how well convergence is proceeding may also be constructed. The Newton-Raphson method is a second order method. This means that in a close neighborhood of the solution, one has that:

$$\delta_{i,k+1} = \sum_{j=1}^{n} p_{ij} \delta_{jk}^2$$  \hspace{1cm} (285)

where the $p_{ij}$ are constants. In practice, there is usually no attempt to actually evaluate them. The significance of this is that in a close neighborhood of the solution, $\delta_{\text{max},k+1}$ should be much less than $\delta_{\text{max},k}$. The function $\delta_{\text{func}}$ (the variable defn) is defined:

$$\delta_{\text{func},k+1} = 1 - \left( \frac{\delta_{\text{max},k+1}}{\delta_{\text{max},k}} \right)$$  \hspace{1cm} (286)

may therefore be expected to approach (from below) a value of unity if the iteration is converging very rapidly (as theory suggests when the cross terms describing the evolution of the correction vector are small; i.e., the $p_{ij}$ are small for the case $i \neq j$). Convergence to a lesser value, say $\approx 0.72$ instead of $\approx 0.99$ is not unknown. This may imply non-negligible cross terms or an error in writing the Jacobian matrix. It also may result from modifications to the basic Newton-Raphson method, such as we have introduced by updating the activity coefficients between Newton-Raphson steps. The function, $\beta_{\text{func}}$ (the variable beta) is defined similarly:

$$\beta_{\text{func},k+1} = 1 - \left( \frac{\beta_{\text{max},k+1}}{\beta_{\text{max},k}} \right)$$  \hspace{1cm} (287)

and has essentially the same properties.

The use of a pure Newton-Raphson method would require the activity coefficients and their associated model equations to be brought directly into the set of $n$ equations and $n$ unknowns solved by the method, either directly or by substitution. In a previous section in this chapter, we noted that there was a problem in expanding the current set of master iteration variables in that the activity coefficients would have to be calculated before the concentrations of the non-basis species, and vice versa. This problem precludes taking care of the activity coefficients by a substitution mechanism that leaves the current set of master iteration variables unchanged. One would have to instead treat the activity coefficients themselves as master iteration variables. These are many, so this would not be very convenient. Alternatively, one could treat the ionic strength as a master iteration variable, but this would only suffice for simple extended Debye-Hückel formalisms that are only valid in dilute solutions. We have instead chosen to hybridize the Newton-Raphson
method by simply updating the activity coefficients between Newton-Raphson steps. In practice, this seems to work quite well, except in some extremely concentrated solutions.

The EQLIB module `newton.f` oversees the Newton-Raphson iteration for EQ3NR. Fellow EQLIB module `nrstep.f` is called to make a single Newton-Raphson step, and fellow EQLIB module `ngcadv.f` recomputes activity coefficients and computes the number of moles of dependent species. The latter module is called between Newton-Raphson steps, in accordance with the single update method that was described earlier in this chapter. The EQ3NR module `betas.f` computes the residual functions, and the EQ3NR module `matrix.f` writes the Jacobian matrix.

The maximum number of iterations in a Newton-Raphson calculation is determined by the input file variable `itermx`. This has a default value of 30 in EQ3NR. Convergence is achieved when $\beta_{\text{max}}$ is less than the tolerance parameter `tolbt`, $\delta_{\text{max}}$ is less than the tolerance parameter `toldl`, and max norms on the changes in the $\Sigma n$ function, the ionic strength, and the activity coefficients are all less than `tolbt`. The tolerance parameters `tolbt` and `toldl` both appear on the input file, and both have a default value of $1 \times 10^{-6}$.

### 9.8. Derivation of Residual Functions and the Jacobian Matrix

In this section, we shall derive the residual functions and the Jacobian matrix for the Newton-Raphson iteration procedures used by the EQ3NR code. Given a set of governing equations and an equal number of unknowns, there is no unique way to formulate residuals and Jacobians. The number of equations and unknowns may be reduced by means of substitutions. Furthermore, one may then construct the residual functions in any number of ways. Once the residual functions have been chosen, the form of the Jacobian is determined according to the partial derivatives of these functions.

We will now take each remaining governing equation, construct a corresponding pair of residual functions ($\alpha$ and $\beta$), and derive the corresponding row of elements in the Jacobian matrix by partial differentiation. The $\alpha$ residuals are the true Newton-Raphson residual functions and are the subject of partial differentiation to define the Jacobian matrix. The $\beta$ residuals are better measures of satisfactory convergence.

#### 9.8.1. Mass Balance

This may be applied to any aqueous species in the basis set ($s = 1$ through $s_Q$) except water (w), $H^+$, and $O_2(g)$ (the $s_B$-th species). Mass balance is specified as the governing equation by setting the corresponding `jflag` value to 0 and entering a total concentration on the molal scale ($m_{T,s}$).

Alternatively, one may enter total concentration in other units using other `jflag` values (molar, `jflag` = 1; mg/L, `jflag` = 2; mg/kg of solution, `jflag` = 3), which EQ3NR will then recompute into molality and set `jflag` to zero. The governing equation can be written as:

$$m_{T,s} = \sum_{s' = 1}^{s_Q} u_{s's} m_{s'} + \sum_{s'' = s_Q + 1}^{s_T} u_{s''s} m_{s''}$$  \hspace{1cm} (288)

The residual functions are defined by:
\[ \alpha_s = -m_{T,s} + \sum_{s'} u_{s's} m_s + \sum_{s'' = s_Q+1} u_{s''s} m_{s''} \]  
(289)

\[ \beta_s = \frac{\alpha_s}{m_{T,s}} \]  
(290)

where in the last part of eqs (288) and (289) it is implied that \( s'' = s_r \). From this point, we may use the relations developed above to derive the following Jacobian elements:

\[ J_{sw} = \frac{\partial \alpha_s}{\partial \log x_w} \]

\[ = \sum_{r=1}^{r_T} u_{s''s} \frac{\partial m_{s''}}{\partial \log x_w} \]

\[ = -2.303 \sum_{r=1}^{r_T} \frac{u_{s''s} m_{s''} b_{w'r}}{b_{s''r}} \]

\[ J_{ssB} = \frac{\partial \alpha_s}{\partial \log f_{O_2}} \]

\[ = \sum_{r=1}^{r_T} u_{s''s} \frac{\partial m_{s''}}{\partial \log f_{O_2}} \]

\[ = 2.303 \sum_{r=1}^{r_T} \frac{u_{s''s} m_{s''} b_{sB'r}}{b_{s''r}} \]

\[ = 2.303 \sum_{r=1}^{r_T} b_{sB'r} H_{sr} \]  
(292)

and for \( s \neq w, s_B \):
\[ J_{ss'} = \frac{\partial \alpha_s}{\partial \log m_{ss'}} \]

\[ = \sum_{s''=1}^{s_Q} u_{s''} \frac{\partial m_{ss''}}{\partial \log m_{ss'}} + \sum_{s''=s_Q+1}^{s_T} u_{s''} \frac{\partial m_{ss''}}{\partial \log m_{ss'}} \]

\[ = -2.303 \left( u_{s',s} m_{ss'} - \sum_{r=1}^{r_T} \frac{u_{s''} m_{ss''} b_{s' r}}{b_{s'' r}} \right) \]

\[ = -2.303 \left( u_{s',s} m_{ss'} - \sum_{r=1}^{r_T} b_{s' r} H_{s r} \right) \]

(293)

Here \( u_{s''} s' = 1.0 \) if \( s' = s'' \), otherwise \( u_{s''} s' = 0 \).

9.8.2. Electrical Balance

This governing equation may be applied to one of the ions in the aqueous species basis set, here denoted by \( s \). Apart from the definition of the \( \beta \) residual, the treatment is exactly analogous to that for mass balance. The governing equation can be written as:

\[ \sum_{s'=1}^{s_Q} z_{s'} m_{ss'} + \sum_{s''=s_Q+1}^{s_T} z_{s''} m_{ss''} = 0 \]

(294)

The residual functions are defined by:

\[ \alpha_s = \sum_{s'=1}^{s_Q} z_{s'} m_{ss'} + \sum_{s''=s_Q+1}^{s_T} z_{s''} m_{ss''} \]

(295)

\[ \beta_s = \frac{\alpha_s}{\sum_{s'=1}^{s_Q} |z_{s'}| m_{ss'} + \sum_{s''=s_Q+1}^{s_T} |z_{s''}| m_{ss''}} \]

(296)

The corresponding Jacobian elements are as follows:
and for \( s \neq w, SB \):

\[
J_{ss'} = \frac{\partial \alpha_s}{\partial \log m_{s'}}
\]

\[
= -2.303 \left( z_{s'} m_{s'} - \sum_{r=1}^{r_T} b_{s'r} H_{zr} \right)
\]  

(299)

9.8.3. The Mole Fraction Of Water

The governing equation can be written as:

\[
x_{w'} = \frac{\Omega_s}{\Omega + \sum_{s=1}^{s_T} m_s}
\]  

(300)

where \( \Omega \) is the number of moles of solvent water comprising a mass of 1 kg (\( \Omega \approx 55.51 \)) and \( s_T \) is the number of aqueous species in the solution. The corresponding residual functions are defined as:
\[
\alpha_w = \log \left( \frac{\Omega}{\Omega + \sum_{s=1, s \neq w}^{sQ} m_s} \right) - \log x_w
\]  

(301)

\[
\beta_s = \alpha_s
\]  

(302)

Because it is necessary to distinguish between basis species and non-basis species, it is helpful to write the equation for the first residual function in the slightly expanded form:

\[
\alpha_w = \log \left( \frac{\Omega}{\Omega + \sum_{s'=1, s' \neq w}^{sQ} \sum_{r=1}^{r_T} m_{s'r}} \right) - \log x_w
\]  

(303)

In the following equations, we will take \( s' \) and \( s'' \) to be basis species other than water. The following Jacobian elements are then obtained:

\[
J_{ww} = \left( \frac{1}{\Omega} \right) \left( \frac{\Omega}{\Omega + \sum_{s'=1, s' \neq w}^{sQ} \sum_{r=1}^{r_T} m_{s'r}} \right) \left( \sum_{r=1}^{r_T} \frac{b_{w'r} m_{s''}}{b_{s''r}} \right) - 1.0
\]  

(304)

\[
J_{w's''} = \left( -\frac{1}{\Omega} \right) \left( \frac{\Omega}{\Omega + \sum_{s'=1, s' \neq w}^{sQ} \sum_{r=1}^{r_T} m_{s'r}} \right) \left( m_{s''} - \sum_{r=1}^{r_T} \frac{b_{s''r} m_{s''}}{b_{s''r}} \right)
\]  

(305)

Note that these Jacobian elements differ from the corresponding set of partial derivatives used in the truncated Taylor's expansion as part of the pre-Newton-Raphson optimization. In the present case, \( \log x_w \) is treated as an independent variable. In the previous case, it was not.
9.8.4. Specified Free Concentration

This represents the $\text{jflag} = 4$ option for $s = 1$ through $s_Q$, except when $s$ is water (w) or $O_2(g)$ ($s_B$). The free concentration is in molality. If it is initially entered in molarity ($\text{jflag} = 5$), EQ3NR will convert it to molality and resets $\text{jflag}$ to 4 before beginning Newton-Raphson iteration. The governing equation is just the identity:

$$m_s = m_s$$

Hence, the corresponding residual functions are given by:

$$\alpha_s = 0$$
$$\beta_s = 0$$

In order to prevent singularity in the Jacobian, we set:

$$J_{ss} = 1.0$$

9.8.5. Specified Thermodynamic Activity

This represents the $\text{jflag} = 16$ option for $s = 1$ through $s_Q$, except when $s$ is water (w) or $O_2(g)$ ($s_B$). This option is most frequently employed with $H^+$ in order to specify a $pH$ value ($pH = -\log a_{H^+}$).

The governing equation is:

$$\log m_s + \log \gamma_s = \log a_s$$

The residual functions are:

$$\alpha_s = -\log a_s + \log m_s + \log \gamma_s$$
$$\beta_s = \alpha_s$$

The only non-zero Jacobian element is:

$$J_{ss} = 1.0$$

9.8.6. Log Activity Combination

Recall that the activity combination parameter is defined by:

$$\kappa_{ij} = |z_j| \log a_i - \frac{z_i z_j}{|z_j|} \log a_j$$

We will identify $i$ as the basis species $s$ to which this constraint is applied, and $s^*$ as the other basis species involved. The governing equation can then be written as:
\[ \log m_s = \frac{\alpha_{ss*}}{|z_{s^*}|} - \log \gamma_s + \frac{z_s}{z_{s^*}} \log m_{s^*} + \frac{z_s}{z_{s^*}} \log \gamma_{s^*} \]  

Hence, the corresponding residual functions are given by:

\[ \alpha_s = \frac{\alpha_{ss*}}{|z_{s^*}|} - \log \gamma_s + \frac{z_s}{z_{s^*}} \log m_{s^*} + \frac{z_s}{z_{s^*}} \log \gamma_{s^*} - \log m_s \]  

\[ \beta_s = \alpha_s \]  

The corresponding non-zero elements of the Jacobian matrix are then:

\[ J_{ss} = -1.0 \]  

\[ J_{ss^*} = \frac{z_s}{z_{s^*}} \]  

9.8.7. Mean Log Activity

The mean log activity of two oppositely charge ions \( i \) and \( j \) can be written as:

\[ \log a_{\pm,ij} = \frac{|z_i| \log a_i + |z_j| \log a_j}{|z_i| + |z_j|} \]  

We will identify \( i \) as the basis species \( s \) to which this constraint is applied, and \( s^* \) as the other basis species involved. The governing equation can then be written as:

\[ \log m_s = \frac{|z_s| + |z_{s^*}|}{|z_{s^*}|} \log a_{\pm,ss} + \log \gamma_s - \frac{z_s}{z_{s^*}} \log m_{s^*} - \frac{z_s}{z_{s^*}} \log \gamma_{s^*} \]  

Hence, the corresponding residual functions are given by:

\[ \alpha_s = \frac{|z_s| + |z_{s^*}|}{|z_{s^*}|} \log a_{\pm,ss} + \log \gamma_s - \frac{z_s}{z_{s^*}} \log m_{s^*} - \frac{z_s}{z_{s^*}} \log \gamma_{s^*} - \log m_s \]  

\[ \beta_s = \alpha_s \]  

The corresponding non-zero elements of the Jacobian matrix are then:

\[ J_{ss} = -1.0 \]  

\[ J_{ss^*} = -\frac{z_s}{z_{s^*}} \]

This option (jflag = 19) may be specified for any aqueous species denoted by \( s = 1 \) through \( s_Q \), except when \( s \) is water (w). Let \( \phi \) denote the mineral in question. The governing equation is:

\[
\log K_\phi = b_{w\phi} (\log x_w + \log \lambda_w) + b_{s_B\phi} \log f_{O_2} + \sum_{s' = 1}^{s_Q} b_{s'\phi} (\log m_{s'} + \log \gamma_{s'})
\]

(326)

The residual functions are defined as:

\[
\alpha_s = \frac{1}{b_{s\phi}} \left( \log K_\phi - b_{w\phi} (\log x_w + \log \lambda_w) - b_{s_B\phi} \log f_{O_2} - \sum_{s' = 1}^{s_Q} b_{s'\phi} (\log m_{s'} + \log \gamma_{s'}) \right)
\]

(327)

\[
\beta_s = \alpha_s
\]

(328)

The corresponding Jacobian elements are then:

\[
J_{ss'} = -\frac{b_{s'\phi}}{b_{s\phi}}
\]

(329)

The residual function \( \alpha_s \) defined in eq (327) has in a sense been normalized by dividing by the stoichiometric reaction coefficient \( b_{s\phi} \). This makes the residual equivalent to the difference between the calculated and current values of \( \log m_s \), independent of how the reaction has been written. This avoids some potential numerical scaling problems. Other options involving mass action equations are treated in the same manner.

