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WOLERY

**EQ3NR:
A Computer Program for Geochemical
Aqueous Speciation-Solubility Calculations:
User's Guide and Documentation**

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PREFACE

This report on the EQ3NR program is the first in a series of reports on computer programs used in modeling aqueous geochemical systems. To aid user understanding of EQ3NR applications, we have included the underlying geochemical theory and the numerical and computational methods by which the theory is implemented in the program. The report also explains EQTL, the data base preprocessor that supports both the EQ3NR and EQ6 programs. Separate reports, explaining the EQ6 and MCRT programs, should be published by the end of 1983. The EQ6 program calculates either reaction paths of reacting aqueous systems or heterogeneous equilibrium with fixed masses of chemical elements and was the subject of previous reports (Wolery, 1978, 1979). MCRT is a thermodynamic data base and temperature extrapolation program.

These programs are available to the public. The MCRT package consists of the MCRT program and related files. EQ3NR, EQ6, EQTL, and related files comprise the EQ3/6 package. These packages can be ordered from either Thomas J. Wolery, L-204, Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, CA, 94550, or the National Energy Software Center, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL, 60439.

Source codes and data files are not included in this report. Those who want to use EQ3NR should read Sections 1-7 and Appendices F-H. Those who are installing EQ3NR and related codes on a computer system for the first time should also read Appendices A-E and I.

The information in this report corresponds to the EQ3NR.3230U48, EQTL.3230U01, and EQ6.3230U01 codes in the EQ3/6.3230 package version. The sample problems we describe in the report were run with the DATA0.3230U01 (also designated DEQPAK9) thermodynamic data file. The internal documentation of this version of the data file is largely incomplete.

The computer programs and data bases in the EQ3/6 and MCRT series are the objects of a continuing effort of improvement and expansion. Comments from program users are welcome. We recommend that users identify the code or data base version for which they have comments so that we can easily respond to their queries.

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GLOSSARY OF SYMBOLS

- a Thermodynamic activity.
- α Debye-Huckel ion size parameter.
- A (a) Thermodynamic affinity. (b) Debye-Huckel A constant.
- Ah Thermodynamic affinity, per electron, of a redox couple with respect to the standard hydrogen electrode; $Ah = F E_h$ (see Section 2.3.5.3).
- A_t Titration alkalinity, equivalents per kilogram of water (see Section 2.3.3). Normally, defined by the pH 4.5--methyl orange--endpoint.
- A_c Carbonate alkalinity, equivalents per kilogram of water.
- B Debye-Huckel B constant. Sometimes called the extended Debye-Huckel constant (not to be confused with B , below).
- \dot{B} Extended Debye-Huckel \dot{B} parameter (Helgeson, 1969).
- B' Factor used in computing the activity of water as a function of equivalent stoichiometric ionic strength ($B' = 1 + w_1 I_E$).
- b Stoichiometric reaction coefficient (e.g., b_{sr} is the number of moles of aqueous species s appearing in reaction r ; b is negative for reactants and positive for products).
- c Stoichiometric mass coefficient (e.g., c_{cs} is the number of moles of element c per mole of aqueous species s).
- C Concentration of aqueous solute on the molar, mg/l., or mg/kg subscripted scales (see m).
- C_{TS} Total dissolved salts, mg/kg solution.
- D' Factor used in computing the activity of water as a function of I_E , the equivalent stoichiometric ionic strength:
- $$D' = 2.303 A / (w_1^3 I_E) .$$
- e^- Electron. In commonly practiced thermodynamic formalism this is a hypothetical aqueous species. (Though real aqueous electrons may actually exist, notably in gamma radiation fields, their thermodynamic properties are not identical to those of the hypothetical aqueous electron.)

E_h Theoretical equilibrium electrical potential of a redox couple,

$$E_h = [2.303RT/(4F)] (\log f_{O_2} - 4 pH - 2 \log a_{H_2O} - \log K_{Eh}) ,$$

where

f_{O_2} is understood to be the hypothetical equilibrium oxygen fugacity in aqueous solution.

f Fugacity.

f_{O_2} (a) Hypothetical equilibrium oxygen fugacity in aqueous solution.
(b) In less common usage in discussions involving aqueous solutions, the fugacity of real oxygen in a gas phase.

g Subscript indexing a gas species.

q_T Total number of gas species.

G_{XS} Excess Gibbs energy of solid solution.

F Faraday constant.

H_{SR} The factor: $m_{S^*} u_{S^*} / b_{S^*r}$, where $s^* = s_r$.

H_{Zr} The factor: $m_{S^*} z_{S^*} / b_{S^*r}$, where $s^* = s_r$.

H_{Tr} The factor: $m_{S^*} \tau_{S^*} / b_{S^*r}$, where $s^* = s_r$.

H_{1r} The factor: $m_{S^*} z_{S^*}^2 / 2b_{S^*r}$, where $s^* = s_r$.

H_{IEr} The factor: $m_{S^*} u_{S^*} / b_{S^*r}$, where $s^* = s_r$.

I Ionic strength.

IAP Ion activity product (see Q).

I_E Equivalent stoichiometric ionic strength of a sodium chloride solution; defined equivalent to the total molal concentration of either Na^+ or Cl^- .

J An element of the Jacobian matrix.

\underline{J} The Jacobian matrix ($\partial \alpha_i / \partial z_j$) used in Newton-Raphson iteration.

J' Factor used in computing the activity of water as a function of I_E , the equivalent stoichiometric ionic strength:

$$J' = B' - 2 \ln B' - 1/B' .$$

- K Thermodynamic equilibrium constant.
- K_{Eh} Thermodynamic equilibrium constant for the half-reaction:

$$2 \text{H}_2\text{O}(l) = \text{O}_2(g) + 4 \text{H}^+ + 4 \text{e}^- .$$
- L_r The quantity: $\sum_{s=2}^{s_Q} b_{sr} \Gamma_s .$
- l_s $\log_{10} m_s$ ($\log f_{\text{O}_2}$ in the special case $s = s_B$) .
- l_{I_E} $\log I$
- l_I $\log I$
- m Molal concentration of an aqueous species.
- m^T Total molal concentration of an aqueous species.
- M Molecular weight, grams per mole.
- n Mass of a species, in moles.
- n^T Total mass of a species, in moles.
- $\text{O}_2(g)$ Oxygen gas. In aqueous solution, this refers to a hypothetical species similar to e^- , also symbolized as O_2 .
- p Partial pressure of a gas.
- P Pressure.
- pe Logarithm of the hypothetical electron activity:
 $pe = F Eh / (2.303 RT) = Ah / (2.303 RT) .$
- Q Activity product of a reaction. IAP is also used for this definition (Parkhurst et al., 1980).
- r Subscript indexing an aqueous reaction.
- r_T Total number of aqueous reactions.
- R The gas constant.
- s Subscript indexing an aqueous species ($s = 1$ implies $\text{H}_2\text{O}(l)$).
- s_A Subscript denoting the master aqueous species (HCO_3^- or CO_3^{2-}) that is constrained by alkalinity balance.

- s_B Number of aqueous master species that formally correspond one-to-one with the chemical elements and charge balance; s_B specifically refers to the hypothetical aqueous species $O_2(g)$.
- s_E Subscript denoting the master aqueous species, either Na^+ or Cl^- , that defines I_E .
- s_g Subscript denoting a master aqueous species whose concentration is adjusted to satisfy solubility equilibrium with the gas denoted by g .
- s_Q The total number of aqueous master species. Depending on the problem at hand, s_Q is equal to or greater than s_B .
- s_T Total number of aqueous species.
- s_r Subscript indexing the aqueous species that formally corresponds to the r -th dissociation or aqueous redox reaction. Reactions are not formally associated with the first s_B aqueous species;
 $s_r = s_B + r$.
- s_z Subscript denoting the master aqueous species whose concentration is adjusted to achieve electrical balance.
- s_ψ Subscript denoting a master aqueous species whose concentration is adjusted to satisfy solubility equilibrium with the fixed composition mineral denoted by ψ .
- $s_{\sigma\psi}$ Subscript denoting a master aqueous species whose concentration is adjusted to satisfy solubility equilibrium with the end member component denoted by σ of the solid solution phase denoted by ψ .
- SI Saturation index for a mineral:
 $SI = \log (Q/K)$,
- where
 Q is the activity product for the dissolution reaction,
 K is the equilibrium constant for the dissolution reaction.
- t Time.
- T Kelvin temperature.
- u Stoichiometric coefficient calculated from the stoichiometric reaction coefficients and the JFLAG options specified for the problem at hand; $u_{s',s}$ relates the stoichiometric equivalence of species s' to master species s such that $u_{s',s} m_{s'}$ is the contribution of s' to mass balance written in terms of s .

w Coefficient for computing the activity of water.

W Solid solution excess of Gibbs energy parameter.

x (a) Mole fraction. (b) A general algebraic variable.

x_{H_2O} Mass fraction of H_2O in aqueous solution.

y Power series coefficient for computing $\gamma_{CO_2(aq)}$.

z (a) Electrical charge. (b) A master iteration variable, an element of the vector \underline{z} .

\underline{z} Vector of master Newton-Raphson iteration variables.

2.303 Symbol for and approximation to $\ln 10$.

\underline{a} Newton-Raphson residual function vector.

$\underline{\beta}$ Newton-Raphson residual function vector, identical to \underline{a} , with the exception that mass balance residual elements are normalized.

β_{max} Largest absolute value of any element of $\underline{\beta}$.

γ Activity coefficient of an aqueous species.

γ_T Stoichiometric activity coefficient of an aqueous species.

Γ_1 $d \log a_{H_2O} / d \log I_E$.

Γ_s $d \log m_s / d \log I$ (for s greater than 1).

$\underline{\delta}$ Newton-Raphson correction term vector.

δ_{max} Largest absolute value of any element of $\underline{\delta}$.

$\delta_{cor.}$ Newton-Raphson convergence function.

e Subscript indexing a chemical element.

ϵ_T Total number of chemical elements in a chemical system.

ξ Reaction progress variable.

κ Under-relaxation parameter in Newton-Raphson iteration.

λ Activity coefficient of a solid solution component.

Λ_{ij} $d \log \lambda_i / d \log x_j$.

μ	Chemical potential.
v_{CO_2}	A function for computing $\log \gamma_{\text{CO}_2(\text{aq})}$ as a function of I .
$v_{\text{H}_2\text{O}}$	A function for computing $\log a_{\text{H}_2\text{O}(i)}$ as a function of I_E .
ρ	Density.
σ	Subscript indexing an end-member component of a solid solution.
σ_T	Total number of end-members in a solid solution.
τ	Alkalinity factor for aqueous species; the number of alkalinity equivalents per mole.
ϕ	Subscript indexing a mineral of fixed composition.
ϕ_T	Total number of minerals of fixed composition.
ϕ'	Osmotic coefficient of water.
χ	Fugacity coefficient.
ψ	Subscript indexing a solid solution.
ψ_T	Total number of solid solutions.
ω	Water constant: $1000/\text{molecular weight of H}_2\text{O}$, = 55.51.