9.8.9. Equilibrium With A Solid Solution End-member Component

This option (jflag = 20) may be specified for any aqueous species denoted by \( s = 1 \) through \( s_Q \), except when \( s \) is water (w). The treatment is closely analogous to that for equilibrium with a pure mineral. Let \( \sigma \) and \( \psi \) denote the end-member and solid solution phase, respectively. The governing equation contains an additional term in the mole fraction and activity coefficient of the solid solution end-member and is given by:
\[ \log K_{\sigma\psi} = b_{\sigma\psi}(\log x_{\sigma\psi} + \log \lambda_{\sigma\psi}) + b_{w\sigma\psi}(\log x_{w} + \log \lambda_{w}) + b_{s_B\sigma\psi}\log f_{O_2} \]

\[
+ \sum_{s' = 1}^{s_Q} b_{s'\sigma\psi}(\log m_{s'} + \log \gamma_{s'}) \quad s' \neq w, s_B
\]

The residual functions are defined as:

\[
\alpha_s = \frac{1}{b_{s\sigma\psi}} \left( \log K_{\sigma\psi} - b_{\sigma\psi}(\log x_{\sigma\psi} + \log \lambda_{\sigma\psi}) - b_{w\sigma\psi}(\log x_{w} + \log \lambda_{w}) - b_{s_B\sigma\psi}\log f_{O_2} - \sum_{s' = 1}^{s_Q} b_{s'\sigma\psi}(\log m_{s'} + \log \gamma_{s'}) \right) \quad s' \neq w, s_B
\]

\[
\beta_s = \alpha_s
\]

The corresponding Jacobian elements are then:

\[
J_{s,s'} = -\frac{b_{s'\sigma\psi}}{b_{s\sigma\psi}}
\]

**9.8.10. Equilibrium With A Gas**

This option (jflag = 21) may be specified for any aqueous species denoted by \( s = 1 \) through \( s_Q \), except when \( s \) is water (w). The treatment is closely analogous to that for equilibrium with a pure mineral. Let \( g \) denote the gas in question. The governing equation contains an additional term in the fugacity of this gas and is given by:

\[ \log K_g = b_{gg}\log f_g + b_{wg}(\log x_w + \log \lambda_w) + b_{s_Bg}\log f_{O_2} + \sum_{s' = 1}^{s_Q} b_{s'g}(\log m_{s'} + \log \gamma_{s'}) \]

The residual functions are defined as:
\[
\alpha_s = \frac{1}{b_{sg}} \left( \log K_g - b_g \log f_g - b_{wg} (\log x_w + \log \lambda_w) \right) - b_{sg} \log f_{O_2} - \sum_{s'=1}^{s_Q} b_{s'g} (\log m_{s'} + \log \gamma_{s'}) \right) \\
\beta_s = \alpha_s 
\]

The corresponding Jacobian elements are then:

\[
J_{ss'} = -\frac{b_{s'g}}{b_{sg}} 
\]

9.8.11. Concentration Fixed By Internal Equilibrium

This option (jflag = 27) excludes the species to which it is applied, which must be in the auxiliary basis set, and its ion-pairs and complexes from the mass balance of the corresponding basis species to which it is linked by its own associated reaction (usually a strict basis species). This is a good choice for dissolved gas species such as \( \text{O}_2(\text{aq}) \) and \( \text{H}_2(\text{aq}) \). If \( \text{HS}^- \) is an auxiliary basis species with jflag = 27 and it is linked to \( \text{SO}_4^{2-} \), then \( \text{HS}^- \) and its “complexes” (other species whose reactions link them to this species) are not included in calculating the \( \text{SO}_4^{2-} \) mass balance. If instead one chooses jflag = 30 for \( \text{HS}^- \), they are included.

Let \( s \) be the auxiliary basis species constrained by jflag = 27, and let \( r \) denote its associated reaction. The governing is then:

\[
\log K_r = b_{sr} (\log m_s + \log \gamma_s) + b_{wr} (\log x_w + \log \lambda_w) \\
+ b_{s'pr} \log f_{O_2} + \sum_{s'=1}^{s_Q} b_{s'r} (\log m_{s'} + \log \gamma_{s'}) \\
\quad s' \neq w, s_{p, r} 
\]

The residual functions are defined as:
\[
\alpha_s = \frac{1}{b_{sr}} \left( \log K_r - b_{sr} (\log m_s + \log \gamma_s) - b_{wr} (\log x_w + \log \lambda_w) \right) \\
- b_{sr} \log f_{O_2} - \sum_{s' = 1}^{s_q} b_{sr} (\log m_{s'} + \log \gamma_{s'}) \right) \\
\beta_s = \alpha_s 
\]

The corresponding Jacobian elements are then:

\[
J_{ss} = - \frac{b_{sr}}{b_{sr}} 
\]

9.8.12. Specified Log Oxygen Fugacity

This option (\textit{iop}t1 = 0) allows direct specification of the log oxygen fugacity. The governing equation is just the identity:

\[
\log f_{O_2} = \log f_{O_2} 
\]

The residuals are:

\[
\alpha_s = 0 \\
\beta_s = 0 
\]

The only non-zero Jacobian element in the corresponding row is:

\[
J_{ss} = 1.0 
\]

9.8.13. Specified \(E_h\)

This option (\textit{iop}t1 = -1) allows indirect specification of the log oxygen fugacity. If \(pe\) is specified (\textit{iop}t1 = -2), EQ3NR converts it to \(E_h\) before it does the Newton-Raphson iteration. Letting \(F\) be the Faraday constant, \(R\) the gas constant, and \(T\) the absolute temperature, the governing equation can be written as:

\[
\log f_{O_2} = \frac{4FE_h}{2.303RT} + \log K_{E_h} + 2 (\log x_w + \log \lambda_w) - 4 (\log m_{H^+} + \log \gamma_{H^+}) 
\]

The residual functions are:
\[
\alpha_s = \frac{4FEh}{2.303RT} + \log K_{Eh} + 2(\log x_w + \log \lambda_w) - 4(\log m_{H^+} + \log \gamma_{H^+}) - \log f_{O_2}
\]  \quad (347)

\beta_s = \alpha_s \quad (348)

The non-zero Jacobian elements in the corresponding row are:

\[J_{sBw} = 2\] \quad (349)
\[J_{sBH^+} = -4\] \quad (350)
\[J_{sB^+} = -1\] \quad (351)


This represents the \texttt{iopt1} = 1 option. Here \(s\) is restricted to \(s_B\). The couple is specified on the input file by setting \texttt{uredox} to the name of the auxiliary basis species which comprises half of the couple (the other half is automatically the corresponding strict basis species). Let \(r\) denote the reaction associated with the auxiliary basis species \((s_r)\) in the desired couple. The governing is then:

\[\log K_r = b_{s,r} (\log m_{s,r} + \log \gamma_{s,r}) + b_{w,r} (\log x_w + \log \lambda_w) + b_{sB} \log f_{O_2} + \sum_{s' = 1}^{s_Q} b_{s'r} (\log m_{s'} + \log \gamma_{s'}) (s' \neq w, s_B, s_r)\] \quad (352)

The residual functions are defined as:

\[\alpha_s = \frac{1}{b_{sB}} \left( \log K_r - b_{s,r} (\log m_{s,r} + \log \gamma_{s,r}) - b_{w,r} (\log x_w + \log \lambda_w) - b_{sB} \log f_{O_2} - \sum_{s' = 1}^{s_Q} b_{s'r} (\log m_{s'} + \log \gamma_{s'}) (s' \neq w, s_B, s_r) \right)\] \quad (353)

\beta_s = \alpha_s \quad (354)
The corresponding Jacobian elements are then:

$$J_{ss'} = \frac{-b_{s't}}{b_{st}}$$

(355)

9.9. Methods for Crash Diagnostics

The iteration procedure is good enough that divergence almost always results from the input of a bad set of input constraints. EQ3NR screens the input prior to Newton-Raphson iteration, but some cases are not sufficiently obvious to be caught at this stage. When the iteration diverges, EQ3NR calls the module ndiagx.f, which examines final state of the iteration process in an attempt to generate diagnostics to write on the screen and output files. Barring the generation of a useful diagnostic, the user should examine the iteration summary on the output file for clues to the cause of the situation.

An iteration crash is generally the result of an iteration variable "blowing up" or, more commonly, "blowing down." "Blowing up" means that the value of an iteration variable or its corresponding residual function, usually a mass balance residual, is increasing to the point where the matrix equation can no longer be solved by the computer and iteration must terminate. Sometimes in this situation the operating system may terminate the code execution due to an overflow condition. If a variable "blows down," it probably means that no physical solution exists for the problem as posed. Because the primary iteration variables are logarithmic, underflow can only occur when these variables are exponentiated. When this happens, the code is usually stopped by encountering what appears to be a singular Jacobian matrix.

"Blow down" occurs for example when the problem calls for the concentration of a species to be adjusted to satisfy electrical balance, but this balance can only be achieved if the resulting concentration takes a negative value. An iteration process which only allows adjustments to log concentrations will never allow the generation of concentration value which is non-positive. What happens instead is that the calculated adjustments to the log concentration become large and negative. These are truncated to a value of -3 (-screwd). As this adjustment truncation parameter has a magnitude of 2.0, the largest adjustment (element of the del array) takes on a value of -2.0. This can be seen in the iteration summary that is printed on the output file as the code executes Newton-Raphson iteration.

An iteration block printed during this iteration is exemplified by the following:

```
iter= 2
del(conc so4-- )= -1.77931F-03, delfnc= 9.34442E-01
beta(conc so4-- )= 8.87762E-05, betfnc= 9.79484E-01
bbig= 8.87762E-05, ubbig= so4--
bbneg= 0.00000E+00, ubneg= none
bqmax= 1.61604E+04, ubqmax= mg4(oh)4++++
bsigm= -1.16619E+04
bxi= -3.19106E+04
btfccr= 9.97838E-01
```

This is taken from the sea water test case that was presented as the first example in Chapter 7. The del element with the largest magnitude and the beta element with the largest magnitude are printed first. We see that in both cases, these are the elements corresponding to the concentration of the basis species $SO_4^{2-}$. "Blow down" would be evident if the del output in this block were to
take on a value of -2.0 (usually for the last several iterations before the process is terminated). "Blow up" would be evident if the \texttt{beta} output in this block were to take on very high positive values. The variables \texttt{delfnc} and \texttt{betfnc} are convergence functions for the \texttt{del} and \texttt{beta} arrays, respectively. They usually start at small positive values less than unity and then approach unity if the iteration process converges. If one or the other takes on sustained negative values, the iteration process usually diverges. Here \texttt{bbig} is the largest positive mass balance residual (\texttt{ubbig} identifying the corresponding species) and \texttt{bneg} is the negative mass balance residual (if any) with the largest magnitude (\texttt{ubneg} identifying the corresponding species). The variable \texttt{bgamx} is an aqueous species activity coefficient residual function (the max norm on the absolute values of the differences between current and previous values of the activity coefficients of the aqueous species); \texttt{ubgamx} identifies the corresponding species. Also, \texttt{bsigm} is a residual on the $\Sigma m$ function (difference between the current and previous values), and \texttt{bxi} is a similar residual on the ionic strength. The variable \texttt{btfncr} is similar to \texttt{betfnc}, but measures the convergence in a pure Newton-Raphson step. Usually \texttt{betfnc} has a smaller value than \texttt{btfncr} because any adjustment of activity coefficient values in between Newton-Raphson steps tends to reduce the overall reduction in the residual functions.

The purpose of the present chapter is to describe 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 EQ3NR modules, see Appendix B of the present report. For EQLIB modules, see Appendix A of the EQ3/6 Package Overview and Installation Guide (Wolery, 1992). 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 main program is the module eq3nr.f. It directs the overall process of code execution. This is illustrated in Figure 4, which is a simplified flow diagram of the code from the point of view of this module. The first function of eq3nr.f 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 passed in calling sequences.

Recall that EQ3NR will run multiple problems stacked on a single input file. The line “20 continue” is a return point in the main program to which execution flows after a single problem has been solved. After this point, the code initializes the relevant arrays and variables, setting their contents to zero or some other appropriate null value equivalent. The purpose of this is to provide a clean slate for the solution of the next problem. The main program then calls module rdinp.f to read the first or a following problem on the input file. If no new problem is found, the problem execution stage is presumed to be finished. The main program then gets the current time and date and writes the starting and ending times and dates to the screen and output files. After that, it makes a “normal exit” and execution stops.

Module rdinp.f does the following. If the input file has not been opened on a previous call, it opens it. Using an EQLIB module called stripl.f, it copies the input file to a file called inputs, deleting any comment lines. The original input file is then closed. The code then subsequently reads the stripped input file instead. Module rdinp.f looks at the first line of this file to see if it is in “W” or “D” form. If it is in “W” or “D” form, it then repositions the file pointer at the top of the file.
Figure 4 (page 1 of 4). Simplified flow diagram of the EQ3NR main program (eq3nr.f).
Read the activity coefficient parameters pertaining to the B-dot equation option (call eqlib/inbdot.f)

Read the activity coefficient parameters pertaining to Pitzer's equations (call eqlib/inupt.f)

Build Pitzer coefficient index arrays (call eqlib/bdsu.f, eqlib/bdmlx.f)

Compute temperature-dependent thermodynamic data (call eqlib/cvdala)

Check redox constraints for conflicts; set default values for numeric parameters

Write echo describing the current problem on the output file (call echox.f)

Convert input concentration data to molalities (call setup.f)

Check the species if any whose concentration is to be adjusted to obtain electrical balance; choose such a species if this is indicated

Make those user-specified basis switches involving strict basis-auxiliary basis pairs (call eqlib/switch.f)

Write a list of inactive species to the output file

Identify the auxiliary basis species, if any, which defines the default redox state (find index corresponding to the uredox input variable)

Check the strict basis species for illegal jflag values of 30

Eliminate from the active basis set all auxiliary basis species with jflag values of 30 (call eqlib/switch.f)

Figure 4 (continued, page 2 of 4). Simplified flow diagram of the EQ3NR main program (eq3nr.f).
Make all remaining user-directed basis switches (call eqlib/switch.f)

Write on the output file the set of constraints as they are presently defined

Compute the activity coefficients of the components of any solid solutions whose compositions were specified on the input file (call eqlib/lambda.f)

Check the input problem constraints for inconsistencies and other obvious errors

Errors found?

Yes

Write a message to the output and screen files; stop

No

Recompute thermodynamic data if necessary because of the elimination and basis switching procedures (call eqlib/evdarr.f)

Yes

Optimization succeeded?

Yes

Optimization failed badly?

No

Write a message to the output and screen files warning that optimization did not succeed

No

Compute starting estimates, refine them to within broad limits using the pre-Newton-Raphson algorithm (call arrset.f)

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Optimization succeeded?

Yes

Optimization failed badly?

No

Write a message to the output and screen files; go back to label 20 (look for another problem)

Figure 4 (continued, page 3 of 4). Simplified flow diagram of the EQ3NR main program (eq3nr.f).
Write a message to the output and screen files; go back to label 20 (look for another problem)

Write results on the output file (call scripx.f)

Write on the pickup file the data necessary to initialize an EQ6 run (call scribaf for "W" format, scribn.f for "D" format); write diagnostic message to the output and screen files if a valid pickup file can not be written

Go back to label 20 (look for another problem)
If the input file is in "W" format, module rdinp.f calls module readx.f to read the next problem. If it is in "D" format, it calls module rdninp.f to oversee the reading of the next problem. Unlike readx.f, rdninp.f carries out its function by calling a fairly large number of other modules, all of which have names beginning with "rd" or "get." Calls to either readx.f or rdninp.f result in the writing of an instant echo of the input file to the output file. If no problem is found at the current position of the file pointer, the main program is notified and it then proceeds as described above to make a normal exit.

If an input problem description is found on the input file, eq3nr.f sets the temperature range flag p*nr calling the EQLIB module gntpr.f. It then gets the name of the chosen activity coefficient option corresponding to the k>pg1 activity coefficient option switch. This is a descriptive character string that will be used subsequently. The code then calls module indatx.f to read the supporting data file, data1. This module checks a flag contained on the data file to insure that the kind of data file provided is consistent with the activity coefficient option selected on the input file. If it is not, this module writes an error message to the screen and output files and execution stops. Otherwise, it proceeds to read the standard state thermodynamic data on the data file. All basis species are loaded into memory (even if they are not needed). All other types of species are loaded into memory only if they are relevant to the current problem.

The primary method of indexing data pertinent to species, reactions, etc., follows from the reading of the data file. Corresponding data read from the input file are stored in holding arrays. For example, the names of the basis species to include in the model and the corresponding "esp" inputs are initially stored in holding arrays called uspecb and cspb, respectively. The names of the aqueous species read from the data file are kept in the uspec array. The actual esp array is constructed by name matching between the uspecb and uspec arrays. This is done by the module gcsp.f, which is called by indatx.f. The module indatx.f also calls the EQLIB module alters.f to execute any nxmod "alter" options that may have been included on the input file.

The main program then calls the EQLIB module gspion.f to find the indices of the hydrogen and chloride ions, and follows this by calling the module fglstx.f to set the species status flags. The latter module may in turn call the EQLIB module supprs.f to execute any nxmod "suppress" options that may have been included on the input file.

Execution then returns to the main program. If iopgl < 0, eq3nr.f calls the module inbdot.f to read from the data file the hard core diameter (azero) and insgfl flag data required for the B-dot activity coefficient model. This is done even if iopgl = -1 (the Davies equation option, in which case these data are not used). If iopgl = 1, eq3nr.f calls the module inupt.f to read from the data file the relevant interaction parameters needed for Pitzer's equations. This is followed by calls to the EQLIB modules bdslx.f and bdmlx.f, which build index arrays used in the evaluation of Pitzer's equations. Only the data needed for the current problem are loaded into memory by either inbdot.f or inupt.f.

The thermodynamic data that have been read in at this point are in various forms which do not generally correspond to the data required at the temperature for the given problem. For example, the equilibrium constants as read from the data file are only represented as the coefficients of interpolating polynomials. The main program then calls the EQLIB module evdata.f to compute the needed data for the temperature specified for the current problem.
The main program then checks the redox constraints for the current problem to see if there are any conflicts. If any are found, it resolves them and writes appropriate warning messages to the screen and output files. It then sets default values as required for some of the input file parameters. The next action of the main program is to call module echox.f. This writes an echo of the current problem to the output file. This echo includes the values of any default parameters that have been assigned.

The next action of eq3nr.f is to call module setup.f. This converts concentration data which are not in terms of molalities to molalities. The main program then identifies the species to be adjusted for electrical balance, or finds one which is suitable for this purpose if that is what the user requested on the input file. A choice made by the user is then checked for suitability. Some warnings and notes may be written to the screen and output files if any problems are apparent, such as the specified species not having any electrical charge (in which case the calculation may well fail, but not necessarily, as the concentrations of charged non-basis species will change in response to adjustments to the concentration of the species defined in the balance constraint).

The main program then executes those basis switches that were specified on the input file and involve switching the roles of strict and auxiliary basis species (other basis switches specified on the input file are done later). In doing this, it makes use of the EQLIB module switch.f. Then it writes a list of inactive species to the output file. These include species which have been suppressed by user options on the input file and species which were loaded from the data file, but for which the requisite thermodynamic data are lacking.

Module eq3nr.f then identifies the auxiliary basis species which defines the redox couple to be used to calculate the default redox state, if this option has been selected on the input file. It then checks to ensure that there are no cases of a jflag value of 30 being assigned to a strict basis species. It then calls the EQLIB module elim.f to eliminate all auxiliary basis species with jflag = 30 from the active basis set. Then it executes (again by calling the EQLIB module switch.f) those basis switches which were specified on the input file and bring non-basis species into the basis set. The main program then writes to the output file a table describing the input constraints as it presently understands them. If solid solution compositions have been entered on the input file, the main program now calls the EQLIB module lambda.f to evaluate the activity coefficients of the components of these phases.

The main program then makes a rather extensive set of tests on the current problem inputs, looking for inconsistencies and other obvious errors. If problems are found, error messages are written to the screen and output files. At the end of this process, if one or more errors have been detected, the code stops execution.

The next action of eq3nr.f is to call the EQLIB module evdatr.f to recompute those thermodynamic data which have to be changed in response to the rewriting of reactions due to elimination of auxiliary basis species from the active basis set and basis switching. During the actual rewriting of reactions associated with such activities, the associated interpolating polynomials are recalculated, but the corresponding equilibrium constants are not immediately recalculated. The equilibrium constants that were evaluated previously by evdata.f (which itself called evdatr.f to do this) are presently not used in any code function. In the past, they have been used to verify that the data were being properly reconstructed in the code prior to the steps in which the reactions
were rewritten. Depending on the choice of the input file option switch \texttt{ippr2}, the reactions and associated data may be written to the output file after these actions have taken place. Module \texttt{eq3nr.f} then calls the EQLIB module \texttt{gests.f}, which computes the stoichiometric mass balance factors, which are kept in the \texttt{stor1} array.

At this point, the code is ready to solve the system of algebraic equations posed by the current problem. The main program calls module \texttt{arrset.f}, which sets up the appropriate computational structures (e.g., the array defining the master iteration variables), assigns starting values, and attempts to refine them using the pre-Newton-Raphson optimization algorithm discussed in Chapter 9. The flow of execution in this module is illustrated in the simplified flow diagram in Figure 5. Note that there is an initial estimation procedure, followed by a fairly complex optimization process. This consists of an outer loop structure (\textit{loops}) in which automatic basis switching is carried out (this happens only if \texttt{iopt2} is set to 1 on the input file). Inside this is a middle loop structure (\textit{passes}) in which \(\Sigma m, I\), and the activity coefficients of aqueous species are updated. Inside this in turn is an inner loop (\textit{cycles}) in which the primary optimization (adjustment of concentrations of the basis species) is carried out. In applying the optimization algorithm, \texttt{arrset.f} calls module \texttt{arrsim.f} to compute refined values for those basis species concentrations which must be determined simultaneously (instead of by successively evaluating individual equations for the basis species concentrations, as is the case in the rest of the algorithm).

The goal of the optimization procedure in \texttt{arrset.f} is only to get the iterated values to within about an order of magnitude of the solution, so that subsequent Newton-Raphson iteration will have sufficiently good values to start with. This optimization process may succeed or not. If not, this module checks to see if any computed basis species concentrations are outrageously high. If this is the case, the problem as stated is almost assuredly ill-posed (has no realistic solution).

If the problem appears to be ill-posed, \texttt{eq3nr.f} writes a note to the screen and output files and gives up on the current problem and loops back to see if there is another problem on the input file. Otherwise, whether or not the optimization step succeeded, it continues by calling the EQLIB module \texttt{newton.f} to compute the final solution. This executes the hybrid Newton-Raphson algorithm that was also discussed in Chapter 9. The flow of execution in \texttt{newton.f} is illustrated in the simplified flow diagram in Figure 6. This module in turn calls the module \texttt{betas.f} and \texttt{matrix.f} to compute, respectively, the residual functions and the Jacobian matrix. These are known to \texttt{newton.f} as \texttt{"betae"} and \texttt{"matrxe"}, respectively. Module \texttt{newton.f} also calls the module \texttt{ncmpx.f} to expand the system. This routine is known to it as \texttt{"nempe."} Module \texttt{newton.f} calls the EQLIB module \texttt{ngcadv.f} to recompute the activity coefficients. It also calls the EQLIB module \texttt{nrstep.f} to execute a single Newton-Raphson step. The flow of execution in \texttt{nrstep.f} is illustrated in the simplified flow diagram in Figure 7. Note that this is actually a fairly complex piece of coding.

If hybrid Newton-Raphson iteration fails, the main program writes an error message to the screen and output files. It then calls module \texttt{ndiagx.f} to examine the results of the failed calculation in an attempt to generate useful diagnostics. If any are generated, they are written to the screen and output files. Most of the possible messages that might be written identify the relevant aspects of ill-posed input. The code then loops back to look for another problem on the input file.
If hybrid Newton-Raphson iteration succeeds, the code continues processing the current problem. The next action of the main program is to call the module scripx.f. This writes a description of all relevant results to the output file. As necessary, it calculates various secondary parameters before writing them. What this module writes is essentially all of what the user sees as the results of the calculation.

The next action of eq3nr.f is to see if a valid pickup file can be written. To be valid for transmittal to EQ6, the aqueous solution model must include each strict basis species which is linked to each auxiliary basis species in the model. If a valid pickup file can not be written, the main program writes a note to the screen and output files. Otherwise, a pickup file is then written. If the input file was in “W” format, the main program calls the module scribo.f, which writes the pickup file in the corresponding format. If the input file was in “D” format, it calls the module scribx.f, which writes the pickup file in the corresponding format.

This terminates all code activity on the current problem. The main program then loops back to look for another problem on the input file.
BEGIN

Initialize the array (uzvecl) refining the active basis set

Set nloop = 0 (automatic basis switching loop counter)

_Label 25: Increment nloop by 1

Make estimates of basis species concentrations (cone) from the input data; concentrations of non-basis species are taken to be zero

Calculate the charge imbalance, $\Sigma m$ (sum of solute molalities) and $I$ (ionic strength)

Calculate the activity coefficients of the aqueous species; also calculate the mole fraction of water (call eqlib/gcoeff.f)

Save "old" values of $\Sigma m$, $I$, and the activity coefficients

_Label 3210: Increment npass by 1

Initialize convergence function (betfnc), negative convergence counter (negbfc), and special residual norms

_LABEL 3220: Increment ncycle by 1

Calculate the charge imbalance, $Em$ (sum of solute molalities) and $I$ (ionic strength)

_Label 3220: Increment ncycle by 1

Initialize the primary vector of unknowns (zvclg1), using current estimates of species concentrations (use module arrsim.f to make estimates in the case of basis species whose constraints involve other basis species)

Save "old" values of $Em$, $I$, and the activity coefficients

Compute the concentrations of the non-basis species (call ncmpx.f)

(author's note: Figure 5 (page 1 of 4). Simplified flow diagram for creation of starting values and pre-Newton-Raphson optimization (from the viewpoint of module arrsel.f).
Compute the residual functions (beta, betamx, bbig, bneg); determine which species dominates each mass balance; if in auto basis switching mode, make list of proposed switches (call betas.f)

Calculate the convergence function (betfnc)

If a species dominates more than one mass balance, resolve the conflict in favor of the balance with the greater residual function (these results are used in the cycle algorithm) (call eqlib/gbfac.f)

no

In auto basis switching mode?

yes

Is loop at maximum value?

no

Disallow candidate switches which are intrinsically impossible due to the nature of the constraints used

Resolve any conflicts in candidate basis switches (call eqlib/gabswx.f)

yes

Make basis switches (call eqlib/autosw.f)

Recompute the thermodynamic data to match the reactions that were rewritten by basis switching (call eqlib/evdalr.f)

Recompute the mass balance stoichiometric factors (call eqlib/gests.f)

Go back to label 25 to make another auto basis switching loop

Calculate the electrical balance residual (bxecor)

Compute cycle convergence test condition (qtestc), based on the values of the residual norms betamx, bbig, bneg, and bxecor

TO PAGE 1

Figure 5 (continued, page 2 of 4). Simplified flow diagram for creation of starting values and pre-Newton-Raphson optimization (from the viewpoint of module arrset.f).
Apply the cycle algorithm to recalculate the concentrations of the basis species.

Go back to label 3220 to do another cycle.

Save "old" values of $\Sigma m$, $\ell$, and the activity coefficients.

Compute new values of $\Sigma m$, $\ell$, and the activity coefficients, applying change limits; compute associated residuals as the difference between new (ignoring change limits) and old values (bsbm, bxi, and bgamx); recalculate the concentrations of the non-basis species (call eqlib/ngeadv.f).

Compute pass convergence test condition (qtestp), based on the values of the residual norms bshm, bxi, and bgamx.

Is the pass test satisfied?

Is $\ell$ at maximum value?

Increment the divergence counter negative, or zero it as appropriate.

Is the cycle iteration diverging?

Applying the cycle algorithm to recalculate the concentrations of the basis species.

Go back to label 3220 to do another cycle.

TO PAGE 1

Optimization has failed; write a message to this effect to the output and screen files; Quit.

EXIT.

Go back to label 3210 to do another pass.

TO PAGE 1

Figure 5 (continued, page 3 of 4). Simplified flow diagram for creation of starting values and pre-Newton-Raphson optimization (from the viewpoint of module arrset.f).
Figure 5 (continued, page 4 of 4). Simplified flow diagram for creation of starting values and pre-Newton-Raphson optimization (from the viewpoint of module arrset.f).
Zero the del array (correction vector) and related variables, such as iter (iteration counter), betfnc and delfnc (convergence functions), upconv (partial convergence counter), and negbfc (divergence counter); set rlxfac (relaxation factor) to 1.0.

Compute the residual functions (beta, betamx, bbig, bnep); determine which species dominates each mass balance; if in auto basis switching mode, make list of proposed switches (call eqlih/betas.f).

Iter > 1?

Both convergence tests satisfied?

Hybrid Newton-Raphson iteration has succeeded}

Figure 6 (page 1 of 2). Simplified flow diagram for hybrid Newton-Raphson iteration (from the viewpoint of the EQLIB module newton.f).
Figure 6 (continued, page 2 of 2). Simplified flow diagram for hybrid Newton-Raphson iteration (from the viewpoint of the EQLIB module newton.f).
Save the current values of beta (the residual function vector) and del (the correction vector); save the current values of the variables delmax (max norm of del) and delfnc (convergence function measuring improvement in delmax).

Are the convergence tests on residuals satisfied?

Yes: Increment npconv (convergence counter) by 1.

No: Are npconv ≥ 42?

Yes: Have pseudo-convergence; do not make another Newton-Raphson step.