EQ3NR
A COMPUTER PROGRAM FOR GEOCHEMICAL
AQUEOUS SPECIATION-SOLUBILITY CALCULATIONS:
USER'S GUIDE AND DOCUMENTATION

ABSTRACT

EQ3NR is a geochemical aqueous speciation-solubility FORTRAN program developed for application with the EQ3/G software package. The program models the thermodynamic state of an aqueous solution by using a modified Newton-Raphson algorithm to calculate the distribution of aqueous species such as simple ions, ion-pairs, and aqueous complexes. Input to EQ3NR primarily consists of data derived from total analytical concentrations of dissolved components and can also include pH, alkalinity, electrical balance, phase equilibrium (solubility) constraints, and a default value for either Eh, pe, or the logarithm of oxygen fugacity.

The program evaluates the degree of disequilibrium for various reactions and computes either the saturation index ($SI = \log Q/K$) or thermodynamic affinity ($A = -2.303 RT \log Q/K$) for minerals. Individual values of Eh, pe, equilibrium oxygen fugacity, and Ah (redox affinity, a new parameter) are computed for aqueous redox couples. Differences in these values define the degree of aqueous redox disequilibrium. EQ3NR can be used alone. It must be used to initialize a reaction-path calculation by EQ6, its companion program.

EQ3NR reads a secondary data file, DATA1, created from a primary data file, DATA0, by the data base preprocessor, EQTL. The temperature range for the thermodynamic data in the file is 0-300°C. Addition or deletion of species or changes in associated thermodynamic data are made by changing only the file. Changes are not made to either EQ3NP or EQTL. Modification or substitution of equilibrium constant values can be selected on the EQ3NR INPUT file by the user at run time. EQ3NR and EQTL were developed for the FTN and CFT FORTRAN languages on the CDC 7600 and Cray-1 computers. Special FORTRAN conventions have been implemented for ease of portability to IBM, UNIVAC, and VAX computers.

1. OVERVIEW

EQ3NR is a geochemical aqueous speciation-solubility FORTRAN program that replaces the EQ3 code in the EQ3/6 software package. Its function is the same as the old code, i.e., to model the thermodynamic state of an aqueous solution by calculating the distribution of aqueous species (simple ions, ion-pairs, and aqueous complexes). EQ3NR is much faster than the old code and its printed output is significantly upgraded.

The relationship of EQ3NR to the EQ6 (Wolery, 1983a), EQTL, and MCRT (Wolery, 1983b) codes is shown in Figure 1. This figure depicts the flow of information involving these codes. MCRT is a thermodynamic data base building code. EQTL is the preprocessor for the EQ3/6 data base. EQ6, which must be initialized by an EQ3NR calculation, computes thermodynamic equilibrium models or reaction-path (kinetic) models.

The output of EQ3NR contains the aqueous species distribution (concentrations and thermodynamic activities of individual species) and the total concentrations of dissolved components in cases where these are output variables instead of input parameters. It also includes the saturation indices ($SI = \log Q/K$) and thermodynamic affinities ($A = -2.303 RT \log Q/K$) of precipitation reactions of minerals in the data base. It estimates the thermodynamic state of each aqueous redox couple, expressing it as couple-specific values of Eh, pe, equilibrium oxygen fugacity, or Ah (redox affinity--see Section 2.3.5.3). Differences in corresponding values of these quantities define the degree of disequilibrium among any two aqueous redox couples. EQ3NR also calculates the equilibrium fugacities of gases in the data base.

The input to the code consists of a chemical analysis of a water and specification of various user-defined options. The descriptive input usually consists mostly of analytical values for concentrations of dissolved components. These inputs represent total values that do not distinguish between contributions from simple ions, ion-pairs, and aqueous complexes. They may or may not distinguish a dissolved component by valence form. Normally, the pH is also an input parameter. Bicarbonate, or carbonate, may be constrained by titration or carbonate alkalinity.

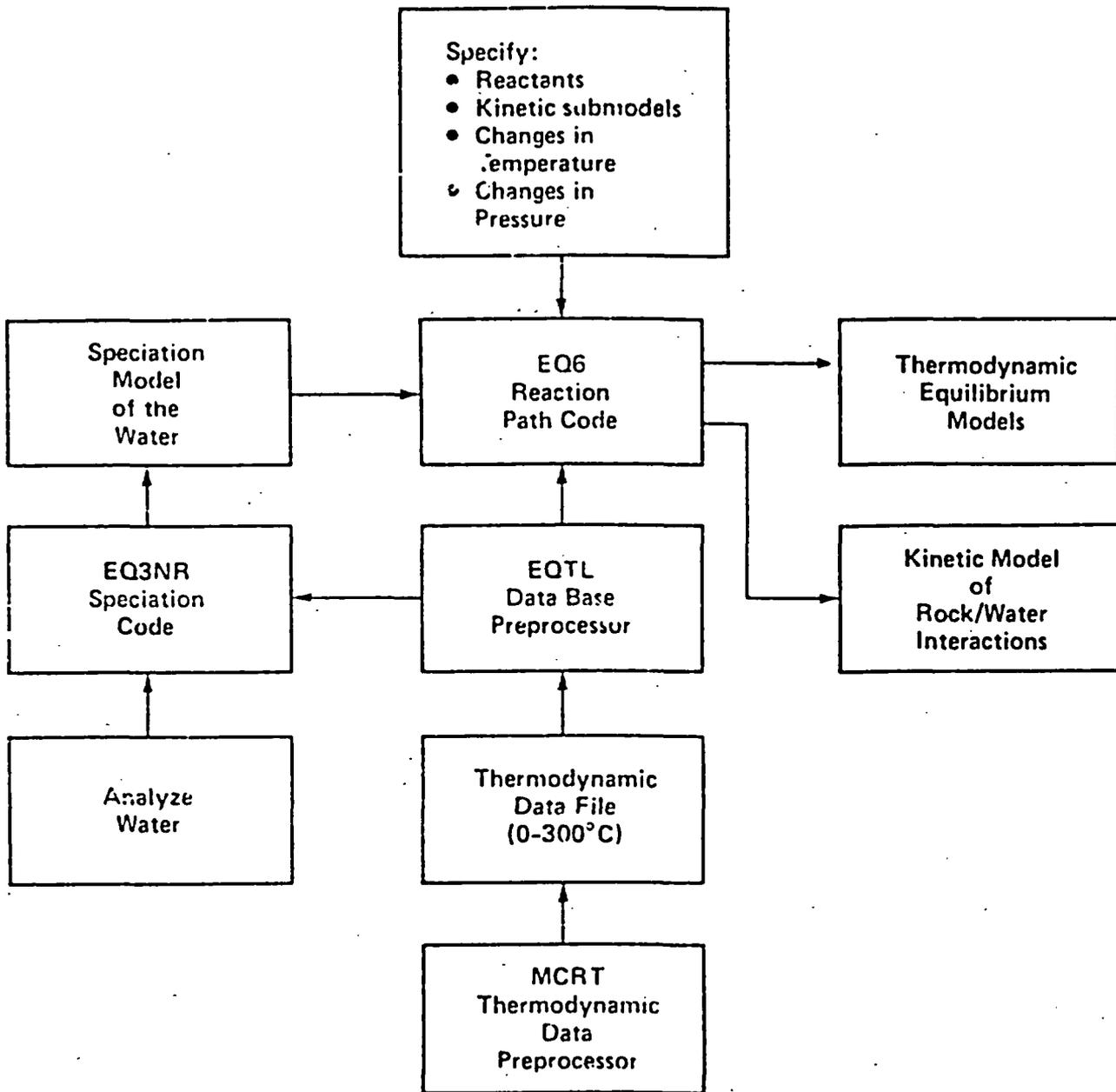


Figure 1. Flow of information between computer codes EQ3NR, EQ6, MCRT, and EQTL.

If desired, a specified ionic solute may be constrained by electrical balance. A default redox parameter (log oxygen fugacity, E_h , or p_{e^-}) may be input to distribute total concentrations that include more than one oxidation state in the corresponding mass balance.

Alternatively, the default redox state may be determined by a specified redox couple for which there is an analytical datum for each oxidation 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 and thereby avoid using a redox default. That way, redox equilibrium can be tested instead of merely assumed. (Section 5.5 gives an example of such calculations.)

The speciation calculation is otherwise based on thermodynamic equilibrium constraints. These data are included on a supporting data file called DATA0. Addition or deletion of species, or changes in associated thermodynamic data, are made on this file without any corresponding changes required in EQ3NR. The temperature range of the thermodynamic data on DATA0 is 0-300°C. The related code/data file package, MCRT (Wolery, 1983b), is an important aid in revising and expanding DATA0.

The data base preprocessor, EQTL, checks the composition, charge, and reaction coefficient data on DATA0 for internal consistency and fits interpolating polynomials to its equilibrium constant-temperature grids. EQTL then writes a secondary data file called DATA1 that is read by EQ3NR. Ad hoc alteration of the values of selected equilibrium constants can subsequently be selected by the user on the INPUT file for EQ3NR.

EQ3NR uses the B equation (Helgeson, 1969) to approximate the activity coefficients of aqueous species. An alternative would be the Davies (1962) equation. These approximations are not applicable to strong brines. Generally speaking, the current set of activity coefficient approximations should be limited to applications in which the ionic strength is no greater than approximately one molal. EQ3NR uses an expression suggested by Helgeson (1969) to estimate the activity of water.

EQ3NR uses a highly efficient modified Newton-Raphson algorithm derived from the one that was developed in the EQ6 code. EQ3NR is much faster than the old EQ3 code, in part, because the equations for ionic strength correction and electrical balance adjustment are solved simultaneously with those describing mass balance, alternative constraints, and mass action

(equilibrium) in aqueous solution. EQ3NR features both user-controlled and automatic basis-switching, a procedure of rewriting the aqueous reactions and redefining the set of aqueous master species. This feature is sometimes essential in getting the iterative calculations to converge. Other convergence aids (pre-iteration optimization and under-relaxation techniques) may also be employed.

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 the Newton-Raphson iteration fails to converge, EQ3NR will analyze the wreckage to generate crash diagnostics. Most of these diagnostics will point to bad input, usually input that is bad in more subtle ways than those which would have been flagged earlier.

Both EQ3NR and its supporting thermodynamic data base are extensively documented internally. They and the INPUT and OUTPUT files are transparent to users since users deal with chemical elements and aqueous, mineral, and gas species by recognizable names rather than index numbers. The EQ3NR OUTPUT file is self-documented and can be effectively controlled by the user by means of print option switches.

EQ3NR can be used by itself. It is required, however, to initialize reaction-path calculations performed by the companion code, EQ6 (Wolery, 1983a). In this case, EQ3NR writes the results into a file called PICKUP, which then forms the bottom half of the EQ6 INPUT file.

EQ3NR, EQTL, and related codes (EQ6, MCRT) were written and tested on the CDC 7600 and Cray-1 computers. Special FORTRAN conventions were followed to maximize portability to IBM, Univac, and VAX machines.