No: EXIT

Set npconv to zero

Iter > 8?

Yes: Does delfnc indicate divergence?

No: Increment negdfc (divergence counter) by 1.

Yes: negdfc ≥ 6?

Yes: Have strong indication of divergence; do not make another Newton-Raphson step.

No: Set negdfc to zero.

EXIT

Figure 6 (page 1 of 4). Simplified flow diagram for a Newton-Raphson step (from the viewpoint of the EQLIB module nrstep.f).
Have strong indication of divergence; do not make another Newton-Raphson step

Have done the maximum number of iterations; do not make another Newton-Raphson step

Figure 6 (page 2 of 4). Simplified flow diagram for a Newton-Raphson step (from the viewpoint of the EQLIB module nrstep.f).
Increment iter by 1

Compute aa, the Jacobian matrix (call eq3nr/matrix.f or eqs/matrixz.f)

Compute rhs, the right hand side vector (rhs = -alpha)

Compute del by solving the matrix equation (call eqlib/insolv.f)

Error flag set?

Have a computationally singular matrix; can not make a Newton-Raphson step

EXIT

Calculate delmax (max norm on del) and the convergence function delfnc

Compute the initial value of rlxfac (the under-relaxation factor)

Set ncut = -1

Label 275: Increment ncut by 1

Apply relaxed Newton-Raphson correction

Compute concentrations or number of moles of the non-basis species (call eq3nr/ncmpx.f or eqs/ncmpz.f)

Compute the residual functions (alpha, beta, betamx, bbig, bneg) (call eq3nr/betas.f or eqs/betas.f)

Compute btfcnr (convergence function, similar to betfnc, but computed prior to any additional under-relaxation)

Figure 7 (page 3 of 4). Simplified flow diagram for a Newton-Raphson step (from the viewpoint of the EQLIB module nrstep.f).
Figure 7 (page 4 of 4). Simplified flow diagram for a Newton-Raphson step (from the viewpoint of the EQLIB module nrstep.f).
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Jackson, K. J., 1988, Verification and Validation Studies of the Addition of Pitzer's Equations to the EQ3/6 Brine Model: UCRL-53841, Lawrence Livermore National Laboratory, Livermore, California.


Appendix A: Glossary of Major Variables in EQ3NR

This glossary covers the major variables in EQ3NR. Almost all of these are also shared by EQ6 (Wolery and Daveler, 1992). Those which are unique to EQ3NR 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.

Some of the entries in this glossary are described as either “data file ordered” or “input file ordered”. The former refers to the indexing of arrays that have been filled by reading the data file, datal. The latter refers to the indexing of arrays that have been filled by reading the input file. Since the two forms of indexing are not equivalent, EQ3NR must correlate them. This is done by mapping “input file ordered” data into a form which corresponds to “data file ordering,” which is the ordering which is used in the code calculations. Most data arrays which are “input file ordered” are therefore treated as holding arrays and play no further role in the calculation once the data in them has been mapped to corresponding arrays which are “data file ordered.”

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 pal. The names of the corresponding dimensioning variables end, respectively, in max, mx, and mxl. Thus, the dimension of the aa matrix is given by the pair kpar/kmax. The maximum number of aqueous species is given by nstpar/nstmax. 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 maximum number of Newton-Raphson iterations.

\[ \] \[ \text{The Jacobian matrix. Dimensioning: aa(kpar,kpar). Usage: aa(krow,kcol) is the element corresponding to the krow-th row and the kcol-th column. Note: In EQ3NR, this is also used as the matrix that is required for simultaneous solutions in pre-Newton-Raphson optimization.} \]

\[ \text{aadh} \] \[ \text{Interpolating polynomial coefficients for computing the Debye-Hückel parameter } A_{y,0} (adh) \text{ as a function of temperature. Dimensioning: aadh(narx,ntpr). Usage: aadh(narx,ntpr) refers to the narx-th coefficient for the ntpr-th temperature range.} \]
**aaphi** Interpolating polynomial coefficients for computing the Debye-Hückel parameter \( A_q \) (aaphi) as a function of temperature. Dimensioning: aaphi(narxpa,ntprpa). Usage: aaphi(narx,ntpr) refers to the narx-th coefficient for the ntpr-th temperature range.

**abdh** Interpolating polynomial coefficients for computing the Debye-Hückel parameter \( B_y \) (bdh) as a function of temperature. Dimensioning: abdh(narxpa,ntprpa). Usage: abdh(narx,ntpr) refers to the narx-th coefficient for the ntpr-th temperature range.

**abdot** Interpolating polynomial coefficients for computing the extended Debye-Hückel parameter \( \tilde{B} \) (abdot) as a function of temperature. Dimensioning: abdot(narxpa,ntprpa). Usage: abdot(narx,ntpr) refers to the narx-th coefficient for the ntpr-th temperature range.


**adh** Debye-Hückel \( A_y \) parameter for computing the base ten logarithm of the molal activity coefficient of an aqueous species.

**aeh** Interpolating polynomial coefficients for computing the special equilibrium constant \( \log K_{eh} \) (xkeh) as a function of temperature. Dimensioning: aeh(narxpa,ntprpa). Usage: aeh(narx,ntpr) refers to the narx-th coefficient for the ntpr-th temperature range.


**afflx** Affinity of a solid solution phase to precipitate, kcal. Dimensioning: afflx(nxtpar). Usage: afflx(nx) refers to the affinity of the nx-th solid solution.

**affx** Affinity of an end-member component of a solid solution. Dimensioning: affx(iktpar,xtpar). Usage: affx(ik,nx) refers to the affinity of the ik-th end-member component of the nx-th solid solution.

**ags** Interpolating polynomial coefficients for computing the array of equilibrium constants \( x_{lkg} \). Dimensioning: ags(narxpa,ntprpa,nstpar). Usage: ags(narx,ntpr,ng) refers to the narx-th coefficient for the ntpr-th temperature range for the ng-th gas species.


2.303 In 10; note: the value 2.303 is generally an insufficient approximation; this parameter should be calculated to the full machine precision to avoid problems with numerical consistency.
\( \text{amn} \) Interpolating polynomial coefficients for computing the array of equilibrium constants \( x_{ikm} \). Dimensioning: \( \text{amn}(\text{narx}, \text{ntpr}, \text{nm}) \). Usage: \( \text{amn}(\text{narx}, \text{ntpr}, \text{nm}) \) refers to the \( \text{narx} \)-th coefficient for the \( \text{ntpr} \)-th temperature range for the \( \text{nm} \)-th pure mineral.

\( A_\phi \) \( \text{aphi} \) Debye-Hückel \( A_\phi \) parameter.

\( \text{apress} \) Interpolating polynomial coefficients for computing the pressure (\( \text{press} \)) as a function of temperature. Dimensioning: \( \text{apress}(\text{narx}, \text{ntpr}) \). Usage: \( \text{apress}(\text{narx}, \text{ntpr}) \) refers to the \( \text{narx} \)-th coefficient for the \( \text{ntpr} \)-th temperature range.

\( \text{ard} \) Holding array used to read in the interpolating polynomial coefficients used to compute equilibrium constants of various kinds of reactions. Dimensioning: \( \text{ard}(\text{narx}, \text{ntpr}) \). Usage: \( \text{ard}(\text{narx}, \text{ntpr}) \) is the \( \text{narx} \)-th coefficient for the \( \text{ntpr} \)-th temperature range of the current reaction.

\( P_{\psi} \) \( \text{apx} \) Solid solution activity coefficient model parameters. Dimensioning: \( \text{apx}(i, \text{nx}) \). Usage: \( \text{apx}(i, \text{nx}) \) refers to the \( i \)-th coefficient for the \( \text{nx} \)-th solid solution.

\( \text{ars} \) Interpolating polynomial coefficients for computing the array of equilibrium constants \( x_{iks} \). Dimensioning: \( \text{ars}(\text{narx}, \text{ntpr}, \text{nst}) \). Usage: \( \text{ars}(\text{narx}, \text{ntpr}, \text{nst}) \) refers to the \( \text{narx} \)-th coefficient for the \( \text{ntpr} \)-th temperature range for the \( \text{nst} \)-th aqueous species.

\( \text{atwt} \) Atomic weight of a chemical element. Dimensioning: \( \text{atwt}(\text{nc}) \). Usage: \( \text{atwt}(\text{nc}) \) refers to the \( \text{nc} \)-th chemical element.

\( \text{azer} \) Hard core diameter of an aqueous species. Dimensioning: \( \text{azer}(\text{nst}) \). Usage: \( \text{azer}(\text{nst}) \) refers to the \( \text{nst} \)-th aqueous species.

\( \text{bbig} \) The mass balance residual (an element of the \( \text{beta} \) array) which has the most extreme positive value; if none is positive, this is assigned a value of zero. The name of the associated basis species is given in the variable \( \text{ubbig} \).

\( B_\gamma \) \( \text{bdh} \) Debye-Hückel \( B_\gamma \) parameter.

\( \beta \) \( \text{beta} \) Residual function vector, with mass balance elements normalized. Dimensioning: \( \text{beta}(\text{kpar}) \). Usage: \( \text{beta}(\text{kcol}) \) refers to the \( \text{kcol} \)-th master iteration variable.

\( \beta_{\text{max}} \) \( \text{betam} \) \( \text{betmax} \) Max norm of \( \beta \).

\( \text{betmxo} \) The previous value of \( \text{betam} \).

\( \dot{\beta} \) \( \text{bdot} \) Extended Debye-Hückel B-dot parameter.

\( \text{bfac} \) Array of \( (\beta + 1)^n \) factors used in pre-Newton-Raphson optimization. Dimensioning: \( \text{bfac}(\text{kpar}) \). Usage: \( \text{bfac}(\text{kcol}) \) refers to the \( \text{kcol} \)-th master iteration variable.
The max norm of activity coefficient residual functions; the name of the associated species is given in the variable abgamx.

Array of third order primitive virial coefficients of Pitzer's equations (25°C values). Dimensioning: bmu(nmupar). Usage: bmu(k) is the coefficient for the k-th species triplet. See dmu1, dmu2, nmu, and pmu.

The mass balance residual (an element of the beta array) which has the most extreme negative value; if none is negative, this is assigned a value of zero. The name of the associated basis species is given in the variable abneg.

Array of second order "short range" primitive virial coefficient parameters of Pitzer's equations (25°C values). Dimensioning: bslm(3,aslpar). Usage: bslm(n,k) is the n-th such parameter for the k-th species pair. See dslm1, dslm2, nslm, and pslm.

The b factor appearing in the Debye-Hückel term in Pitzer's equations; it is assigned a constant value of 1.2.


Reaction coefficient for dissolution reactions of gas species. Dimensioning: cdrg(nsqpar,ngipar). Usage: cdrg(ns,ng) is the coefficient of the ns-th aqueous basis species appearing in the dissolution reaction for the ng-th gas; cdrg(nsq1,ng) is the coefficient of the ng-th gas itself.

Reaction coefficient for the dissolution reactions of pure minerals. Dimensioning: cdrm(nsqpar,nmtpar). Usage: cdrm(ns,nm) is the coefficient of the ns-th aqueous basis species appearing in the dissolution reaction of the nm-th pure mineral; cdrm(nsq1,nm) is the coefficient of the nm-th pure mineral itself.

Reaction coefficient for aqueous redox and dissociation reactions. Dimensioning: cdrs(nsqpar,nrtpar). Usage: cdrs(ns,nrs) is the coefficient of the ns-th aqueous basis species appearing in the nrs-th aqueous dissociation/destruction reaction; cdrs(nsq1,nrs) is the coefficient of the associated species (of index nsc = nrs + nsb). If the ns-th species is an auxiliary basis species and nrs is its own formally associated reaction, cdrs(ns,nrs) = 0 and cdrs(nsq1,nrs) is its coefficient.

Holding array used to read in the coefficients of reactions listed on the data file. Dimensioning: cdrsd(nsqpar). Usage: cdrsd(n) is the n-th coefficient in the current reaction as it is written on the data file; it corresponds to the species whose name is udrxd(n).

Array containing the elemental composition coefficients of aqueous species. Dimensioning: cess(nctpar,nstpar). Usage: cess(ne,ns) is the coefficient of the ne-th chemical element for the ns-th aqueous species.

Holding array used to read in the elemental composition coefficients of species listed on the data file. Dimensioning: cessd(nsqpar). Usage: cessd(n) is the n-th coef-
ciss
Temporary storage array used to decode the elemental composition coefficients of species listed on the data file. Dimensioning: ciss(nsqpal). Usage: ciss(nc) is the coefficient for the nc-th element. This array is used to transfer data between the cissd array and the ciss array.

$m_i$
Molar concentration of an aqueous species. Dimensioning: conc(nstpar). Usage: conc(ns) is the molar concentration of the ns-th aqueous species. This is defined as zero for water, even its molality is technically fixed at $\Omega (= 55.51)$.

$log m_i$
Log molar concentration of an aqueous species. Dimensioning: conclg(nslpar). Usage: conclg(ns) is the log molar concentration of the ns-th aqueous species.

$m_j$
Molar concentrations of the aqueous species, sorted in order of increasing value. Dimensioning: csort(nstpar). Usage: primarily as a storage array required for the sorting; csort(n) = conc(jsort(n)). It is unique to EQ3NR.

csp
Constraining parameter array; the meaning of each member of this array is determined by the corresponding member of the jflag array. Dimensioning: csp(nsqpal). Usage: cspfns) is the constraining parameter for the ns-th aqueous basis species. This array is data file ordered. It is unique to EQ3NR.

cspb
Holding array into which the csp values are read from the input file. Dimensioning: cspb(nsqpal). Usage: cspb(n) is the constraining parameter for the n-th aqueous basis species listed on the input file. This array is input file ordered. It is unique to EQ3NR.

cstor
Stoichiometric mass balance factors of aqueous species for oxygen in the $O^{2-}$ valence form and hydrogen in the $H^+$ valence form. Dimensioning: cstor(2,nstpar). Usage: cstor(1,ns) is the factor for the ns-th aqueous species in the mass balance for $O^{2-}$; cstor(2,ns) is the corresponding factor in the mass balance for $H^+$. This array is used to set up the corresponding parts of the csts array. It is unique to EQ3NR.

$
\mu s's$
Mass balance coefficient array. Dimensioning: csts(nsqpal,nstpar). Usage: csts(nse,ns) is the coefficient of the ns-th aqueous species in the mass balance equation for the nse-th basis species. It is unique to EQ3NR.

crer
Equivalent total molality of a chemical element in a given valence form or combination of valence forms in mutual equilibrium. Dimensioning: cte(nsqpal). Usage: cte(ns) is the equivalent total molality of the ns-th aqueous basis species.

$\delta$
Newton-Raphson correction term vector. Dimensioning: del(kpar). Usage: del(kcol) is the correction term for the kcol-th master iteration variable.

$\delta_{func}$
Convergence function that measures the improvement in delmax, defined as $(1.0 - (delmax/delmax0))$. 

$\delta_{max}$
Max norm of $\delta$.

delmaxo
The previous value of delmax.
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W$</td>
<td>Array of partial derivatives of the log mole fraction of water with respect to the log molalities of the solute basis species. Dimensioning: $\text{dlogxw}(\text{nsqpar})$. Usage: $\text{dlogxw}(\text{ns})$ is the partial derivative with respect to the $\text{ns}$-th basis species.</td>
</tr>
<tr>
<td>$\frac{d\mu_{ijk}}{dT}$</td>
<td>Array of first derivatives with respect to temperature of third order primitive virial coefficients of Pitzer's equations (25°C values). Dimensioning: $\text{dmu1}(\text{nmupar})$. Usage: $\text{dmu1}(k)$ is the derivative for the $k$-th species triplet. See $\text{bmu}$, $\text{dmu2}$, $\text{nmux}$, and $\text{pmu}$.</td>
</tr>
<tr>
<td>$\frac{d^2\mu_{ijk}}{dT^2}$</td>
<td>Array of second derivatives with respect to temperature of third order primitive virial coefficients of Pitzer's equations (25°C values). Dimensioning: $\text{dmu2}(\text{nmupar})$. Usage: $\text{dmu1}(k)$ is the derivative for the $k$-th species triplet. See $\text{bmu}$, $\text{dmu1}$, $\text{nmux}$, and $\text{pmu}$.</td>
</tr>
<tr>
<td>$\frac{d\Sigma_{\lambda_{ij}}^{(n)}}{dT}$</td>
<td>Array of first derivatives with respect to temperature of second order &quot;short range&quot; primitive virial coefficient parameters of Pitzer's equations (25°C values). Dimensioning: $\text{dsm1}(3,\text{nsqpar})$. Usage: $\text{dsm1}(n,k)$ is the $n$-th such parameter for the $k$-th species pair. See $\text{bslm}$, $\text{dsm2}$, $\text{nslx}$, $\text{pslm}$, and $\text{pslam}$.</td>
</tr>
<tr>
<td>$\frac{d^2\Sigma_{\lambda_{ij}}^{(n)}}{dT^2}$</td>
<td>Array of second derivatives with respect to temperature of second order &quot;short range&quot; primitive virial coefficient parameters of Pitzer's equations (25°C values). Dimensioning: $\text{dsm2}(3,\text{nsqpar})$. Usage: $\text{dsm2}(n,k)$ is the $n$-th such parameter for the $k$-th species pair. See $\text{bslm}$, $\text{dsm1}$, $\text{nslx}$, $\text{pslm}$, and $\text{pslam}$.</td>
</tr>
<tr>
<td>$\text{ee}$</td>
<td>A work array used in solving matrix equations. Dimensioning: $\text{ee}(\text{kpar})$.</td>
</tr>
<tr>
<td>$\text{efac}$</td>
<td>Array of reciprocal stoichiometric weighting factors used in pre-Newton-Raphson optimization; this is the $\frac{1}{\beta^n}$ which appears in the array of $1$ factors used in this optimization method. Dimensioning: $\text{efac}(\text{nsqpar})$. Usage: $\text{efac}(\text{ns})$ is the factor for the $\text{ns}$-th basis species.</td>
</tr>
<tr>
<td>$\text{Eh}$</td>
<td>Redox potential, volts.</td>
</tr>
<tr>
<td>$\text{F}$</td>
<td>Faraday, The Faraday constant, 23062.3 cal/equivalent-volt.</td>
</tr>
<tr>
<td>$\text{f02}$</td>
<td>Oxygen fugacity, bars.</td>
</tr>
</tbody>
</table>
Log oxygen fugacity.

Array of fugacities of gas species. Dimensioning: \texttt{fug(ngtpar)}. Usage: \texttt{fug(ng)} is the fugacity of the \texttt{ng}-th gas species.

Array of log fugacities of gas species. Dimensioning: \texttt{fuglg(ngtpar)}. Usage: \texttt{fuglg(ng)} is the log fugacity of the \texttt{ng}-th gas species.

The function \( g(x) \) which appears in Pitzer's equations. Dimensioning: \texttt{g(2)}. Usage: 
\[
g(1) = g(\alpha_1 \sqrt{f}) \quad \text{and} \quad g(2) = g(\alpha_2 \sqrt{f}) .
\]

The function \( g'(x) \) which appears in Pitzer's equations. Dimensioning: \texttt{gp(2)}. Usage: 
\[
gp(1) = g'(\alpha_1 \sqrt{f}) \quad \text{and} \quad gp(2) = g'(\alpha_2 \sqrt{f}) .
\]

Array of log activity coefficients of aqueous species; this is a mole fraction activity coefficient for water and a molal activity coefficient for all solute species. Dimensioning: \texttt{glg(nstpar)}. Usage: \texttt{glg(ns)} is the log activity coefficient of the \texttt{ns}-th aqueous species.

Array of previous values of log activity coefficients of aqueous species. Dimensioning: \texttt{glgo(nstpar)}.

A work array that is used to store a copy of \texttt{aa}, the Jacobian matrix. Dimensioning: \texttt{gm(kpar,kpar)}.

Maximum number of coefficients for determining activity coefficient parameters per solid solution in the \texttt{apx} array. This is the variable equivalent to the parameter \texttt{iapxpa}.

Dimensioning parameter: the maximum number of coefficients for determining activity coefficient parameters per solid solution in the \texttt{apx} array. See \texttt{iapxmx}.

Array that contains a record of basis switching. Dimensioning: \texttt{ibasis(nstpar)}. Usage: if \texttt{ibasis(ns)} is not 0, then the \texttt{ns}-th species was switched with the species whose index is given by \texttt{ibasis(ns)}.

The index of the element of the \texttt{beta} array corresponding to the max norm (\texttt{betamx})

Array that contains the indices of species which are candidates for switching into the basis set. This is a part of the automatic basis switching mechanism. Dimensioning: \texttt{ibswx(nsqpar)}. Usage: if \texttt{ibswx(ns)} is not 0, then it gives the index of a species to switch with the \texttt{ns}-th basis species.

The index of the aqueous species chosen for electrical balancing.

Flag controlling whether or not higher order electrostatic terms are used in Pitzer's equations. It is set by the \texttt{ueltam} flag on the supporting data file and has the following meanings:

- \texttt{-1} Higher order electrostatic terms are not used
- \texttt{1} They are used
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.

iindex

Array containing the indices of the basis species for which the starting iteration values must be estimated simultaneously. Dimensioning: iindex(nsqpar). Usage: iindex(n) is the n-th such species.

iindx1

Array that contains the indices of the species for which the master iteration variables are defined. Dimensioning: iindx1(kpar). Usage: iindx1(kcoel) is the index of the species corresponding to the kcoel-th master iteration variable.

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 iktpar.

insgfl

Flag array for determining how to compute the activity coefficient of a neutral solute species in conjunction with the B-dot equation. Dimensioning: insgfl(nstpar). Usage: insgfl(ns) is the flag for the ns-th aqueous species:

= 0 Set log \( \gamma_i \) = 0 (polar species)
= -1 Use the Drummond (1981) polynomial (non-polar species).

ioo, etc.

Debugging print option switches; see Chapter 6. Some of these switches differ from those used in EQ6.

iopg1, etc.

Activity coefficient option switches; see Chapter 6.

ioprl, etc.

Print option switches; see Chapter 6. Some of these switches differ from those used in EQ6.

ioptl, etc.

Model option switches; see Chapter 6. Some of these switches differ from those used in EQ6.

ir

A work array used in solving matrix equations. Dimensioning: ir(kpar).

irang

The real*8 machine exponent range parameter (the exponent range is \(+irang\)).

istack

A work array used to sort aqueous species in increasing order of concentration. Dimensioning: istack(nstpar).

itermx

Limit on the number of Newton-Raphson iterations.

izm

The max norm on the electrical charges of the aqueous species.

jcf slg

Status flag array for chemical elements. Dimensioning: jcf slg(nctpar). Usage: jcf slg(nc) is the flag for the nc-th element:

= 0 An element does not appear in the current model
= 1 It does appear
**jflag**
Switch array that defines the type of constraint (governing equation) applied to each basis species. Dimensioning: `jflag(nsqpar)`. Usage: `jflag(ns)` is the flag for the `ns`-th basis species. See Chapter 6.

**jflagb**
Array used to read in `jflag` values from the input file. Dimensioning: `jflagb(nsqpar)`. Usage: `jflagb(n)` is the `jflag` value for the `n`-th basis species read from the input file. This array is thus input file ordered. It is unique to EQ3NR.

**jgflag**
Status switch array for gas species. Dimensioning: `jgflag(ngtpar)`. Usage: `jgflag(ng)` is the flag for the `ng`-th gas:
- `0` The gas species appears in the current model
- `2` It is thermodynamically suppressed

**jkflag**
Status switch array for solid solution end-member components. Dimensioning: `jkflag(iktpar,iutpar)`. Usage: `jkflag(ik,nx)` is the flag for the `ik`-ili end-member component of the `nx`-th solid solution:
- `0` The component appears in the current model
- `2` It is thermodynamically suppressed
- `4` It could not be found among the pure minerals

**jmflag**
Status switch array for pure minerals. Dimensioning: `jmflag(nmtpar)`. Usage: `jmflag(nm)` is the flag for the `nm`-th pure mineral:
- `0` The mineral appears in the current model
- `2` It is thermodynamically suppressed

**jrs**
The indices of the aqueous reactions, sorted in increasing order of concentration of the associated species. Dimensioning: `jrs(nrstpa)`. Usage: `jrs(n)` is the index of the reaction which corresponds to the non-basis aqueous species whose concentration is `n`-th in this order. This array is used in making sorted summations.

**jsflag**
Status switch array for aqueous species. Dimensioning: `jsflag(nstpar)`. Usage: `jsflag(ns)` is the flag for the `ns`-th aqueous species:
- `0` The species appears in the current model
- `2` It is thermodynamically suppressed
- `3` It does not appear in the current model

**jsol**
Array whose values define chosen models of activity coefficients in solid solutions. Dimensioning: `jsol(nxtpar)`. Usage: `jsol(nx)` is the flag for the `nx`-th solid solution:
- `0` Ideal solution
(The data files currently support no other options.)

**jsort**
The indices of the aqueous species, sorted in increasing order of concentration. Dimensioning: `jsort(nstpar)`. Usage: `jsort(n)` is the index of the aqueous species whose concentration is `n`-th in this order. This array is used in making sorted summations.

**jstack**
A work array used in sorting aqueous species in increasing order of concentration. Dimensioning: `jstack(nstpar)`.  

**jxflag**
Status switch array for solid solutions. Dimensioning: `jxflag(nxtpar)`. Usage: `jxflag(nx)` is the flag for the `nx`-th solid solution:
- `0` The phase appears in the current model
- `4` It has no active end-member components
**jxmod**  Flag specifying the type of a species/reaction affected by an alter/suppress option specified on the input file. Dimensioning: jxmod(nxmdpa). Usage: jxmod(n) is the flag for the n-th such option specified (see kxmod, uxmod, xlkmod, and nxmod):

- 0  Aqueous species/reaction
- 1  Pure mineral
- 2  Gas
- 3  Solid solution

**kct**  Number of chemical elements present in the aqueous system currently being modeled.

**kction**  A pointer array used in pre-Newton-Raphson optimization. It points to entries in the subset of master iteration variables which must be solved simultaneously which correspond to basis species used to complete the definition of input constraints for other basis species. Dimensioning: kction(nsqpar). Usage: kction(n) is the index in this subset for the basis species which completes the constraint definition for the basis species whose index in this subset is n. It is unique to EQ3NR.

**kdim**  Dimension of the Jacobian matrix; kdim = ksq in EQ3NR.

**kebal**  Variable denoting the position of the species selected for electrical balancing in the set of master iteration variables. It is unique to EQ3NR.

**khydr**  Variable denoting the position of $H^+$ in the set of master iteration variables.

**kkndex**  Array which marks those basis species whose concentrations must be initially estimated simultaneously. Dimensioning: kkndex(nsqpar). Usage: kkndex(n) is the flag for the n-th such species:

- 0  Do not estimate simultaneously
- 1  Estimate simultaneously

It is unique to EQ3NR.

**kmax**  The maximum number of master variables readable by EQ6. This is the variable corresponding to the parameter kpar.

**kpar**  Dimensioning parameter: the maximum number of master variables readable by EQ6. See kmax.

**ksb**  Variable denoting the position of the species used as the redox variable, currently $O_{2(g)}$ only; ksb = kct + 1.

**ksq**  The number of active basis species.

**kxmod**  Flag defining the type of alter/suppress option specified on the input file. Dimensioning: kxmod(nxmdpa). Usage: kxmod(n) is the flag for the n-th such option specified (see jxmod, uxmod, xlkmod, and nxmod):

- -1  The corresponding species/reaction is suppressed
- 0  Its log $K$ is replaced by xlkmod
- 1  Its log $K$ is augmented by xlkmod
- 2  Same as = 1, but xlkmod is given in units of kcal/mole

**$\log \lambda_{nw}$**  Array of log activity coefficients of solid solution end-member components. Dimensioning: lamlg(iktpar,nsxpar). Usage: lamlg(ik,nx) is the activity coefficient for the ik-th end-member component of the nx-th solid solution.
<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m_{\text{te}}$</td>
<td>Array of total molalities of dissolved chemical elements. Dimensioning: $m_{\text{te}}(\text{nctpar})$. Usage: $m_{\text{te}}(\text{nc})$ is the molality of the $\text{nc}$-th element.</td>
</tr>
<tr>
<td>$M_i$</td>
<td>Array of molecular weights of aqueous species. Dimensioning: $m_{\text{wtss}}(\text{nstpar})$. Usage: $m_{\text{wtss}}(\text{ns})$ is the molecular weight of the $\text{ns}$-th aqueous species.</td>
</tr>
<tr>
<td>$n_{\text{adi}}$</td>
<td>The unit number of the data file.</td>
</tr>
<tr>
<td>$n_{\text{alpha}}$</td>
<td>A pointer array used to find the $\alpha_f$ and $\alpha_2$ parameters of Pitzer's equations for a species pair for which $\delta_{ij}$ and $\delta_{i}^{j}$ values are to be calculated. Dimensioning: $n_{\text{alpha}}(\text{ns})$. Usage: $p_{\text{alpha}}(1,n_{\text{alpha}}(n)) = \alpha_f$ and $p_{\text{alpha}}(2,n_{\text{alpha}}(n)) = \alpha_2$ for the $n$-th such solute species pair.</td>
</tr>
<tr>
<td>$n_{\text{appar}}$</td>
<td>Dimensioning parameter: the maximum number of distinct pairs of $\alpha_f$, $\alpha_2$ parameters of Pitzer's equations. See $n_{\text{apt}}$.</td>
</tr>
<tr>
<td>$n_{\text{apt}}$</td>
<td>The maximum number of distinct pairs of $\alpha_f$, $\alpha_2$ parameters of Pitzer's equations. This is the variable corresponding to the dimensioning parameter $n_{\text{appar}}$.</td>
</tr>
<tr>
<td>$n_{\text{arxmx}}$</td>
<td>The maximum number of coefficients per temperature range for an interpolating polynomial coefficient array such as $\text{ars}$ and $\text{amn}$. This is the variable corresponding to the parameter $n_{\text{arxpa}}$.</td>
</tr>
<tr>
<td>$n_{\text{arxpa}}$</td>
<td>Dimensioning parameter: the maximum number of coefficients per temperature range for an interpolating polynomial coefficient array. See $n_{\text{arxmx}}$.</td>
</tr>
<tr>
<td>$n_{\text{chlor}}$</td>
<td>The index of the species $\text{Cl}^-$.</td>
</tr>
<tr>
<td>$n_{\text{comp}}$</td>
<td>Array giving the number of end-member components in a solid solution. Dimensioning: $n_{\text{comp}}(\text{nxtpar})$. Usage: $n_{\text{comp}}(\text{nx})$ is the number of such components for the $\text{nx}$-th solid solution.</td>
</tr>
<tr>
<td>$n_{\text{compb}}$</td>
<td>Array giving the number of solid solution end-member components of solid solutions for which mole fractions are read from the input file. Dimensioning: $n_{\text{compb}}(\text{nxbpar})$. Usage: $n_{\text{compb}}(\text{nxb})$ is the number of such components for the $\text{nxb}$-th solid solution so listed on the input file.</td>
</tr>
<tr>
<td>$n_{\text{et}}$</td>
<td>Total number of chemical elements.</td>
</tr>
<tr>
<td>$n_{\text{etmax}}$</td>
<td>The maximum number of chemical elements. This is a variable which corresponds to the parameter $n_{\text{etpar}}$.</td>
</tr>
<tr>
<td>$n_{\text{etpar}}$</td>
<td>Dimensioning parameter: the maximum number of chemical elements. See $n_{\text{etmax}}$.</td>
</tr>
<tr>
<td>$n_{\text{end}}$</td>
<td>Array that stores the indices of pure minerals that correspond to end-member components of solid solutions. Dimensioning: $n_{\text{end}}(\text{iktpar},\text{nxtpar})$. Usage: $n_{\text{end}}(\text{ik},\text{nx})$ is the pure mineral index for the $\text{ik}$-th component of the $\text{nx}$-th solid solution.</td>
</tr>
<tr>
<td>$n_{\text{fac}}$</td>
<td>Array of indices of dominant species. Dimensioning: $n_{\text{fac}}(\text{nsqpar})$. Usage: $n_{\text{fac}}(\text{ns})$ is the index of the dominant species in the mass balance for the $\text{ns}$-th basis species.</td>
</tr>
</tbody>
</table>
\( \eta \)

\( \eta_T \)

\( \eta_T \) Total number of gas species.