This report describes the assumptions underlying the use of EQ3NR and documents the mathematical derivations and the numerical techniques used by the code. The EQ3NR INPUT file is described in detail. Several examples, each of successful and unsuccessful uses of the code, including the full INPUT and OUTPUT files for each example, are presented and discussed. The limitations and possible misuses of the code are pointed out.

The remaining parts of this report that are of primary interest to code users are Sections 2-7 and Appendices F-H. Appendices A-E and I contain information that can help in getting EQ3NR and EQTL up and running on a new system. Section 8 documents the mathematical derivations in complete detail. Many readers may wish to skip it. Appendices A-E contain information mainly of interest to programmers. Readers knowledgeable about geochemical modeling of aqueous systems should at least skim the sections providing background information on the geochemical theory and principles used in EQ3NR, if for no other reason than to familiarize themselves with our notation and the contents of the code.

2. CHEMICAL MODELING OF AQUEOUS SOLUTIONS

2.1. INTRODUCTION

2.1.1. Types of Geochemical Models for Aqueous Systems

"Chemical modeling," when applied to aqueous solutions, implies attempting to understand the properties of these solutions in terms of aqueous species: simple ions, oxyions, hydroxyions, neutral species, and ion-pairs and complexes like NaSO_4^- , CaSO_4^0 , and $\text{UO}_2(\text{CO}_3)_2^{2-}$. This report will not attempt to present a thorough review of the subject. Reviews of the basic principles may be found elsewhere (Garrles and Christ, 1965; Krauskopf, 1967; Freeze and Cherry, 1979; Snoeyink and Jenkins, 1980; Stumm and Morgan, 1981; Drever, 1982). Nordstrom et al. (1979b), Wolery (1979), Potter (1979), and Jenne (1981) review the state of the art in chemical modeling, especially with regard to the application of computer codes.

It is important to distinguish speciation-solubility models from reaction path or kinetic models. A speciation-solubility model is a static model of an aqueous solution. It estimates the concentrations and activities of all the important aqueous species in this fluid and calculates the saturation indices for various minerals. A reaction path or kinetic model is a dynamic model. It predicts the path of a reacting system, i.e., it calculates changes in total concentrations, concentrations of individual aqueous species and their

thermodynamic activities, and the appearance and disappearance of reactants and products as a reaction progress or time variable advances.

Ordinarily, a reaction path model must contain one or more reactions that are not in a state of thermodynamic equilibrium. Without any of these so-called irreversible reactions, there would exist no driving force for any rock/water interaction process. The exception to this rule occurs when there are changes in temperature or pressure. Driving forces then occur even in the absence of irreversible reactions.

Speciation-solubility models are commonly used as a method to test whether heterogeneous reactions are at or near a state of thermodynamic equilibrium. The saturation indices of the fluid with respect to mineral phases ($\log Q/K$) are measures of thermodynamic disequilibrium. Too often, these models ignore the possibility that some homogeneous reactions (reactions involving only aqueous species) may also be in disequilibrium. The homogeneous reactions that are most likely to be suspect are those involving oxidation-reduction and the formation/dissociation of complexes that are actually small polymers (oligomers), such as $(\text{UO}_2)_3(\text{OH})_7^-$. Speciation-solubility models are better used when employed to test the degree of disequilibrium for these types of reactions than when they are forced to merely assume that such reactions are in equilibrium.

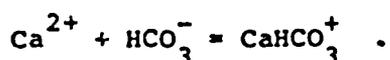
A speciation-solubility model can not, by itself, predict the change in aqueous solution composition in response to rock/water interactions. Nevertheless, this type of modeling can be a powerful tool for elucidating such interactions when it is applied to a family of related waters. Such a family might 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 during a rock/water interactions laboratory experiment.

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 the Nordstrom et al. (1979a) study of controls on the concentration of iron in acid mine waters. To minimize the chances of misusing geochemical modeling codes, would-be users of EQ3NR and other geochemical modeling codes should familiarize themselves with several studies of this type to increase their understanding of the approaches that can be taken in chemical modeling.

EQ3NR is a speciation-solubility code without the capability to calculate reaction-path models. That function is reserved for its companion code, EQ6 (Wolery, 1983a); however, EQ3NR can use phase equilibrium (solubility) constraints to construct a given chemical model. In such cases, a solubility equilibrium replaces a total concentration or other type of analytical datum on the INPUT file (see Section 4). The solution in the resulting model will then be saturated with respect to the heterogeneous reactions that were specified; however, EQ3NR only assumes that the solution has been saturated. EQ3NR does not calculate chemical models in which the state of the aqueous solution is changed by a process, such as the dissolution of a mineral, until saturation is reached.

2.1.2. Specific Interactions vs Ion Pairing/Complexing: An Alternate Approach

EQ3NR follows the traditional approach in geochemical modeling that emphasizes the role of ion-pairing and complexing in an aqueous solution. This approach is based on the classical model of sea water devised by Garrels and Thompson (1962), and to deeper roots in inorganic chemistry, and biochemistry. Ion pairs and complexes are considered as physical entities present in solution, formed by reactions, such as:



We refer to this concept as "species-including-ion-pairs-and-complexes-as-components."

An alternate approach is the "specific interactions" formalism (Pitzer, 1973, with references therein, and Whitfield, 1975a,b). This concept could be termed "species-excluding-ion-pairs-and-complexes-as-components." From a purely formal viewpoint, the dissolved components are assumed to be fully dissociated. Here the chemistry of ionic interactions is treated as a factor affecting the activity coefficients of the ions. These coefficients are not identical to the activity coefficients of the same ions under the traditional approach discussed above. To avoid confusion, they are sometimes called "total" or "stoichiometric" activity coefficients, and symbolized by γ^T . For the i -th ion,

$$a_i = m_i^T \gamma_i^T = m_i \gamma_i ,$$

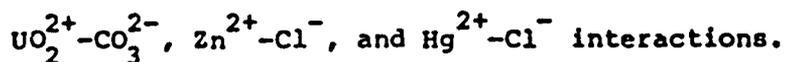
where m^T is the "total" and m the "free" concentration. Hence,

$$\gamma_i^T = \gamma_i (m_i/m_i^T) .$$

The specific interactions approach has been treated mostly in terms of "salts-as-components." Here one deals not with individual ionic components and their properties, but electrically neutral combinations, the "salts", and their corresponding (combined) properties. The activities and activity coefficients of salt components are experimentally measurable, while the corresponding individual ionic properties that contribute to them are not separately observable. Whitfield (1975a,b) and Harvie and Weare (1980) present formulations for single-ion activities in the context of a specific interactions approach utilizing Pitzer's equations (see below).

The two principal advantages of the specific interactions approach are fewer components with which to deal and all parameters can be directly experimentally measured. An ionic splitting convention is still required to obtain single-ion activity coefficients. It is a sometimes frustrating fact that the thermodynamic properties, and often even the identities of many aqueous ion pairs and complexes, must be largely inferred from measurements of gross solution properties such as vapor pressure, conductivity, or solubility. On the other hand, there is sufficient hard evidence (e.g., spectrophotometric) that aqueous complex formation is, in general, a very real and important phenomenon.

As one might expect, the dissolved salt approach tends to work best in systems where there is only weak ion-pairing and no strong complexing. This approach has been successfully applied to aqueous systems where this assumption holds true (e.g., Pitzer, 1973). Its primary disadvantage is that aqueous complexing is extremely important in some cases, e.g.,



This approach has been most extensively developed by Pitzer (1973, and subsequent papers). Pitzer's approach, like several other attempts to develop this concept, is based on the idea of fitting a virial coefficient expansion to experimental measurements. In simple terms, this expansion is a type of multivariable power series. Pitzer made two major improvements over previous

works in this area. First, he used improved modifications of the Debye-Huckel term. Second, he treated the first order virial coefficient as a function of ionic strength instead of as a constant.

The "specific interactions" approach has been developed to the point where it has appreciable, but limited, applicability to brine systems (i.e., systems involving aqueous solutions of high ionic strength). For example, Harvie and Weare (1980), have applied Pitzer's equations to the study of equilibria among brines and evaporite minerals in the Na-K-Mg-Ca-Cl-SO₄-H₂O system.

A workable approach to modeling brines using ion pairs and complexes as components has yet to be demonstrated; however, there is no reason that Pitzer's equations could not be developed using these as components. Pitzer's model has been modified somewhat in this direction with regard to the treatment of acid-base equilibria of phosphate (Pitzer and Silvester, 1976), sulfate (Pitzer et al., 1977), and carbonate (Peiper and Pitzer, 1982).

The present version of the EQ3NR code does not contain approximations for estimating activity coefficients that are valid in brines. Consequently, calculations should be limited to modeling aqueous solutions with ionic strengths no greater than approximately one molal. (Work is now in progress to extend EQ3NR's applicability to systems that include brines--Wolery, 1983c.)

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 the number of moles of that substance per kilogram of solvent (water). Other common measures of aqueous solute concentration are the molarity (moles of substance per liter of aqueous solution), the parts-per-million or ppm by volume (mg/L, milligrams 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 Section 4), but converts non-molal concentrations to molalities before computing the aqueous speciation model.

The conversion equations in all three cases require a value for the total dissolved salts in mg/kg solution (C_{TS}). The density of the aqueous

solution in g/L (ρ) is also required to convert molarities and mg/L concentrations to molalities.* Let us define the weight fraction of solvent

$$X_{H_2O} = (1,000,000 - C_{T\text{S}})/1,000,000 .$$

Then letting C_{molar} be the molar concentration, the molality is given by

$$m = C_{\text{molar}} / (\rho X_{H_2O}) .$$

Letting $C_{\text{mg/L}}$ be the concentration in mg/L, the conversion is

$$m = (0.001 C_{\text{mg/L}}) / (M\rho X_{H_2O})$$

where M is the molecular weight of the solute in grams per mole. Letting $C_{\text{mg/kg}}$ be the concentration in mg/kg solution, the conversion is

$$m = (0.001 C_{\text{mg/kg}}) / (MX_{H_2O}) .$$

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 can include total (analytical) concentrations, alkalinity, an electrical balance requirement, free concentrations, activities, pH, Eh, pe, oxygen fugacity, phase equilibrium requirements, activity coefficient corrections, homogeneous equilibria, and values for the necessary thermodynamic functions. The governing equations are the corresponding

* In principle, both $C_{T\text{S}}$ and ρ are model-dependent quantities (ρ being related to the species distribution and partial molal volumes of the dissolved species). In practice, water analyses often include estimates of $C_{T\text{S}}$ and ρ , or values sufficient for the purpose of converting concentration units are estimable without great difficulty. EQ3NR expects values of $C_{T\text{S}}$ and ρ on the INPUT file if such conversions are necessary (see Section 4).

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 (e.g., pH, a species concentration, a total concentration) are to be inputs to the model and which are to be outputs. This, in turn, is a function of the available data on a given water, the form of the data, and the hypothetical assumptions the modeler would prefer to apply.