\( \eta_T \max \)

The maximum number of gas species. This is a variable which corresponds to the parameter \( \eta_T \par \).

\( \eta_T \par \)

Dimensioning parameter: the maximum number of gas species. See \( \eta_T \max \).

\( \eta_{hydr} \)

The index of the species \( H^* \).

\( \eta_{inpt} \)

The unit number of the input file.

\( \eta_{inpts} \)

The unit number of the file which is a copy of the input file that has been stripped of comment lines.

\( \eta_{mlx} \)

The number of entries in the \( \eta_{mlxx} \) pointer array, which is used in evaluating terms in the \( \mu_{ijk} \) coefficients in Pitzer's equations.

\( \Phi_T \)

\( \Phi_T \) Total number of pure minerals.

\( \Phi_T \max \)

Maximum number of pure minerals.

\( \Phi_T \par \)

Dimensioning parameter: the maximum number of pure minerals. See \( \Phi_T \max \).

\( \Phi_{mu} \)

The number of species triplets with \( \mu_{ijk} \) coefficients specified for use in evaluating Pitzer's equations.

\( \Phi_{mut} \)

The maximum number of species triplets with \( \mu_{ijk} \) coefficients specified for use in evaluating Pitzer's equations. This is the variable corresponding to the dimensioning parameter \( \Phi_{mu} \).

\( \Phi_{mu} \par \)

Dimensioning parameter: the maximum number of entries in the \( \Phi_{mlxx} \) pointer array, which is used in evaluating terms in the \( \mu_{ijk} \) coefficients in Pitzer's equations. To be absolutely safe, one could set \( \Phi_{mxpar} \) equal to \( 3*\Phi_{mu} \par \). See \( \Phi_{mxpar} \).

\( \Phi_{mx} \)

Array identifying the species in triplets with \( \mu_{ijk} \) coefficients specified for use in evaluating Pitzer's equations. Dimensioning: \( \Phi_{mx}(3,\Phi_{mnpar}) \). Usage: \( \Phi_{mx}(i,kk) \) is the index of the \( i \)-th species in the \( k \)-th triplet.

\( \Phi_{mx} \par \)

Dimensioning parameter: the maximum number of entries in the \( \Phi_{mlxx} \) pointer array, which is used in evaluating terms in the \( \mu_{ijk} \) coefficients in Pitzer's equations. For a given species whose index is \( ns \), the corresponding range in the \( \Phi_{mx} \) array is defined by \( kk \) in the range from \( \Phi_{mx}(1,ns) \) to \( \Phi_{mx}(2,ns) \). This combination of
pointer arrays is useful in evaluating the sum, \(3 \sum_{j} \sum_{k} \mu_{ijk} m_j m_k\), which appears in the expression for the solute activity coefficient.

**nmxt**
The maximum number of entries in the *nmxx* pointer array, which is used in evaluating terms in the \(\mu_{ijk}\) coefficients in Pitzer's equations. This is the variable corresponding to the dimensioning parameter *nmxpar*.

**noutput**
The unit number of the output file.

**npkup**
The unit number of the pickup file.

**nrst**
The maximum number of reactions among aqueous species.

**nrstmx**
The maximum number of aqueous reactions. This is a variable corresponding to the parameter *nrstpa*.

**nrstpa**
Dimensioning parameter: the maximum number of aqueous reactions. See *nrstmx*.

**nsb**
The number of strict basis species. Also the index denoting the aqueous redox species (currently \(O_2\)); \(nsb = \text{net} + 1\).

**nsb1**
Index denoting the first species in the auxiliary basis set; \(nsb1 = nsb + 1\).

**nslpar**
Dimensioning parameter: the maximum number of species pairs having \(S_{ij}^{(n)}\) parameters specified for evaluation of Pitzer's equations. See *nslmt*.

**nslm**
The number of species pairs with \(S_{ij}^{(n)}\) parameters specified for use in evaluating Pitzer's equations.

**nslmt**
The maximum number of species pairs with \(S_{ij}^{(n)}\) parameters specified for evaluation of Pitzer's equations. This is the variable corresponding to the dimensioning parameter *nslpar*.

**nslmx**
Array identifying the species in pairs with \(S_{ij}^{(n)}\) parameters specified for use in evaluating Pitzer's equations. Dimensioning: \(nslmx(2,nslpar)\). Usage: \(nslmx(i,k)\) is the index of the \(i\)-th species in the \(k\)-th pair.

**nslx**
The number of entries in the *nslx* pointer array, which is used in evaluating terms in the \(S_{ij}^{(n)}\) parameters in Pitzer's equations.

**nsp**
Array containing the indices of the aqueous, mineral, solid solution end-member component, or gas species that are required to define certain kinds of constraints on basis species on the input file. Dimensioning: \(nsp(nspar)\). Usage: \(nsp(ns)\) is the index of the species for the constraint place on the \(ns\)-th basis species. This never refers to the \(ns\)-th basis species itself, but always a second species. Phase equilibrium (solubility) constraints and log activity combination and mean log activity constraints all require the specification of such second species. This array is data file ordered. It is unique to EQ3NR.
**nspec**

Array that contains the indices of the basis species which appear on the input file. 
Dimensioning: `nspec(nsqpar)`. Usage: `nspec(n)` is the index of the n-th basis species appearing on the input file. It is thus input file ordered. It is unique to EQ3NR.

**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, `cels(nsq1,nrs)` refers to the coefficient of the associated aqueous species destroyed in the nrs-th reaction.

**nsqb**

Number of basis species which appear on the input file.

**nsqmax**

The maximum number of aqueous basis species. This is the variable corresponding to the parameter `nsqpar`.

**nsqmx1**

A variable equal to `nsqmax + 1`. This corresponds to the parameter `nsqpar1`.

**nsqpar**

Dimensioning parameter: the equivalent of `nsqpar + 1`. See `nsqmax`.

**nst**

Total number of aqueous species; this currently includes all basis species but only those non-basis species appearing in the system for a given problem defined on the input file.

**nstmax**

The maximum number of aqueous species. This is a variable corresponding to the parameter `nstpar`.

**nstpar**

Dimensioning parameter: the maximum number of aqueous species. See `nstmax`.

**nsxi**

A pointer array which gives the range in the `nsxx` array. Dimensioning: `nsxi(2,nstpar)`. Usage: `nsxi(1,ns)` to `nsxi(2,ns)` is the range in the `nsxx` array corresponding to the species whose index is `ns`.

**nsxpar**

Dimensioning parameter: the maximum number of entries in the `nsxi` pointer array, which is used in evaluating terms in the \( S_{ij} \) coefficients in Pitzer's equations. To be absolutely safe, one could set `nsxpar` equal to `2*MUPAR`. See `nsxt`.

**nsx**

The maximum number of entries in the `nsxi` pointer array, which is used in evaluating terms in the \( S_{ij} \) coefficients in Pitzer's equations. This is the variable corresponding to the dimensioning parameter `nsxpar`.

**nsxx**

An ordered pointer array constructed from the `nstmax` array which, when used in connection with the `nsxi` pointer array, gives for each solute species the index of the other species appearing in a pair for the \( S_{ij} \) coefficients in Pitzer's equations and also the index of the pair itself. Dimensioning: `nsxx(2,nsxpar)`. Usage: `nsxx(1,kk)` is the index of the other species in the kk-th entry and `nsxx(2,kk)` is the pair itself. For a given species whose index is `ns`, the corresponding range in the `nsxx` array is defined by `kk` in the range from `nsxi(1,ns)` to `nsxi(2,ns)`. This combination of point-
er arrays is useful in evaluating the sum, $\sum_j \lambda_j m_j$, which appears in the expression for the solute activity coefficient.

`ntitl` The number of lines of the title on the input file.

`ntild` The number of lines of the title on the data1 file.

`ntitm` The maximum number of lines of the title on the input or data1 file. This is a variable corresponding to the parameter `ntitpa`.

`ntitpa` Dimensioning parameter: the maximum number of lines of the title on the input or data1 file. See `ntitm`.

`ntpr` The index of the temperature range corresponding to the temperature specified on the input file.

`ntprm` The maximum number of temperature ranges for an interpolating polynomial coefficient array such as `ars` and `amn`. This is a variable corresponding to the parameter `ntprpa`.

`ntprpa` Dimensioning parameter: the maximum number of temperature ranges for an interpolating polynomial coefficient array such as `ars` and `amn`. See `ntprm`.

`nttyo` The unit number of the screen file.

`nxmdm` The maximum number of alter/suppress options that can be specified on the input file. This is a variable corresponding to the parameter `nxmdpa`.

`nxmdpa` Dimensioning parameter: the maximum number of alter/suppress options that can be specified on the input file. See `nxmdm`.

`nxmod` The number of species/reactions affected by alter/suppress options specified on the input file. See `jxmod`, `kxmod`, `uxmod`, and `xlkmod`.

`nxt` Total number of solid solution phases.

`nxtb` Number of solid solutions whose compositions are read from the input file. It is unique to EQ3NR.

`nxtmax` The maximum number of solid solutions. This is a variable corresponding to the parameter `nxtpar`.

`nxtpar` Dimensioning parameter: the maximum number of solid solutions. See `nxtmax`.

`om` The water constant, $1000 +$ the molecular weight of water ($\Omega = 55.51$).

`omlg` Log water constant.

`oscoff` The osmotic coefficient.

$\alpha_1$, $\alpha_2$ The $\alpha_1$ and $\alpha_2$ parameters of Pitzer's equations. Dimensioning: `palpha(2,nappar)`.

Usage: `palpha(1,k) = \alpha_1` and `palpha(2,k) = \alpha_2` for the $k$-th distinct pair of $\alpha_1$, $\alpha_2$. 

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values; \( k = n\alpha(n) \) for the \( n \)-th solute species pair for which \( \gamma_{ij} \) and \( \delta_{ij} \) coefficients are to be computed.

\( pe \)  
The electron activity function; \( pe = -\log a_e \).

\( \mu_{ij,k} \)  
Array of third order primitive virial coefficients of Pitzer's equations (values at the current specified temperature). Dimensioning: \( \mu_{ij,k}(nmupar) \). Usage: \( \mu_{ij,k}(k) \) is the coefficient for the \( k \)-th species triplet. See bmu, dmu1, dmu2, and nmux.

\( P \)  
Pressure, bars.

\( S_{\gamma_{ij}} \)  
Array of second order "short range" primitive virial coefficients of Pitzer's equations (values at the current specified temperature). Dimensioning: \( S_{\gamma_{ij}}(nslpar) \). Usage: \( S_{\gamma_{ij}}(n,k) \) is the \( n \)-th such coefficient for the \( k \)-th species pair. See bslm, dslm1, dslm2, nslmx, and pslam.

\( S_{\delta_{ij}} \)  
Array of second order "short range" primitive virial coefficient parameters of Pitzer's equations (values at the current specified temperature). Dimensioning: \( S_{\delta_{ij}}(nslpar) \). Usage: \( S_{\delta_{ij}}(n,k) \) is the \( n \)-th such parameter for the \( k \)-th species pair. See bslm, dslm1, dslm2, nslmx, and pslam.

\( qbassw \)  
Logical flag indicating whether or not basis switching has taken place.

\( qbswx \)  
Logical flag indicating whether or not there are candidates for automatic basis switching.

\( r \)  
The gas constant, 1.98726 cal/mol·K.

\( \rho_{gml} \)  
Density of aqueous solution, g/ml. It is unique to EQ3NR.

\( -a \)  
A negative copy of the array alpha. Dimensioning: \( -a(kpar) \).

\( J(x) \)  
The \( J(x) \) function used in Pitzer's equations.

\( J(x) \)  
The \( J(x) \) function used in Pitzer's equations.

\( screwd \)  
Under-relaxation parameter that bounds delmax.

\( log QlK \)  
Saturation index of a solid solution end-member component. Dimensioning: \( si(iktpar,nxtpar) \). Usage: \( si(ik,mx) \) is the saturation index for the \( ik \)-th component of the \( mx \)-th solid solution.

\( log QlK \)  
Array of saturation indices of solid solutions. Dimensioning: \( siss(nxtpar) \). Usage: \( siss(mx) \) is the saturation index of the \( mx \)-th solid solution.

\( H_{sr}, H_{sr} \)  
The \( H_{sr} \) or \( H_{sr} \) factors defined in Chapter 9. Dimensioning: \( stor1(arstpa) \). Usage: \( stor1(nrs) \) is the factor for the \( nrs \)-th reaction. Note that these are defined in terms of molalities in EQ3NR, whereas they are defined in terms of moles in EQ6.
tdamax The nominal upper temperature limit of the data file, °C.

tdamin The nominal lower temperature limit of the data file, °C.

$C_{75, mg/kg}$ Total dissolved salts, mg/kg. This is unique to EQ3NR.

$C_{75, mg/L}$ Total dissolved salts, mg/L. This is unique to EQ3NR.

tempc Temperature, °C.

tempk Temperature, °K.

tolbt Convergence bound on betamx.

toldl Convergence bound on delmax.

tol saturated Limit on the absolute value of the affinity of a mineral of fixed composition for the mineral to be listed as "saturated" on the output file. This is unique to EQ3NR.

tolxat Limit on the absolute value of the affinity of a solid solution for the phase to be listed as "saturated" on the output file. This is unique to EQ3NR.

uactop Character string describing the model selected by the user for computing the activity coefficients of aqueous species; this is set by the iopgl value read from the input file.

ubasis Array of names of aqueous species that are to be switched into the basis set. Dimensioning: ubasis(nsqpar). Usage: ubasis(ns) is the name of the species to be switched into the basis set in place of the ns-th basis species.

ubbig The name of the basis species corresponding to the mass balance residual with the most extreme positive value; if none is positive, ubbig is assigned a value of 'none'.

ubgamx The name of the species corresponding to the max norm (bgamx) of activity coefficient residual functions.

ubneg The name of the basis species corresponding to the mass balance residual with the most extreme negative value; if none is negative, ubneg is assigned a value of 'none'.

ucode A variable containing the name of the code.

udrxd Holding array used to read in the names of species appearing in reactions listed on the data file. Dimensioning: udrxd(nsqpal). Usage: udrxd(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. See cdrsd.

uelam Flag read from the supporting data file indicating whether or not higher order electrostatic terms are to be used in Pitzer's equations:

- 'off' Higher order electrostatic terms are not used
- 'on' They are used

uelem Array of names of chemical elements (their chemical symbols). Dimensioning: uelem(nctpar). Usage: uelem(nc) is the name of the nc-th element.
uelnd  Holding array of names of chemical elements. Dimensioning: uelnd(nctpar). Usage: uelnd(n) is the name of the n-th element listed for the current species. See cessed.

uendt  The string 'endt.'.

ueqlrn  A string containing the release number of the supporting EQLIB library.

ueqlst  A string containing the stage number of the supporting EQLIB library.

ugas  Array of names of gas species. Dimensioning: ugas(nqpar). Usage: ugas(n) is the name of the n-th gas species.

ujtype  Array of character strings that describe the jflag options. Dimensioning: ujtype(nsqpar).

umemb  Array of names of solid solution end-member components appearing on the input file. Dimensioning: umemb(iktpar,nxtpar). Usage: umemb(ikb,nxb) is the name of the ikb-th component in the nxb-th solid solution whose composition is given on the input file. It is thus input file ordered. It is unique to EQ3NR.

umin  Array of name of pure minerals. Dimensioning: umin(nmtpar). Usage: umin(n) is the name of the n-th pure mineral.

undms  Array of names of data file basis species appearing on the EQ3NR pickup file and the EQ6 input file. Dimensioning: undms(nsqpar). Usage: undms(n) is the name of the n-th such species appearing on one of these files.

unone  The string 'none'.

unrms  Array of names of run basis species appearing on the EQ3NR pickup file and the EQ6 input file. Dimensioning: unrms(nsqpar). Usage: unrms(n) is the name of the n-th such species appearing on one of these files. If unrms(n) refers to a different species than undms(n), then the former is to be switched into the basis set in place of the latter.

uphas1  Array of names of aqueous basis species or mineral, solid solution, or gas species required to complete the definition of an input constraint under the jflag = 17, 18, 19, 20, and 21 options. Dimensioning: uphas1(nsqpar). Usage: uphas1(n) is the name of such a species required to complete the constraint for the n-th basis species appearing on the input file. This array is input file ordered. It is unique to EQ3NR.

uphas2  Array of names of solid solution end-member components required to complete the definition of an input constraint under the jflag = 20 option. Dimensioning: uphas2(nsqpar). Usage: uphas2(n) is the name of such a species required to complete the constraint for the n-th basis species appearing on the input file. This array is input file ordered. It is unique to EQ3NR.

uredox  The name of an auxiliary basis species which is part of an aqueous redox couple used to calculate the default redox state of aqueous redox couples. It is unique to EQ3NR.

urelno  A string containing the release number of the code it is contained in.
usolb Array of names of solid solution phases whose composition are specified on the input file. Dimensioning: usolb(nxpar). Usage: usolb(nx) is the name of the nx-th such phase. This array is input file ordered. It is unique to EQ3NR.

usolx Array of names of solid solutions. Dimensioning: usolx(nxpar). Usage: usolx(nx) is the name of the nx-th solid solution.

uspec Array of names of aqueous species. Dimensioning: uspec(nstpar). Usage: uspec(ns) is the name of the ns-th aqueous species.

uspecb Array of names of aqueous basis species listed on the input file. Dimensioning: uspecb(ns). Usage: uspecb(ns) is the name of the ns-th such species. This array is input file ordered. It is unique to EQ3NR.

ussnp Array of names of solid solution end members listed on the data1 file which fail to correspond to any pure mineral on the same file. Dimensioning: ussnp(nxpar). Usage: ussnp(nx) is the name of the nx-th solid solution.

ustage A string containing the stage number of the code it is contained in.

util The title (text) from the input file. Dimensioning: util(ntitpa). Usage: util(n) is the n-th line of this title.

utild The title (text) from the data1 file. Dimensioning: utild(ntitpa). Usage: utild(n) is the n-th line of this title.

uxmod The name of a species for which an alter/suppress option is specified on the input file. Dimensioning: uxmod(nxmdpa). Usage: uxmod(nx) is the name of the species for the nx-th such option specified (see jxmod, kxmod, xlkmod, and nxmod).

uxtype Array of character strings that describe the solid solution activity coefficient models defined by the jsol flag. Dimensioning: uxtypel(10). Usage: uxtypel(n) is the string which describes the model identified by jsol(n).

uzvec1 Array containing the names of the species corresponding to master iteration variables. Dimensioning: uzvec1(kpar). Usage: uzvec1(k) is the species name corresponding to the k-th master iteration variable.

vmin0 Array containing the molar volumes of the pure minerals. Dimensioning: vmin0(nmtpar). Usage: vmin0(nm) is the molar volume of the nm-th pure mineral.

\[ V_g \]

volg The volume of a perfect gas at 298.15°C K and 1 bar pressure; \( V_g = 22413.6 \text{ cm}^3 \). It is unique to EQ3NR.

\[ W_i, W_{i'j'}, W_{ij} \]

w Array of solid solution activity coefficient model parameters. Dimensioning: w(i,x). Usage: w(i,nx) is the i-th parameter for the nx-th solid solution. These are computed from the coefficients in the apx array.

weight A work array containing weighting factors for aqueous species used in evaluating balance equations. Dimensioning: weight(nstpar). Usage: weight(ns) is the factor for the ns-th aqueous species.
weight fraction of solvent water in aqueous solution.

Array of mole fractions of solid solution end-member components. Dimensioning: $x_{\text{bar}}(ik, nx)$. Usage: $x_{\text{bar}}(ik, nx)$ is the mole fraction of the $ik$-th component of the $nx$-th solid solution.

Array of mole fractions of solid solution end-member components read from the input file. Dimensioning: $x_{\text{barb}}(ik, nx)$. Usage: $x_{\text{barb}}(ik, nx)$ is the mole fraction of the $ik$-th component given for the $nx$-th solid solution listed. This array is input file ordered. It is unique to EQ3NR.

Array of mole fractions of solid solution end-member components corresponding to the compositions that maximize the saturation indices of the corresponding phases. Dimensioning: $x_{\text{barh}}(ik, nx)$. Usage: $x_{\text{barh}}(ik, nx)$ is the mole fraction of the $ik$-th component of the $nx$-th solid solution which maximizes the saturation index of this phase.

Array of log mole fractions of solid solution end-member components. Dimensioning: $x_{\text{barlg}}(ik, nx)$. Usage: $x_{\text{barlg}}(ik, nx)$ is the log mole fraction of the $ik$-th component of the $nx$-th solid solution.

The mole fraction of solvent water.

The log mole fraction of solvent water.

Ionic strength, molal.

Log equilibrium constant of the half reaction relating the hypothetical electron and $O_2(g)$.

Array of log equilibrium constants of the dissolution reactions of gas species. Dimensioning: $x_{\text{lk}}(ng)$. Usage: $x_{\text{lk}}(ng)$ is the log equilibrium constant for the $ng$-th gas.

Array of log equilibrium constants of the dissolution reactions of pure minerals. Dimensioning: $x_{\text{lm}}(nm)$. Usage: $x_{\text{lm}}(nm)$ is the log equilibrium constant for the $nm$-th pure mineral.

The log $K$ alter option parameter for an alter/suppress option specified on the input file. Dimensioning: $x_{\text{lkmod}}(nxmd)$. Usage: $x_{\text{lkmod}}(n)$ is the parameter for the $n$-th such option specified (see $jxmod$, $kxmod$, $uxmod$, and $rxmod$).

Array of log equilibrium constants of the dissociation/destruction reactions of aqueous species. Dimensioning: $x_{\text{ls}}(nrs)$. Usage: $x_{\text{ls}}(nrs)$ is the log equilibrium constant for the $nrs$-th such species.

Array of saturation indices of pure minerals. Dimensioning: $x_{\text{lk}}(nm)$. Usage: $x_{\text{lk}}(nm)$ is the saturation index for the $nm$-th pure mineral.

Array of saturation indices of solid solution end-member components. Dimensioning: $x_{\text{qkx}}(ik, nx)$. Usage: $x_{\text{qkx}}(ik, nx)$ is the saturation index for the $ik$-th component of the $nx$-th solid solution.
Array of electrical charges of the aqueous species. Dimensioning: \( z(nstpar) \). Usage: \( z(ns) \) is the electrical charge of the \( ns \)-th aqueous species.

Array of values equal to one half the charge squared of the aqueous species. Dimensioning: \( zsq2(nstpar) \). Usage: \( zsq2(ns) \) is one half the charge squared for the \( ns \)-th aqueous species.

Array of logarithmic master iteration variables. Dimensioning: \( zvelg1(kpar) \). Usage: \( zvelg1(kcol) \) is the value of the \( kcol \)-th logarithmic master iteration variable.
Appendix B. Glossary of EQ3NR Modules

EQ3NR is a moderately large code. The source code consists of the main program and a number of subroutines. In addition, EQ3NR uses a number of modules from the EQLIB library. These are described in Appendix B of the EQ3/6 Package Overview and Installation Guide (Wolery, 1992). 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 10.

arrset.f  This module is called by eq3nr.f. It sets up the matrix structure for Newton-Raphson iteration and estimates starting values for the iteration variables. The initial estimates are refined according to a pre-Newton-Raphson optimization algorithm. They may also be refined by automatic basis switching, if this feature is enabled.

arrsim.f  This module is called by arrset.f to compute those basis species concentrations which by the nature of the chosen constraints must be estimated simultaneously.

balcon.f  This module is called by matrix.f. It writes the part of the Jacobian matrix that consists of rows corresponding to balance equations (mass and charge balance).

betas.f    This module is called by arrset.f and the EQLIB modules newton.f and nrstep.f (these latter two modules call it as betae). It computes the residual functions (\( \phi \), \( \beta \), and \( f_{\text{max}} \)).

dawfix.f  This module is called by arrsim.f. It determines whether or not the problem input constraints directly fix the activity of water, as for example would happen if one constrained dissolved calcium by equilibrium with gypsum and dissolved sulfate by equilibrium with anhydrite.

echox.f   This module is called by eq3nr.f. It writes a description of the input problem on the output file. Unlike the "instant echo" of the input file, this description includes data file statistics, any default values that were chosen by EQ3NR, and any changes in the input constraint options made by the code to resolve inconsistencies among these constraints or with truncation limits imposed on certain run parameters.

eq3nr.f  This is the main program of EQ3NR. It supervises the speciation-solubility calculation. It connects the necessary files (input, data1, output, pickup, and rlist). It initializes key arrays and sets default values for important run parameters. It also does an extensive checking of the problem that has been input, looking for inconsistencies and missing inputs that are required by the options chosen.

figstx.f  This module is called by eq3nr.f. It sets up the species status switch arrays jsflag, jmflag, jkflag, jxflag and jgflag.

gases.f  This module is called by scripx.f. It computes the equilibrium fugacities of gas species.

gcsp.f The module is called by ndatx.f. It interprets the constraints (jflag, csp) for basis species listed on the input file by matching the species names with those read from the supporting data file.

getrdx.f  This module is called by rdtyp4.f. It gets the redox constraints specified on the input file in "D" format.

getspc.f  This module is called by both getrdx.f and rdtyp4.f. It gets input constraints for the basis species listed on the input file in "D" format.

getss.f  This module is called by both getspc.f and rdtyp5.f. It gets solid solution data that are part of constraints listed on the input file in "D" format.
indatx.f  This module is called by eq3nr.f. It reads the data file data1.

init3v.f  This module is called by rdninp.f.

matrix.f  This module is called by the EQLIB routine nrslep.f (which calls it by the name of matrxe). It computes the Jacobian matrix (J).

ncmpx.f  This module is called by arrset.f and the EQLIB modules nrgadv.f and nrslep.f (which call it by the name of ncmpe). It computes all parameters that derive from the primary iteration variables and are necessary to write the Jacobian matrix (e.g., all aqueous species concentrations and activities).

ndiagx.f  This module is called by eq3nr.f. If Newton-Raphson iteration fails, it attempts to generate diagnostics.

rd3lds.f  This module is called by rdninp.f. It gets the input for total dissolved salts from the input file in “D” format.

rdinp.f  This module is called by eq3nr.f. It oversees reading the input file. If the input file is in “W” format, it calls readx.f to carry out this function. If the input file is in “D” format, it calls rdninp.f to do this.

rdninp.f  This module is called by rdinp.f. It carries out reading the input file in “D” format.

rdtyp1.f  This module is called by rdninp.f. It gets the input for temperature and density from the input file in “D” format.

rdtyp2.f  This module is called by rdninp.f. It gets the input for electrical balancing from the input file in “D” format.

rdtyp4.f  This module is called by rdninp.f. It gets the input for the basis species constraints from the input file in “D” format. It does this by calling getrdx.f and getspef.f.

rdtyp5.f  This module is called by rdninp.f. It gets the input for solid solutions from the input file in “D” format. It calls getss.f.

rdtyp9.f  This module is called by rdninp.f. It gets the input for tolbt, toldt, tolsat, and itermx from the input file in “D” format.

readx.f  This module reads the input file in “W” format. It writes an “instant echo” of this input data on the output file. It contains full internal documentation.

scribo.f  This module is called by eq3nr.f. It writes the pickup file in “W” format.

scribx.f  This module is called by eq3nr.f. It writes the pickup file in “D” format.

scripx.f  This module is called by eq3nr.f. This module writes the results of the speciation-solubility calculation on the output file.

setup.f  This module is called by eq3nr.f. This module converts input concentration data other than molalities to molalities.
Appendix C. EQ3NR 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 input 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 which could possibly indicate an error, but normally does not. All three types of messages are written to both the screen file and the output file. If an error message is issued, analysis of the problem may be facilitated by checking any preceding error, warning, or note messages.

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, eq3m, 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 usingAAAAA to stand for a character variable, IIII for an integer, and RRRR for a floating point number.

Most of the error messages that users are likely to encounter deal with problems regarding the input file, the data file, or both of these. 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. If this does not suffice to identify corrective action, compare the instant echo of the input file on the output file with the original input file. You may find that certain data were not entered in the correct fields, that certain inputs fail to correspond with the necessary lines to follow, or that a line is missing or you have an extra line. In addition, it may help to re-run the problem with the debugging option switch iodbl set to 1 or 2. This will trigger the printing of additional information which should help to identify the problem. A small number of messages deal with installation errors. These should also be quite clear.