Chemical analysis mainly provides 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 from all of them. This leads to a mass balance equation of the form

$$m_{Ca^{2+}}^T = m_{Ca^{2+}} + m_{CaOH} + m_{CaCO_3} + m_{CaHCO_3} + m_{CaHPO_4} + \dots$$

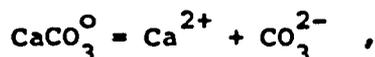
where $m_{Ca^{2+}}^T$ is the total concentration. The summations must be weighted by the appropriate stoichiometric equivalences, e.g.,

$$m_{F^-}^T = m_{F^-} + m_{HF^0} + 2m_{H_2F_2^0} + 2m_{HF_2^-} + 3m_{AlF_3^0} + 2m_{AlF_2^+} + \dots$$

The total concentration is the most common type of input parameter to an aqueous speciation model. The mass balance constraint that 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, ion-triplets, etc., and complexes. For some investigators, the term "ion-pair" implies a species 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 carbonate ion-pair dissociates according to the reaction



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

$$K_{\text{CaCO}_3^{\circ}} = (a_{\text{Ca}^{2+}})(a_{\text{CO}_3^{2-}})/(a_{\text{CaCO}_3^{\circ}}) ,$$

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

$$\log K_{\text{CaCO}_3^{\circ}} = \log a_{\text{Ca}^{2+}} + \log a_{\text{CO}_3^{2-}} - \log a_{\text{CaCO}_3^{\circ}} ,$$

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

$$a = m_{\gamma} .$$

where γ is the activity coefficient, a function of the composition of the aqueous solution. As the solution approaches infinite dilution, the value of γ for each species approaches unity. (Activity coefficients are the subject of Section 2.3.4.) The following subsections discuss the formulation of aqueous speciation problems in general terms.

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. To make sense of the various ways of setting up a model, we will define a reference formulation for the aqueous speciation problem. This reference formulation will serve as a springboard for discussing the information entered into speciation models, the output from the model, and the modeling options. It will also be used to compare the

formulation of the aqueous speciation problem in EQ3NR, and other speciation-solubility codes, with the formulation in a reaction-path code such as EQ6.

In the reference formulation, we will ignore activity coefficient corrections and assume that the activity of the solvent, water, is unity. 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 will assume that there are c_T chemical elements in the model. To further simplify the reference formulation, we will assume that each element is present in only one oxidation state. Therefore, suppose that chemical analysis has given us $c_T - 2$ total concentration values with one corresponding to each chemical element except oxygen and hydrogen. That gives us $c_T - 2$ mass balance equations as governing equations.

The charge balance equation will play 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

s is overall aqueous species,

z is the electrical charge of a species,

m is the molal concentration of a species.

The hydrogen mass balance equation can not be used as a governing equation to calculate the pH. 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.

To sum up, the reference formulation consists of (1) $c_T - 2$ mass balance equations/total concentrations, one pair for every element except oxygen and hydrogen, and (2) the charge balance equation (to calculate pH). Each element is present in only one oxidation state. Activity coefficient corrections, including one for calculating the activity of water, are ignored.

Before proceeding, we will contrast this framework (in general, common to speciation-solubility codes) with that employed in the EQ6 code. In the

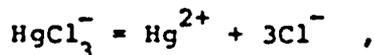
corresponding problem for that code, we would be given c_T masses (in moles) and the same number of mass balance equations written in terms of masses instead of concentrations. There we have a mass balance equation for oxygen, and we must calculate the mass of the solvent, water. In the case where each 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 code problem has one less unknown and, 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 us 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).

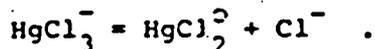
The number of aqueous complexes is usually much greater than the number of balance equations. This is especially true when there are a very large number of balance equations. A useful approach is facilitated when the number of equations and unknowns is reduced by substituting the aqueous mass action equations into the balance equations (see Section 8). 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.,



not



We will also use this format to write dissolution reactions for minerals and gases and their associated heterogeneous mass action equations. (See Section 3.1 for further discussion of master species and reaction formats.)

2.3.3. Alternative Constraints

The reference formulation of the aqueous speciation problem consists of the $c_T - 2$ mass balance equations/total concentrations and the charge balance equation (to calculate pH) mentioned earlier.

We have discussed adding activity coefficient corrections and corrections for the activity of water. Now we will discuss alternative constraints to the balance equations in the reference formulation. Insertion of the oxidation-reduction options into the formulation will be discussed in the following subsection.

The alternative constraints are:

- Specifying $\log a$ for a species (recall, $\log a_{\text{H}^+} = -\text{pH}$).
- Applying the charge balance constraint to a master species other than H^+ .
- Alkalinity balance (carbonate or bicarbonate only).
- 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).
- Specifying the individual concentration of a master aqueous species.

When a mass balance constraint is replaced by one of the above constraints, we will continue to reduce the number of unknowns to a master set, as previously discussed. The corresponding total concentrations become

parameters to be calculated. We can calculate, for example, the total mass/concentration of hydrogen with sufficient relative accuracy to permit the EQ6 code to use the result as a constraint to solve for pH.

It is appropriate that the first substitution we will discuss concerns 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 (recalling, $\text{pH} = -\log a_{\text{H}^+}$). 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. This means that the code expects to see $-\text{pH}$, not pH , on the INPUT file when the option is invoked. The new governing equation is just

$$m = a/\gamma$$

We recommend routinely calculating pH from electrical balance only in cases of synthetic salt solutions where the ionic totals are exact with respect to charge balance (see the example in Section 5.4). In other circumstances, this practice is potentially dangerous because the result is affected by the error in every analytical value put into the model and by every analytical value not entered, but required by the model. In general, apart from the case of synthetic salt solutions, it is only safe to calculate pH this way if the pH is low (acid solutions) or high (alkaline solutions where $\text{pOH} = -\log a_{\text{OH}^-}$ is low and electrical balance would effectively be constraining OH^-).

The charge balance constraint 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.

Carbonate, including bicarbonate, generally contributes nearly all of the alkalinity of an aqueous solution. EQ3NR allows titration alkalinity to be input for carbonate instead of total concentration. An alkalinity balance equation 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

A_t is the titration alkalinity,
 τ -values are the corresponding alkalinity factors.

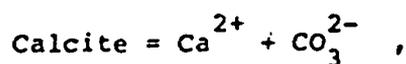
There is more than one type of alkalinity and consequently more than one set of alkalinity factors. EQ3NR offers two choices. The first is titration alkalinity to the methyl orange endpoint at pH 4.5. This is the same definition of titration alkalinity given by Parkhurst et al. (1980) for use in the PHREEQE code. The user is warned, however, that other titration alkalinity standards exist, corresponding to different end points, and they require a different set of titration factors.

The titration alkalinity balance equation corresponding to the methyl orange end point is

$$A_t = m_{\text{HCO}_3^-} + m_{\text{CaHCO}_3^+} + \dots + 2m_{\text{CO}_3^{2-}} + 2m_{\text{CaCO}_3^0} + \dots \\ + m_{\text{OH}^-} + m_{\text{CaOH}^+} + \dots + m_{\text{HS}^-} + 2m_{\text{S}^{2-}} + \dots$$

The second alkalinity option in EQ3NR does not correspond to a different end point. It merely includes only the carbonate/bicarbonate species in the alkalinity balance. It is of limited usefulness because there is not an experimental procedure for determining the alkalinity attributable only to carbonate.

A mass balance constraint may also be replaced by a specified mineral or gas equilibrium. For instance, 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 $\text{CaCO}_3(c)$ at 25°C). The dissolution reaction may be written



and the corresponding governing equation is then

$$K_{\text{calcite}} = (a_{\text{Ca}^{2+}})(a_{\text{CO}_3^{2-}})$$

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 $(\text{Ca},\text{Mg})\text{CO}_3(\text{c})$. The governing equation becomes

$$K_{\text{calcite}} = (a_{\text{Ca}^{2+}})(a_{\text{CO}_3^{2-}})/(a_{\text{calcite}})$$

The activity of a solid solution component, like that of calcite above, is given by

$$a = \gamma x$$

where

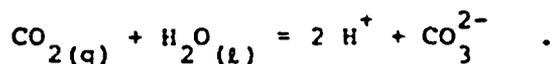
γ is the activity coefficient,

x is the mole fraction of the component in the solid solution.

The current version of EQ3NR deals only with solid solutions that are composed of end-member components. For ideal solutions of this type, the activity coefficients (γ) all have values of unity. For non-ideal solutions, the activity coefficients are functions of the composition of the solid solutions. As the mole-fraction (x) of a component approaches unity, so does its activity coefficient. Hence, the activity of pure calcite is unity and need not explicitly appear in the mass action equation for its solubility equilibrium.

In order to use this type of constraint, one must complete the input to the speciation model by including the mole fractions of the end members of the solid solution. The type of solid solution (the "law" that relates the activity coefficients to the mole fractions of the end members) is specified on the EQ3/6 data file. For examples of such solid solution "laws," see Wolery (1979, Table 3, pp. 12-13).

Suppose we want to know how much dissolved carbonate would be in solution if it were in equilibrium with $\text{CO}_2(\text{g})$. The $\text{CO}_2(\text{g})$ dissolution reaction may be written



The corresponding governing equation is

$$K_{\text{CO}_2(\text{g})} = (a_{\text{H}^+})^2 (a_{\text{CO}_3^{2-}}) / (a_{\text{H}_2\text{O}}) (f_{\text{CO}_2})$$

where f_{CO_2} is the fugacity of $\text{CO}_2(\text{g})$. To use this option, the user must provide this fugacity as an input value 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

$$f = \gamma p ,$$

where

p is the partial pressure,

γ is the fugacity coefficient, analogous to the activity coefficient γ .

At low pressures γ approaches unity, and fugacities can be equated with partial pressures.

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 the choice is an extremely poor one, the equilibrium concentration of a species so constrained may be very large (see the example in Section 6.3). Furthermore, the expressions for the logarithm of the ion activity products for all such reactions 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 what we call the "apparent" or "mineralogic" 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. (See Section 6.2 for an example of an apparent phase rule violation.)

EQ3NR allows input of the individual concentrations of master species. The governing equation in this case is

$$m = m .$$

It is largely appropriate only for master species that form no complexes, such as $\text{O}_2(\text{aq})$ and other dissolved gases.

2.3.4. Activity Coefficients and the Activity of Water

The thermodynamic activities (a) of aqueous solutes are the product of their molal concentrations (m) and their activity coefficients; i.e.,

$$a = m\gamma$$

The activity coefficients are functions of the composition of the aqueous solution. In dilute solutions, this can be described solely as an ionic strength dependence. The ionic strength is

$$I = 0.5 \sum_{s=1}^{s_T} m_s z_s^2$$

where the summation is over all aqueous species and z is the electrical charge.

EQ3NR uses the B equation of Helgeson (1969) for electrically charged species:

$$\log \gamma_s = -Az_s^2 \frac{I}{(1 + a_s B \sqrt{I})} + BI$$

A possible alternative, though not yet implemented in EQ3NR, would be the Davies (1962) equation:

$$\log \gamma_s = -Az_s^2 \left[\frac{I}{(1 + I)} - dI \right]$$

The value of the d parameter is usually taken as 0.3 (e.g., Parkhurst et al., 1980; Stumm and Morgan, 1981).