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. Users of EQ3NR may also encounter error messages from EQLIB modules. These messages are listed in similar format in the EQ3/6 Package Overview and Installation Guide (Wolery, 1992). The errors are listed first, then the warnings and finally the notes.

Message: * error - (eq3nr/arrset) Have encountered an automatic basis switching error in loop IIII.

Comment: This is a programming error.
Message: * error - (eq3nr/arrsim) The phase assemblage by the specified solubility constraints fixes the activity of water. The code is presently unable to solve problems of this type.

Message: * error - (eq3nr/arrsim) The specified counterfoil "AAAA" in the jflag = 17 or 18 option for "AAAA" is not in the basis set.

Message: * error - (eq3nr/arrsim) The speciation model appears to be singular. There is probably a violation of the mineralogic phase rule in the set of solubility constraints specified on the input file.

Message: * error - (eq3nr/arrsim) Have encountered an illegal jflag value = IIII for the species "AAAA".

Message: * error - (eq3nr/arrsim) Can not use the jflag= III option for "AAAA" because this species is suppressed.

Message: * error - (eq3nr/arrsim) Can not use the jflag= III option for "AAAA" because this species has no charge.

Message: * error - (eq3nr/arrsim) Can not use the jflag= III option for "AAAA" because the specified counterion "AAAA" is not in the active basis set.

Message: * error - (eq3nr/arrsim) Can not use the jflag= III option for "AAAA" because the specified counterion "AAAA" is not in the present system.

Message: * error - (eq3nr/arrsim) Can not use the jflag= III option for "AAAA" because the specified counterion "AAAA" is suppressed.

Message: * error - (eq3nr/arrsim) Can not use the jflag= III option for "AAAA" because the specified counterion "AAAA" has zero charge.

Message: * error - (eq3nr/arrsim) Choosing ioptl = -3 requires setting jflag(o2(g)) to 19, 20, or 21. The input file has jflag(o2(g)) = Iin.

Message: * error - (eq3nr/arrsim) The species "AAAA" was selected to determine the redox state, but the associated reaction is not a redox reaction.

Message: * error - (eq3nr/arrsim) The species "AAAA" was selected to determine the redox state, but it is not in the present system.

Message: * error - (eq3nr/arrsim) The species "AAAA" was selected to specify the redox state, but it has a jflag value of IIII. The jflag for such species can not have a value of 27 or 30.

Comment: You have to enter some actual data for this species. The jflag = 27 and 30 options do not correspond to input of actual data.

Message: * error - (eq3nr/arrsim) The species "AAAA" was selected to specify the redox state, but the necessary corresponding strict basis species representing the complementary oxidation state is not in the present system.

Comment: To use this option for the redox state, you must enter data for both the auxiliary basis species whose associated reaction defines the couple, and the strict basis species which represents the other half of the redox couple and appears in that reaction.
Message: * error - (eq3nr/eq3nr) Have illegal negative csp value of RRR for the basis species "AAAA".

Message: * error - (eq3nr/eq3nr) Did you mean to specify alkalinity for "AAAA"? Because of theoretical problems with the concept and not uncommon analytical difficulties, EQ3/6 no longer allows the use of alkalinity.

Comment: If you have not already done so, read the section on alkalinity in Chapter 2.

Message: * error - (eq3nr/eq3nr) The species "AAAA" cannot be constrained by the reaction.

Comment: This is followed by the reaction in question.

Message: * error - (eq3nr/eq3nr) The species "AAAA" cannot be constrained by equilibrium with a solid solution because iopt4 = III, not 2.

Comment: In order to use such a constraint, it is necessary to input the composition of the solid solution.

Message: * error - (eq3nr/eq3nr) The species "AAAA" has a jflag value of III. This is not permitted. This species is in the strict basis set and therefore has no associated reaction in which it is destroyed.

Message: * error - (eq3nr/eq3nr) The following heterogeneous reaction constraint has been used more than once.

Comment: This is followed by the reaction in question.

Message: * error - (eq3nr/eq3nr) The input file has jflag(o2(g) = III). This requires iopt1 to be -3, but iopt1 is now set to III.

Message: * error - (eq3nr/eq3nr) Hybrid newton-raphson iteration failed after III steps. Calling diagnostics routine.

Message: * error - (eq3nr/eq3sp) The basis species "AAAA" was specified more than once on the input file.

Message: * error - (eq3nr/getrdx) When specifying redox parameters, column four must contain "eh", "pe", "o2(g)" or "redox couple". Check INPUT file line: IIII

Message: * error - (eq3nr/getrdx) Break line or end-of-file found where redox couple input was expected. Check INPUT file line: IIII

Message: * error - (eq3nr/getspc) Species was not specified in column 1. Check INPUT file line: IIII

Message: * error - (eq3nr/getspc) Maximum number of allowed entries: IIII. Have exceeded this value on INPUT file line IIII

Message: * error - (eq3nr/getspc) The "pH" species can only be "h+". Check INPUT file line: IIII

Message: * error - (eq3nr/getspc) The "pHCl" species can only be "h+". Check INPUT file line: IIII

Message: * error - (eq3nr/getspc) Column 2 can not be blank for the "gas", "mineral", "log activity combo", and "log mean activity" constraints. Check INPUT file line: IIII

Message: * error - (eq3nr/getspc) Column 2 must left blank for the "log activity", "ph", and "phcl" constraints. Check INPUT file line: IIII

Message: * error - (eq3nr/getss) Maximum number of allowed entries: IIII. Have exceeded this value on INPUT file line: IIII
Message: * error - (eq3nr/getss) Must specify all end-members of a solid solution (mole fractions must sum to 1.0). Check above INPUT file line: III

Message: * error - (eq3nr/getss) Solid solution name can not be blank. Check INPUT file line: III

Message: * error - (eq3nr/getss) End-member names can not be blank. Check INPUT file line: III

Message: * error - (eq3nr/getss) Maximum number of end-members per solid solution: IIII. Check above INPUT file line: III

Message: * error - (eq3nr/indatx) Have wrong file header = "AAAA" on the data file. The first five characters must be 'data'.

Comment: Make sure you have not defined data to be a data file.

Message: * error - (eq3nr/indatx) The number of chemical elements on the data file is IIII. This exceeds the dimensioned limit (ncipar) of IIII.

Message: * error - (eq3nr/indatx) The number of basis species on the data file is IIII. This exceeds the dimensioned limit (nsqpar) of IIII.

Message: * error - (eq3nr/indatx) The composition of species "AAAA" on the data file is described in terms of an unrecognized chemical element called "AAAA". If this is an actual element, it is not in the list of chemical elements on this data file.

Message: * error - (eq3nr/indatx) The maximum number of aqueous species (nstpar) is IIII. This has been exceeded while trying to read the data file.

Message: * error - (eq3nr/indatx) The reaction for the destruction of the species "AAAA" is written on the data file in terms of an unrecognized basis species called "AAAA". If this is an actual species, it is not among the basis species on this data file.

Message: * error - (eq3nr/indatx) The maximum number of pure minerals (nmtpar) is IIII. This has been exceeded while trying to read the data file.

Message: * error - (eq3nr/indatx) The maximum number of gas species (nglpar) is IIII. This has been exceeded while trying to read the data file.

Message: * error - (eq3nr/indatx) The basis species "AAAA" was referenced on the input file but was not read from the data file.

Comment: The name of the basis species may contain a typographical error. Otherwise, the data file does not contain this species. You may be using the wrong data file.

Message: * error - (eq3nr/indatx) The maximum number of solid solutions (nxtpar) is IIII. This has been exceeded while trying to read the data file.

Message: * error - (eq3nr/indatx) The species "AAAA" is specified in user-directed basis switches to switch with both "AAAA" and "AAAA".

Message: * error - (eq3nr/indatx) The species "AAAA" is specified in a user-directed basis switch to switch with "AAAA", but is not in the list of aqueous species read from the data file.
Message: * error - (eq3nr/indatx) The species "AAAA" is required for an abs(zj)*log ai +/- abs(zi)*log aj constraint but was not read from the data file.

Message: * error - (eq3nr/indatx) The species "AAAA" is required for a log a(+/-,ij) constraint but was not read from the data file.

Comment: "a(+/-,ij)" denotes the mean activity of ions i and j.

Message: * error - (eq3nr/indatx) The species "AAAA" is required for a heterogeneous equilibrium constraint but was not read from the data file.

Message: * error - (eq3nr/matrix) Have encountered an illegal jflag value = IIII for the species "AAAA".

Comment: This is a programmer error.

Message: * error - (eq3nr/rdninp) Looking for heading: "AAAA" Found string: "AAAA" See INPUT file line: IIII

Message: * error - (eq3nr/rdninp) End-of-file unexpectedly encountered. See INPUT file line: IIII

Message: * error - (eq3nr/rdninp) Errors encountered while reading the INPUT file. Process stopped

Message: * error - (eq3nr/rdninp) The electrical balancing species "AAAA" was not found among the basis species listed on the input file.

Message: * error - (eq3nr/rdninp) The species "h+" must be specified in the species list on the input file.

Message: * error - (eq3nr/rdtyp2) Only one electrical balancing option can be selected. Check INPUT file line: IIII

Message: * error - (eq3nr/rdtyp9) Unrecognized tolerance variable "AAAA". Check INPUT file line: IIII

Message: * error - (eq3nr/rdtyp9) Invalid tolerance descriptor string "AAAA". Check INPUT file line: IIII

Message: * error - (eq3nr/readx) The input file has no title.

Message: * error - (eq3nr/readx) The maximum number of axmod options (axmdpa) is IIII. This has been exceeded while trying to read the input file.

Message: * error - (eq3nr/readx) The maximum number of basis species (nsqpar) is IIII. This has been exceeded while trying to read the data file.

Message: * error - (eq3nr/scribo) Bad pickup file has been written. The basis species "AAAA" appears on it but is not in the model.

Comment: The pickup file contains a strict basis species that is not in the model. You used an auxiliary basis species which is linked to this strict basis species. The EQ3NR calculation is still valid, but you cannot use the pickup file to input the solution model to EQ6. If you want to do this, re-run the problem switching the auxiliary basis species in question into the strict basis set.

Message: * error (eq3nr/setup) An undefined jflag value of IIII was specified for the basis species "AAAA".

Message: * warning - (eq3nr/eq3nr) The input file contains conflicting redox options - ioptl = IIII overrides jflag(o2(g)) = IIII.
Message: * warning - (eq3nr/eq3nr) The input file contains conflicting redox options - iopt1 = III overrides uredox = "AAAA".

Message: * warning - (eq3nr/eq3nr) The species "AAAA" was specified to be adjusted for electrical balance, but it is not in the set of basis species.

Message: * warning - (eq3nr/eq3nr) The species "AAAA" was specified to be adjusted for electrical balance, but it has no electrical charge. Success will depend on its concentration affecting that of one or more charged species with which it is in equilibrium.

Message: * warning - (eq3nr/eq3nr) The species "AAAA" was specified to be adjusted for electrical balance, but it is not in the present model.

Message: * warning - (eq3nr/eq3nr) Tried to pick a species to be adjusted for electrical balance, but did not succeed.

Message: * warning - (eq3nr/eq3nr) The species "AAAA" was specified to define the default redox state, but is not in the active auxiliary basis set.

Message: * warning - (eq3nr/eq3nr) The strict basis species "AAAA" has an illegal jflag value of IIII.

Message: * warning - (eq3nr/eq3nr) The input line for o2(g) will be ignored because iopt1 is not set to -3.

Message: * note - (eq3nr/arrsim) Can not switch the species "AAAA" out of the basis because it is tied up in a jflag = 17 or 18 option for another species.

Message: * note - (eq3nr/arrset) Optimization ended outside requested limits.

Comment: Don't panic. Hybrid Newton-Raphson iteration may still succeed. If so, the results of the run are still perfectly good. If it doesn't succeed, see the comment following the following message.

Message: * note - (eq3nr/arrset) Optimization ended far outside requested limits.

Comment: Don't panic. Hybrid Newton-Raphson iteration may still succeed, though the probability of this is significantly diminished. If it does succeed, the results of the run are still perfectly good. If it doesn't succeed, re-run with iodb set to 1 or 2 in order to see what is going on during the optimization stage. You may be able to get the problem to converge by directing the code to make certain basis switches.

Message: * note - (eq3nr/arrsim) The matrix solver routine (eqlib/msolvrt) failed.

Message: * note - (eq3nr/arrsim) The species "AAAA" has a required concentration near RRRR molal.

Comment: Don't panic. This is not always fatal. If the code fails to solve the problem, however, this probably means that one or more equilibrium constraints (jflag = 19, 20, 21, or 27) are such that no sensible answer exists to the problem currently posed. Think about what you are asking the code to do.

Message: * note - (eq3nr/echox) The species "AAAA" is not in the model.

Message: * note - (eq3nr/eq3nr) The input value for the iopr9 print option flag is inconsistent with the specified value of iopgl (choice of model for activity coefficients of aqueous species). The iopr9 flag has been reset to 0.

Message: * note - (eq3nr/eq3nr) Have picked the species "AAAA" to be adjusted for electrical balance. Any other specified constraint will be overridden.
Message: * note - (eq3nr/eq3nr) Could not compute acceptable starting estimates for Newton-Raphson iteration. Will therefore not attempt it.

Comment: Re-run with iodb set to 1 or 2 in order to see what is going on during the optimization stage. You may be able to get the problem to converge by directing the code to make certain basis switches.

Message: * note - (eq3nr/eq3nr) Can not write a valid pickup file for the current problem because the auxiliary basis species in each of the following strict-auxiliary basis species pair(s) is present in the model while the corresponding strict basis species is not. Add a trivial amount of each such strict basis species to the model, or switch it from the strict set to the auxiliary set and suppress it if necessary.

Comment: The relevant data follow this message. The pickup file contains a strict basis species that is not in the model. You used an auxiliary basis species which is linked to this strict basis species. The EQ3NR calculation is still valid, but you can not use the pickup file to input the solution model to EQ6. If you want to do this, re-run the problem switching the auxiliary basis species in question into the strict basis set.

Message: * note - (eq3nr/getspe) A non-zero concentration should not be specified as an input parameter for a "mineral", "solid solution", "dependent", or "eliminated" species. Check INPUT file line: IIII

Message: * note - (eq3nr/ndiagx) The ion being adjusted to achieve electrical balance is crashing to zero. Electrical balancing must be done on an ion of opposite charge.

Message: * note - (eq3nr/ndiagx) The oxygen fugacity is crashing, probably because a bad electrical balance constraint on H+ is causing the concentration of that species to crash to zero.

Message: * note - (eq3nr/ndiagx) The oxygen fugacity is crashing, probably because of a bad constraint on one of the aqueous species appearing in the redox reaction that is being used to constrain the redox state.

Message: * note - (eq3nr/ndiagx) No diagnostics were generated from the failed iteration. Look at the del and beta data in the iteration summary for clues to why it did not work.
Appendix D. Notes on Known Bugs and Such

This appendix presents notes on known bugs and other known unusual phenomena concerning EQ3NR.

1. The code tends to converge slowly or not at all in dealing with extremely concentrated electrolyte solutions. Roughly speaking, these are solutions whose ionic strengths are greater than about 12 molal. However, there is no simple way to accurately categorize the code's performance envelope.

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, 1992).