Neither the B equation nor the Davies equation is generally dependable at ionic strengths of greater than roughly one molal. Below an ionic strength of about 0.5, the results of the two equations are pretty much equivalent.

EQ3NR uses one of two treatments for neutral aqueous species. One treatment suggested by Garrels and Thompson (1962), and reiterated by Helgeson (1969), suggests assigning the value of the activity coefficient of aqueous CO_2 . This function is represented by a power series:

$$\log \gamma_s = v_{\text{CO}_2,1} I + v_{\text{CO}_2,2} I^2 + v_{\text{CO}_2,3} I^3 + v_{\text{CO}_2,4} I^4$$

The first term on the right-hand side dominates the others. Its coefficient is positive, so the activity coefficient of CO_2 increases with increasing ionic strength, the so-called "salting-out" phenomenon. EQ3NR only applies this approximation to species that are essentially nonpolar (e.g., $\text{O}_2(\text{aq})$, $\text{H}_2(\text{aq})$, $\text{N}_2(\text{aq})$), for which salting-out would be expected.

Reardon and Langmuir (1976) showed that the activity coefficients of two polar neutral species (CaSO_4^0 and MgSO_4^0) decrease with increasing ionic strength, the so-called "salting in" phenomenon. There is insufficient understanding of the activity coefficients of polar neutral aqueous species to suggest a general mathematical description. EQ3NR sets the activity coefficients of such species to unity; i.e.,

$$\log \gamma_s = 0 .$$

In principle, if one has a model of the behavior of activity coefficients in aqueous solution, one immediately has a model for the behavior of the activity of water through the Gibbs-Duhem equation of thermodynamics. Any different model for the activity of water would be inconsistent with the laws of thermodynamics. The following approximations are not thermodynamically consistent with the activity coefficient approximations given above; however, the activity of water is so close to unity, outside the case of strong brines, that it makes no practical difference if the formulation for the activity of water is inconsistent with the formulation for the activity coefficients of the solutes.

EQ3NR uses the following approximation from Helgeson (1969), which is essentially a fit to data from the system sodium chloride-water up to a 2-molal concentration. It uses a parameter called the equivalent stoichiometric ionic strength of a sodium chloride solution (I_E), taken as equivalent to the total concentration of either Na^+ or Cl^- . The equation is

$$\log a_{\text{H}_2\text{O}} = -2I \varphi' / (2.303w) ,$$

where

$$\varphi' = 1 - D'J' + w_2 I_E / 2 + 2w_3 I_E^2 / 3 + 3w_4 I_E^3 / 4 ,$$

and

$$D' = 2.303 A / (w_1^3 I_E) ,$$

$$J' = B' - 2 \ln B' - 1/B' ,$$

$$B' = 1 + w_1 I_E ,$$

where

$w_1, w_2, w_3,$ are constants adjusted to fit experimental data,
and w_4

w is 1000 divided by the molecular weight of water,
 φ' is the osmotic coefficient of water.

A more elementary approximation, not presently used in EQ3NR, was suggested by Garrels and Christ (1965):

$$\log a_{H_2O} = 1 - (1/w) \sum_{s=2}^{s_T} m_s .$$

where the summation is over all aqueous species, except the solvent ($s = 1$).

Corrections for activity coefficients and the activity of water are treated in EQ3NR by including I and I_E in the set of master iteration variables. The other master iteration variables correspond to the aqueous master species. For a detailed discussion of the mathematical derivations in which the activity coefficient and activity of water corrections are folded in with the rest of the governing equations, see Section 8.

2.3.5. Redox Constraints

2.3.5.1. There is No Such Thing as a "System" Eh

The high degree of emphasis on trying to understand the geochemistry of natural waters in terms of pure equilibrium thermodynamics has misled many people to believe that the redox state of real aqueous systems can be characterized by a single parameter called Eh (a redox potential, given in volts). The related parameter called 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 exists 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 extremely inaccurate for real systems, including probably all natural systems, all such systems perturbed by man, and all but the most trivial laboratory systems (Morris and Stumm, 1967). Stumm and Morgan (1981) introduce their chapter on oxidation-reduction with a warning to this effect. Jenne (1981) also points out the problem. By and large, however, even the more recent textbooks and monographs on aqueous geochemistry fail to effectively state this caveat.

Redox disequilibrium in natural aqueous systems is primarily the consequence of two factors. First, biological activity (as in the case of photosynthesis) acts to perturb these systems away from redox equilibrium (although by means of other reactions, it may also catalyze an approach toward equilibrium). Secondly, oxidation-reduction of compounds of the light elements (e.g., C, H, O, N, S) usually involves the breaking of covalent bonds; hence, many such reactions tend to occur very slowly.

A third factor may be important in the disposal of nuclear waste. Radiolysis of aqueous solutions by gamma radiation is a very effective process in perturbing such systems away from redox equilibrium, because it promotes the formation of thermodynamically unstable mixtures of strong oxidizing and strong reducing agents.

Several well known examples of redox disequilibrium in natural aqueous systems can be cited. One example is the coexistence of dissolved oxygen and organic carbon in nearly all natural waters. Another is the disequilibrium of dissolved methane and bicarbonate with dissolved sulfide and sulfate in many marine sediments (Thorstenson, 1970). In another case, Berner (1971, p. 119) cites the disequilibrium of dissolved nitrogen and nitrate with dissolved oxygen and water in marine surface waters.

How then does one characterize the redox state of aqueous solutions if the concepts of "system" Eh and "system" pe are inadequate? Berner (1981) has proposed an interesting geochemical classification scheme for waters in sediments that depends on first, the presence or absence of measurable dissolved oxygen, and secondly, in the absence of dissolved oxygen, the presence or absence of measurable dissolved sulfide. One approach to

characterization would be to generalize Berner's scheme to include a broader range of natural waters, including those perturbed by man.

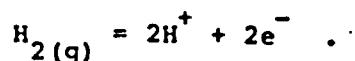
A more quantitative approach, however, is to recognize that each redox couple can have its own redox state that can be expressed as a couple-specific Eh or pe. We can define and calculate these parameters for any couple by using the Nernst equation in conjunction with chemical analyses that are specific with respect to oxidation state. In the following discussion, we will discuss this concept and make it clear why the idea of a system Eh or pe requires the generally implausible assumption that there is thermodynamic equilibrium among all redox couples.

2.3.5.2. 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 systems include $\text{HS}^-/\text{SO}_4^{2-}$, $\text{Fe}^{2+}/\text{Fe}^{3+}$, $\text{CH}_4(\text{aq})/\text{HCO}_3^-$, $\text{O}_2(\text{aq})/\text{H}_2\text{O}$, and $\text{H}_2(\text{aq})/\text{H}_2\text{O}$. The half-reaction is illustrated in the case of the very important dissolved oxygen-water couple



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



If we multiply this half-reaction by two and subtract it from the first one, we get the following complete redox reaction (which has no electrons among the reactants or products)



The thermodynamic convention describing the state of electrical potentials of half-reactions as Eh values takes the electrical potential of the standard hydrogen electrode as zero at all temperatures and pressures. This is consistent with the following thermodynamic conventions, where the superscript "o" denotes the standard state:

$\Delta G_{f,H_2(g)}^{\circ} = 0$ at all temperatures (the fugacity is one bar in the standard state),

$\Delta G_{f,H^+}^{\circ} = 0$ at all temperatures and pressures,

$\Delta G_{f,e^-}^{\circ} = \Delta G_{f,e^-} = 0$ at all temperatures and pressures.

Gibbs energies are related to electrical potentials by the Nernst equation

$$\Delta G = +nFE \quad ,$$

where

n is the number of electrons in the half-reaction,

F is the Faraday constant.

This is the form of the Nernst equation presented by Garrels and Christ (1965).

An alternative treatment, almost equivalent to the approach in the above Nernst equation, is writing the half-reactions as reduction reactions, so that the electron appears on the left side. One then reverses the sign on the right side of the equation. Development is equivalent to that of the original Nernst equation, except the signs of the Gibbs energies and corresponding equilibrium constants and activity products are reversed (Stumm and Morgan, 1981, Chapter 7).

Applying the thermodynamic relation

$$\Delta G = \Delta G^{\circ} + 2.303 RT \log Q \quad ,$$

to half-reactions and substituting it into the positive convention version of the Nernst equation, we get

$$E = E^{\circ} + (2.303 RT/nF) \log Q_{1/2} \quad ,$$

where

E° is the standard state potential,

$Q_{1/2}$ is the activity product of the half-reaction,

R is the gas constant,

T is the absolute temperature.

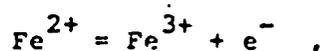
If we use the negative convention version of the Nernst equation, we get

$$E = E^{\circ} - (2.303 RT/nF) \log Q'_{1/2} ,$$

where $Q'_{1/2}$ is the activity product of the reverse half-reaction. These relations are equivalent because $\log Q'_{1/2} = -\log Q_{1/2}$. 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 does not need to explicitly appear in the activity product expressions for half-reactions.

2.3.5.3. Background: Eh, Ah, pe, and Equilibrium Oxygen Fugacity

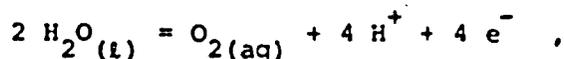
We can write a modified Nernst equation for any redox couple. In the case of the ferrous-ferric couple, whose corresponding half-reaction is



this is

$$E = E^{\circ}_{\text{Fe}^{2+}/\text{Fe}^{3+}} + (2.303 RT/nF) \log (a_{\text{Fe}^{3+}})/(a_{\text{Fe}^{2+}}) .$$

Similarly, for the dissolved oxygen-water couple, whose half-reaction is



this relation is

$$E = E^{\circ}_{\text{O}_2(\text{aq})/\text{H}_2\text{O}(\text{l})} = (2.303 RT/nF) \log (a_{\text{O}_2(\text{aq})}) (a_{\text{H}^{+}})^4 / (a_{\text{H}_2\text{O}(\text{l})})^2 .$$

Under the thermodynamic conventions adopted above, the potential E on the left side of each of the above equations equates with Eh.

If the two couples shown above are in equilibrium with each other, they must have the same Eh. If they have the same Eh, they are in equilibrium. Conversely, if they do not have the same Eh, they must be in 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, we can create a complete reaction by multiplying the

second half-reaction by $-n_1/n_2$ and adding the result to the first. Then n_1 electrons are transferred in the complete reaction. The Gibbs energy of reaction is then given by

$$\Delta G_r = n_1 F E_{h_1} - (n_1/n_2) n_2 F E_{h_2} = n_1 F (E_{h_1} - E_{h_2}) .$$

The condition of zero Gibbs energy of reaction (thermodynamic equilibrium) is met only if $E_{h_1} = E_{h_2}$.

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

$$pe = -\log a_{e^-} ,$$

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 often given (e.g, Thorstenson, 1970; Stumm and Morgan, 1981) between pe and Eh is

$$pe = (F/2.303 RT) Eh .$$

One may derive that this requires the thermodynamic convention

$$\Delta G_{f,e^-} = 1/2 \Delta G_{H_2(g)} - \Delta G_{H^+} \text{ at all temperatures and pressures, which}$$

requires that

$$\Delta G_{f,e^-}^{\circ} = 0 \text{ at all temperatures and pressures, whereas the } Eh \text{ convention for the hypothetical electron was}$$

$$\Delta G_{f,e^-}^{\circ} = \Delta G_{f,e^-} = 0 \text{ at all temperatures and pressures.}$$

It should be clear to the reader that pe is not a perfect analog to pH because pH is defined with respect to H^+ , a real aqueous species, whereas pe is defined with respect to a hypothetical species. (In calling H^+ a real aqueous species, we ignore the potential issue of whether or not H_3O^+ is the real species that defines pH. The point here is that pH is defined by a

real species.) Each redox couple can have its own pe , just as it can have its own Eh , with both 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 pe .

The state of an aqueous redox couple is described in terms of an electrical potential by a couple-specific Eh . It can also be expressed in terms of a chemical affinity by a new parameter we define here and call the redox affinity, Ah . This is a special case of the thermodynamic affinity function, viz., application of this function to redox half-reactions. This quantity is related to Eh by the relation:

$$Ah = F Eh \quad .$$

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

$$A = 2.303 RT \log (K/Q) = -2.303 RT \log (Q/K) \quad .$$

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 by multiplying the second half-reaction by $-n_1/n_2$ and adding it to the first. The thermodynamic affinity of the complete reaction, in which n_1 electrons are transferred, is then related to the Ah values (Ah_1 and Ah_2 , respectively) of the two half-reactions by the equation:

$$A = n_1 (Ah_1 - Ah_2) \quad .$$

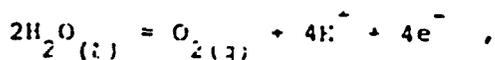
Thermodynamic equilibrium ($A = 0$) among two redox couples is the case if and only if both couples have the same value of Ah .

The redox affinity has no fundamental advantage over Eh as a redox descriptor as long as one understands that Eh is couple-specific and not a "system" parameter. In the geochemical literature, however, Eh has received so much attention as a "system" parameter that this connotation is difficult to disregard.

Alternatively, the state of a redox couple may be expressed in terms of an equilibrium oxygen fugacity. Recall that fugacities are properties of gas

species. Gas species can 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:



where we now take $O_2(aq)$ 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 half-reaction 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:

$$\log f_{O_2} = (4F/2.303 RT) Eh - 4 \log a_{H^+} + 2 \log a_{H_2O(l)} + \log K_{Eh}$$

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.

1.1.3.4. Redox Options: Testing vs 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, pe, 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, Ah, pe, 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.
- Ah in terms of a chemical potential.
- pe.
- Equilibrium oxygen fugacity.

Generally, analytical techniques do not discriminate between a simple species and its ion-pairs and complexes; however, there are techniques in many cases to discriminate between different oxidation states. For example, to calculate the couple-specific Eh of the ferrous-ferric half-reaction, we must have an analytical datum for each of Fe^{2+} and Fe^{3+} (Nordstrom et al., 1979a). If these data are both total concentrations (e.g, total Fe^{2+} , total Fe^{3+}), we simply have two master species and two corresponding mass balance equations for iron in the aqueous speciation model instead of one master species and one mass balance equation.

This is the preferred approach to treating oxidation-reduction in aqueous speciation modeling (Nordstrom et al., 1979b). 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 section could be used to 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, a pe, or log oxygen fugacity. Alternatively, it can 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.

2.3.6. 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

$$SI = \log (I/K)$$

where it is understood that Q is the activity product and K the equilibrium constant for a dissolution reaction. 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 the equation:

$$A = 2.303 RT \log (K/Q) = -2.303 RT \log (Q/K) .$$

Because $\log Q/K$ changes sign when the reaction is reversed, the affinity to precipitate is related to the saturation index by

$$A_{\text{precipitation}} = 2.303 RT SI .$$

Following these conventions, both SI and A are positive for supersaturated minerals, zero for saturated minerals, and negative for undersaturated minerals.

In the case of solid solution minerals with end-member components, the saturation index of the σ -th end member is related to that of the corresponding pure phase ψ by

$$SI_{\sigma} = SI_{\psi} + \log a_{\sigma} = SI_{\psi} + \log x_{\sigma} + \log \lambda_{\sigma} .$$

where

a is the thermodynamic activity of the end member,

x is the end-member mole fraction,

λ is the end-member activity coefficient.

Consideration of an overall dissolution reaction of a solid solution of given composition suggests that the saturation index of the ψ -th solid solution should be defined:

$$SI_{\psi} = \sum_{\sigma=1}^{\sigma_T} x_{\sigma} SI_{\sigma} .$$

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 is to find the compositions that maximizes the SI. Another is to search for those compositions that are either in equilibrium with the fluid (SI = 0) or are closest to the minimum absolute value of SI.

The present version of EQ3NR has very little capability for dealing with the saturation states of solid solutions of unspecified compositions. The current coding for this was taken directly from the old EQ3 code. The approach taken here requires estimation of the saturation index or affinity on the basis of a composition for which all end members, except the last, would be in equilibrium with the aqueous solution. This approach fails when such a composition does not exist, which is the case when any pure end member but the last has a positive saturation index.

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. Many heterogeneous and aqueous redox reactions are likely to behave this way.

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. (1979b) that ". . . no model is better than the assumptions on which it is based."

The EQ3/6 data base is designed to make it very convenient to add or delete species or change their associated thermodynamic data. Furthermore, the EQ3NR code permits changing the values of equilibrium constants at run time (see Section 4). The code offers the user no excuses for not addressing the above questions.

If thermodynamic data are not available for species known or suspected to be important in a given application, then such data should be estimated by empirical or semiempirical methods. EQ3NR's capability to modify equilibrium constants at run time makes it convenient to make 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 acidified samples that were inadequately filtered and contained colloidal particles of these two components. These particles then dissolve and "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) performed more detailed studies on 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 $\text{Fe}(\text{OH})_3$ 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 because of factors such as crystallinity (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 in a solution assuming appropriate solubility equilibria. For example, one might constrain dissolved aluminum to satisfy equilibrium with gibbsite $[\text{Al}(\text{OH})_3(\text{c})]$, or constrain iron to satisfy equilibrium with

amorphous $\text{Fe}(\text{OH})_3$ or a nontronite (ferric-rich smectite) clay; however, this is by no means a substitute for analysis of carefully filtered samples.

Certain analytical operations, such as filtering, should nearly always be performed immediately upon collection of a water sample. Measurement of pH, platinum electrode Eh, titration alkalinity, dissolved sulfide, and other parameters subject to possible significant change during transportation and storage should also be performed as soon as possible upon collection. Water samples should be inspected after transportation and storage for the formation of precipitates.

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 performs these calculations to provide a meaningful test (providing 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.

2.5. OTHER SPECIATION-SOLUBILITY CODES OF INTEREST

It would be nice to provide a detailed and comprehensive comparison of EQ3NR with other speciation-solubility codes. Unfortunately, a comparison of this sort is not feasible. This would require not only getting a fairly large number of such codes up and running in one place, but would also require familiarity and development of expertise with each. Such an effort would be further complicated by the development of many local or personalized versions of some widely distributed codes. Discussion here will be limited to listing some of the other major speciation-solubility codes used in geochemistry while pointing out some previous attempts to review and compare them. We will also note a few of the important points to consider in evaluating such codes.

Any list of the major speciation-solubility codes now in use should include:

WATEQ (Truesdell and Jones, 1974) and its derivatives:

WATEQF (Plummer et al., 1976)

WATSPEC (Wigley et al., 1977)

WATEQ2 (Ball et al., 1979, 1980)

SOLMNEQ (Kharaka and Barnes, 1973)

REDEQL (Morel and Morgan, 1972) and its derivatives:

REDEQL2 (McDuff and Morel, 1973)

GEOCHEM (Mattigod and Sposito, 1979)

MINEQL (Westall et al., 1976)

PHREEQE (Parkhurst et al., 1980)

EQ3 (Wolery, 1978, 1979)

SOLVEQ (Reed, 1977, 1982)

There are other codes (and derivatives of the above codes) that do not appear in the above list. The codes that were chosen for discussion here were primarily picked because they have received a significant level of distribution and use in the geochemistry community. Similar codes are used in the fields of inorganic chemistry and biochemistry.

The reader is referred elsewhere for more extensive guides to the available codes. In a study by Nordstrom et al. (1979b), the existing speciation-solubility codes were compared (only PHREEQE and SOLVEQ, in the above list, were not included). Wolery (1979) reviewed some aspects of several of the the major geochemical modeling codes, and Potter (1979) gives a short, but wide-ranging, review; however, Jenne's (1981) report is the most up-to-date. In these sources, the reader will find references in these sources to codes not included in the above list.

We will consider here only the speciation-solubility modeling capabilities of these codes. For instance, PHREEQE and SOLVEQ both have full reaction-path capabilities. Codes in the REDEQL/MINEQL series have limited reaction-path capabilities. In the EQ3/6 package, all reaction-path modeling functions are reserved for the EQ6 code.

The major points of evaluation for speciation-solubility codes are:

- "Hard coding" vs generalized coding.
- Range of allowable options.

- Reliability of the numerical algorithm.
- Ease of use and level of documentation.
- Quality and range of activity coefficient corrections.
- Ease of extending existing capabilities.
- Quality, extent, and temperature competency of the data base.
- Ease of portability to a different computer.

"Hard coding" here refers to the practice of writing specific lines of code for specific aqueous species and minerals. One then must write such new lines when adding additional species. This practice carries a high probability of introducing a small number of errors that may be difficult to locate. With generalized coding, there are not any lines specific to individual species; hence, a much smaller number of lines is required for the same job. Adding or deleting species from the chemical model is accomplished by changing only the data base. WATEQ, WATEQF, WATSPEC, WATEQ2, and SOLMNEQ are hard coded speciation-solubility computer programs. EQ3, EQ3NR, PHREEQE, REDEQL, and MINEQL use generalized coding.

A good speciation-solubility code should offer the user a wide range of model options to test alternative assumptions and accept various types of input data expressed in different types of units. All such codes known to this writer accept total concentrations and pH as model inputs. Other types of model input capabilities can be equally desirable; e.g, using alkalinity as a constraint on carbonate or constraining one dissolved component by electrical balance, allowing for redox disequilibrium modeling or permitting the use of heterogeneous equilibrium constraints. EQ3NR and PHREEQE can do all of these things.

Nearly all of the above codes use reasonably reliable numerical algorithms; however, there are two functions to consider: first, choosing starting estimates for the iteration variables and, second, iterating to a solution. Most codes, including EQ3NR, automatically generate their own starting estimates. A few, like EQ3, provide the user with the option of entering his own values. There is no need for this feature in codes with generally reliable algorithms for generation of starting estimates and subsequent convergence.

There are two main classes of iteration algorithms. The so-called "first-order" methods (Van Zeggeren and Storey, 1970) have a higher tendency toward impractically slow convergence for some problems than does the

Newton-Raphson method (a "second-order" method, see Chapter 8). These problems usually involve cases of very strong complexing, such as between mercuric ion and chloride, or uranyl and carbonate. The EQ3 code uses a first-order method developed by Wolery and Walters (1975). The technique of basis-switching, i.e., making an important species in a mass balance the corresponding master species (see Chapter 8), eliminates most convergence problems of this type. The WATEQ, WATEQ2, and SOLMNEQ codes also use first-order algorithms, but do not have basis-switching.

EQ3NR, REDEQL, MINEQL, SOLVEQ, and to some extent, PHREEQE, all use Newton-Raphson algorithms. The typical behavior of the unmodified Newton-Raphson method is that of quick convergence when converging. The behavior is further characterized by occasional extreme sensitivity to the values used for the starting estimates. The success of this iteration algorithm may depend on the quality of the algorithm that generates the starting estimates; however, other techniques (see Van Zeggeren and Storey, 1970; Wolery, 1979; and Section 8.4 in this report) may also be employed. EQ3NR uses the techniques (optimization of starting estimates and under-relaxation) that were developed for use in the EQ6 code (Wolery, 1979). It also offers both user-controlled and automatic basis-switching. In testing, EQ3NR has effectively manipulated some problems that were beyond the capability of EQ3.

EQ3NR is easier to use than EQ3. EQ3 requires the user to deal with index numbers for species. EQ3NR requires the user to deal only with names. All indexing is set up during execution and is generally not seen by the user. The INPUT and OUTPUT files have been organized to make them easily used. EQ3NR is fully documented internally using comment lines. In contrast, internal documentation is nearly non-existent in REDEQL. External manuals exist for nearly all codes (EQ3 being an exception) and they vary considerably in scope and quality.

Neither EQ3NR nor any of the other speciation-solubility codes listed above can make activity coefficient corrections for aqueous solutions more concentrated than approximately one molal in ionic strength, which rules out application to geochemical modeling of most brines. This problem was discussed at some length in Section 2.3.3, and directions toward its solution were discussed in Section 2.1.2.

Most codes, including EQ3NR, EQ3, WATEQ, WATEQ2, SOLVEQ, and PHREEQE correct the ionic strength for the effects of aqueous complexing. MINEQL, as described by Westall et al. (1976), does not do this unless the user alters the main program to create an "ionic strength" loop around the species distribution coding such as that used in EQ3. In EQ3NR, the ionic strength correction is made simultaneously with the species distribution calculation.

Most geochemical codes are not sufficiently well written to accept additional capabilities at a later time. All EQ3/6 software has been written with the idea of accepting future expansion. EQ3NR was specifically written for later incorporation of Pitzer's (1973) equations to produce activity coefficient corrections in solutions of high ionic strength. As discussed earlier in Section 2.1.2, Pitzer's equations represent the current state-of-the-art approach to calculating activity coefficients in concentrated electrolyte solutions.

Activity coefficients in concentrated aqueous salt solutions depend, in a general way, on the solution compositions rather than only the ionic strength. All realistic equations for describing these functions must reflect this fact. Incorporation of equations, such as Pitzer's, into most of the existing geochemical speciation-solubility codes, including EQ3, would be difficult because the iteration structures of these codes are built on the assumption that the activity coefficients depend only on the ionic strength.

There are four important factors to consider for the thermodynamic data that support geochemical modeling calculations pertaining to aqueous solutions. The first is the number of species represented. The greater the number, the more likely that all the important species will be represented in a given application. The data base of WATEQ2 (Ball et al., 1979, 1980) is noteworthy in this respect. The second factor pertains to the issue of temperature competency, i.e., does the supporting data base allow modeling over a useful range of temperature? Most of the data bases for codes in the REDEQL/MINEQL series are restricted to a single temperature, usually 25°C. EQ3NR's data base supports calculations over the range 0-300°C (it will automatically extrapolate its data base to higher temperatures, but this is not recommended). The SOLMNEQ data base extends over the range 0-350°C while the WATEQ and PHREEQE data bases are sufficient to support calculations roughly over the range 0-75°C. The third factor, at least ideally, is that any set of supporting data would be both accurate and internally (i.e.,

thermodynamically) consistent. In general, no existing speciation-solubility code data base is generally superior to others on these counts, however, the WATEQ2 data base (Ball et al., 1979, 1980) is one of the more noteworthy examples. It is the basis of the PHREEQE data base. Parts of the WATEQ2 data base have been used as a starting point and as a benchmark in building sections of the EQ3/6 data base. The fourth factor requires that a good data base be well documented. WATEQ2's data base is well documented externally (i.e., in reports separate from the data file itself). The data bases for many other codes, especially in the REDEQL and MINEQL series, are usually poorly documented. The EQ3/6 data base is designed to be documented internally by the inclusion of references in the data file (DATA0) with full citations of sources in journal-style format either at the end of this file or at the end of the MCRT data files used to build DATA0 (see Wolery, 1983b). The documentation in the current version (DATA0.3230U01; see Appendix H for a description of version nomenclature) is still largely incomplete. A new version is being prepared with full internal documentation.

EQ3NR is one of the most portable speciation-solubility codes. It has been designed for fast and easy transfer among CDC, Cray, IBM, UNIVAC, and VAX computers. MINEQL is also very portable, though WATEQ2 is not so portable because it was written in PL/1 instead of FORTRAN.

3. ORGANIZATION OF AQUEOUS SPECIES AND SUPPORTING DATA

3.1. MASTER SPECIES AND BASIS SWITCHING

In the EQ3/6 system, there is a set of either master (or basis) aqueous species (see Section 2.3.2). Every remaining species (aqueous, mineral, or gas) is formally associated with a reaction that destroys it. For example, an aqueous complex is paired with its dissociation reaction, and a mineral with its dissolution reaction. The reactions are written in terms of only the associated species and the set of master aqueous species (Section 2.3.2); thus, no more than one nonaqueous phase can appear in each reaction.

The set of master or basis species on the EQ3/6 data file is divided into two parts: the strict basis and the auxiliary basis. The species in the strict basis set have a one-to-one correlation with the chemical elements,

except $O_{2(g)}$, which is used here as a hypothetical aqueous species and corresponds to charge balance. These species first appear in the overall organization of aqueous species. The solvent, $H_2O_{(l)}$, is the first aqueous species, and $O_{2(g)}$, the hypothetical aqueous species, is the last in the strict basis. The master species in the strict basis set are not formally paired with any reactions. They play the role of building blocks, and appear as the first sub-block of aqueous species on the data file.

The auxiliary master species follow (the second sub-block of aqueous species). These master species, for the most part, represent the chemical elements in different valence forms. They may also include OH^- , and either CO_3^{2-} or HCO_3^- , depending on which, for convenience, is in the strict basis. Including such species in the master species set is necessary so that they can be used as general components in writing chemical reactions on the supporting data file. Auxiliary master species either act as master species ("building blocks") or as nonmaster ("derivative") species, depending on the specifications for a given speciation-solubility problem. The nonmaster aqueous species follow the auxiliary master species.

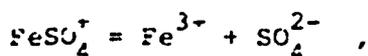
The following restriction applies to the master aqueous species as the set is defined on the data file. The master species must consist of no elements except the formally associated chemical element, oxygen, and hydrogen. They may represent any valence state. Any number of other valence states may be represented in the auxiliary master set, each by a separate species. The number and arrangement of master aqueous species is limited only by the code dimensions and the restrictions that: (a) water must be the first aqueous species, and (b) the hypothetical oxygen gas species is the last in the strict basis set.

In order to perform a speciation-solubility calculation, an input model constraint, such as a total concentration, is required for each master aqueous species. There are, however, limitations on the constraints that can be placed on a given master species, depending on whether the species is in the strict basis or the auxiliary basis. The user needs to be aware which aqueous species are in the strict master set and which species are in the auxiliary set. Users should consult either the DATA0 file or a copy of the SLIST file, produced by the data base preprocessor (see Section 3.2).

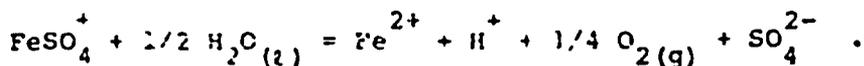
The user can specify selected examples of basis switching on the I:PUT file. This provides a method to change the set of master aqueous species at run time. For example, a strict basis species can be exchanged with an auxiliary basis species, placing the latter in the strict basis and the former in the auxiliary set. Other types of basis switching, involving an exchange with a nonmaster species, are also possible. A basis switch causes reactions to be rewritten for consistency with the modified basis set of aqueous species. The stoichiometric restrictions on master species on the EQ3/6 data file do not apply to basis switching.

A basis switch involving a nonbasis species causes the corresponding input constraints (CSP and UPHASE parameters; see Section 4), to be reassigned to the species brought into the basis set. For example, if $\text{Al}(\text{OH})_4^-$ is to be switched with Al^{3+} , for which JFLAG = 16 (log activity constant) and CSP = -5.0 (the desired value), the model specified is one in which the log activity of $\text{Al}(\text{OH})_4^-$ is -5.0.

Setting the JFLAG parameter of an auxiliary master species to 30 effectively removes the species from the set of master species (see Section 4). For example, if Fe^{2+} is the strict basis species corresponding to dissolved iron, and Fe^{3+} is in the auxiliary basis, setting the JFLAG parameter of the latter to 30 effectively makes Fe^{3+} , and all its complexes (in the loosest sense of the word), a set of derivative species of Fe^{2+} . For example, the reaction



is rewritten



The JFLAG parameters for the strict basis species (i.e., those in the strict basis before EQ3NR sets up for Newton-Raphson iteration) can not be set to 30.

For any species in the auxiliary set purely for convenience, such as OH^- , it is important that the JFLAG parameters be set to 30. If the flag is incorrectly set, unintended disequilibria may be introduced into the speciation-solubility model (e.g., OH^- not in equilibrium with H^+ and $\text{H}_2\text{O}_{(l)}$).

3.2. DATA0 AND EQTL: DATA FILE AND PREPROCESSOR

The primary data file that supports EQ3NR and EQ6 is called DATA0. This file contains thermodynamic data corresponding to the temperatures 0-25-60-100-150-200-250-300°C, a pressure of 1.013 bar (1 atmosphere) up to 100°C, and the steam/liquid water equilibrium pressure at higher temperatures. All other necessary supporting data are also on this file.

EQTL, a data base preprocessor, reads DATA0 and writes three secondary data files, DATA1, DATA2, and DATA3 as shown in Figure 2. In referring to the figure, we see that DATA1 is read directly by EQ3NR, DATA2 and DATA3 by EQ6. EQTL checks each reaction for mass and charge balance and fits interpolating polynomials to all data on temperature grids. It also reformats the information on DATA0 into forms suitable for direct reading by EQ3NR and EQ6. EQ3NR and EQ6 read the coefficients of the interpolating polynomials from DATA1 and DATA3, respectively, instead of the gridded data.

MCRT (Wolery, 1983b) is a data base building program whose data base consists of Gibbs energies and enthalpies of formation, entropies, heat capacities, etc., and the log K function of specified reactions on the temperature-pressure grid used in DATA0. To ease the job of building or revising DATA0, MCRT writes complete individual data blocks for a reaction/species (see Section 3.4 for an example and discussion of the format). These blocks can then be directly merged into DATA0.

It is not the purpose of this report to present the contents of the data file, but rather to discuss its format. We will, however, describe some of the major sources of data in the current version of DATA0 (DATA0.3230U01; see Appendix H for a description of version nomenclature). Most of the log K values for aqueous redox reactions and mineral dissolution reactions involving the major geochemical elements Na, K, Ca, Mg, Fe, Al, Si, C, S, O, and H were generated from the SUPCRT program/data base (Helgeson and Kirkham, 1974a, 1974b, 1976; and Helgeson et al., 1978). A significant number of log K values for aqueous complex dissociation involving these and other elements were taken from Helgeson (1969).

These data are supplemented by estimates of the thermodynamic properties of some clay minerals, mostly smectite compositions, taken from Wolery (1978). These values are based on a modification of the estimation method of Tardy and Garrels (1974). Wolery (1980) added Langmuir's (1978) data for

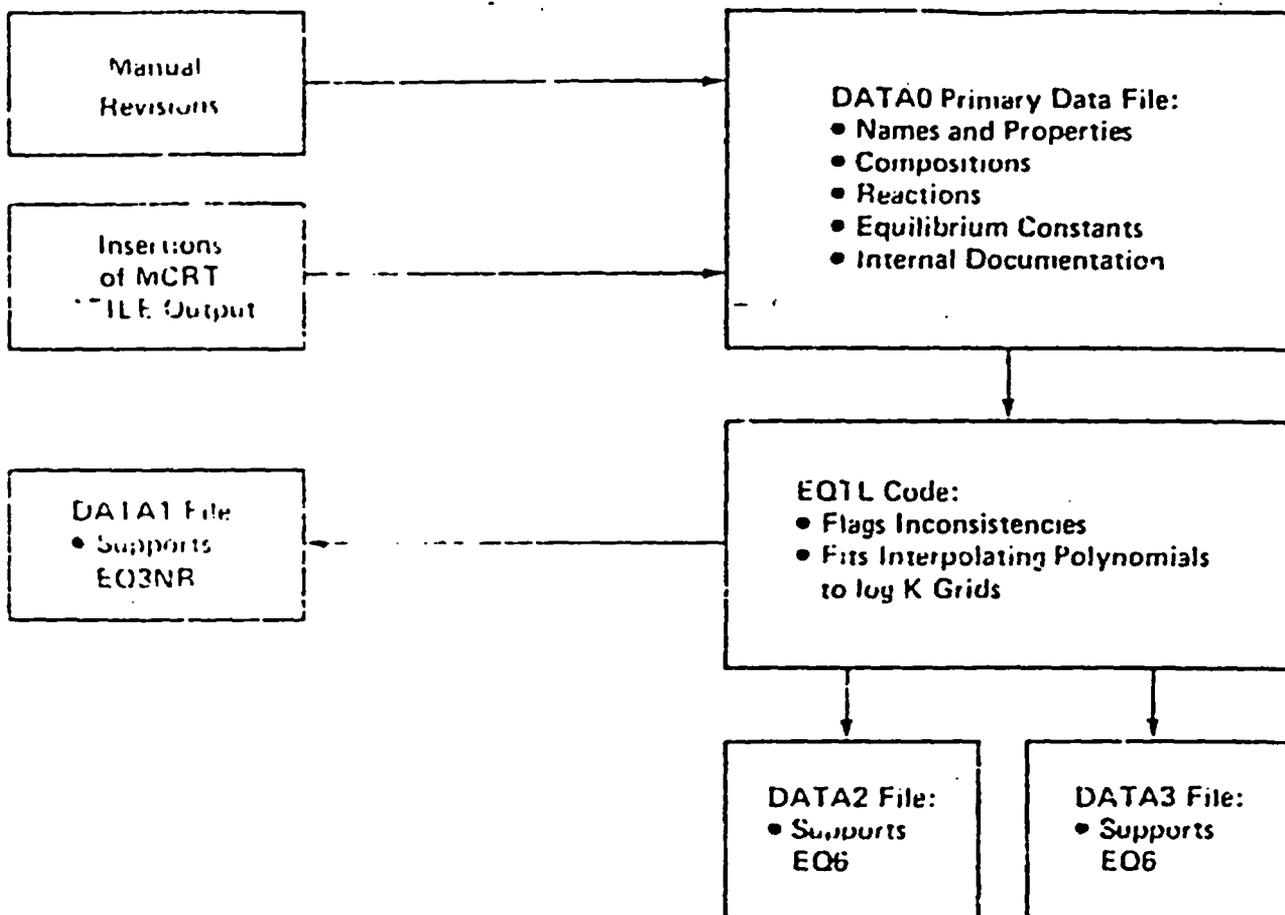


FIGURE 2. Relationship between the EQTL data base preprocessor, primary data file (DATA0), and secondary data files (DATA1, DATA2, and DATA3).

chemical species. Wolfe and Iremaine's (1990) data on plutonium and supplementary data on uranium have also been included, as have data on reactions for sulfuric and phosphoric species generated through MCRT. The internal documentation of DATA0:3230001 is mostly incomplete. Revision of DATA0 is in progress to address the problem.

The first line of DATA0 contains the name and release number of the file (see Appendix B). The release number is followed by a block of data for the chemical elements, giving the symbol for each, atomic weight, name of a corresponding oxide, and the gravimetric factor relating the oxide to the pure element.

Following the chemical element block in DATA0 is the standard temperature grid, 0-25-60-100-150-200-250-300°C. The temperature grid is followed by the pressure grid, corresponding to one atmosphere pressure (1.013 bar) up to 100°C and the liquid/vapor equilibrium curve for water at higher

temperatures. These are followed by temperature grids the Debye-Huckel A and B parameters, the B parameter, the v_{Cu} coefficients, the v_{H_2O} coefficients, and $\log K_{FH}$. This part of DATA0 is followed by four superblocks, one for aqueous species, one for minerals of fixed composition, one for gases, and one for solid solutions. Each superblock is terminated by a line containing the character string "ENDIT." in the name field. The solid solution superblock is followed by the references section.

As the term implies, each superblock consists of individual data blocks for species/reactions. The data blocks for aqueous species, minerals, and gases are very similar in format (mineral and gas blocks are identical), and will be discussed in some detail. Data blocks for aqueous species in the strict basis set are shorter than those for other aqueous species, because these species do not have formally associated reactions.

An aqueous species data block is shown in Figure J. Its contents should be transparent to the reader. The first line contains the name of the species, in this case "mah2m4+", the name of the person responsible for the data in the data block, the date of entry or last revision, a source indicator, and an estimate of the quality of the data. The source indicator identifies major data sources, and should be blank or read "see below" unless the data are taken from a major data source. Sources of isolated data should be identified in comment lines, which begin with an asterisk in column 1, and can appear anywhere in the data block. In this case, the data block was written by MCRT. The comment line identifies the name of the MCRT file from which the data was taken (in this case, "mdaqsp") and the method MCRT used to make the temperature extrapolation of the thermodynamic data ("criss-cobble method").

The use of the "quality" parameter is optional. Valid entries include "good," "poor," "bad," "restricted," "speculative," "uncertain," and "unspecified." The entry "good" implies that log K data have uncertainties of less than one or two units. A "poor" entry implies that the log K data have uncertainties greater than several units. A "bad" entry marks data that should not be used except in demonstrative calculations. A "restricted" entry marks data which have been shown to be consistent with specific observations, but which may not be generally valid. Appropriate caveats should be given in comment lines. A "speculative" entry marks cases where the existence of the species, as well as the values of the corresponding thermodynamic data, are both inferred by analogy to known substances and their thermodynamic

properties. An "uncertain" entry is used to mark cases in which significantly different values of the data have been reported by different sources, and these differences have not been resolved. The alternate data values should be given in comment lines. A blank entry is equivalent to an "unspecified" entry.

Following in the aqueous species data block are the electrical charge, the titration factor, the Debye-Huckel ion size parameter, and the hydration number of the species. Hydration numbers are not presently used. After these, the chemical formula, the associated reaction, the log K grid, and a similar grid for the standard partial molal volume of the reaction "delvr" are listed. The volume of reaction grid is presently not used, and its contents now consist of zeros. In the course of future development, we intend to support the minor pressure corrections necessary for calculations off the standard temperature-pressure grid.

The data block format for minerals and gases is illustrated in Figure 4. Its format is identical to that of the aqueous species data block, except there is an entry for the molar volume (at 298.15°K and 1.013 bar pressure) in lieu of entries for electrical charge, titration factor, ion size, and hydration number. (These latter quantities are not relevant to minerals and gases.)

The exact formats used in this data block can be obtained from either the EQTL or MCRT source codes. Users should either generate data blocks using the MCRT code or use copies of existing blocks as templates and modify the contents with a editor.

The solid solution blocks contain the name of the solution, the number of end-member components, a number indicating the equations used to describe the end-member activity coefficients, the names of the components, limits on the mole fractions, and the parameters from which EQ3NR or EQ6 can calculate the activity coefficient functions of the end members.

We do not recommend direct user modification of the secondary data files (DATA1, DATA2, and DATA3). Modification of the data base should be accomplished by making revisions to DATA0, followed by running EQTL to generate new versions of DATA1, DATA2, and DATA3.

To assist the user in maintaining a record of the species in the data file (as well as the position of aqueous species with respect to the strict and auxiliary basis sets), EQTL writes a relatively short listing on a file called SLIST. It may be helpful to keep a printed copy of this list near the user's computer terminal.

Figure 4. Example of a mineral species data block.

```

-----
anorthite          cca12si2o8
entered by= t.j. wolery          date= 07/14/82
  source= supcrl                quality= good
  volume= 100.790 cc/mol
  4 chemical elements=
    8.000 o                    1.000 ca                    2.000 al
    2.000 si
  6 species in reaction=
    -1.000 anorthite          4.000 h2o                    1.000 ca++
    2.000 al+++                2.000 sio2(aq)              -8.000 h+
  • log k grid (0-25-60-100/150-200-250-300 c)=
    31.7527  27.0626  21.6136  16.7017
    11.9653   8.2178   4.9259   1.3252
  • delvr grid (0-25-60-100/150-200-250-300 c)=
    0.0000   0.0000   0.0000   0.0000
    0.0000   0.0000   0.0000   0.0000
  • supcrl data for anorthite          , no. 1030, run 7/14/82
-----

```

4. THE EQ3NR INPUT FILE: SETTING UP THE PROBLEM

In this section, we examine the INPUT file for EQ3NR. This file is the only means, apart from changing the thermodynamic data file, by which the user specifies a problem to be solved by the code. The reader will find examples of INPUT files for EQ3NR, along with the corresponding OUTPUT files, in Sections 5 and 6.

The recommended way of creating a new INPUT file is to use an old file as a template. This is particularly effective if the user has access to a cursor editing capability. At Lawrence Livermore National Laboratory, an on-line cursor editing capability exists, using HP2645A terminals. The TRIX AC editor for this system is implemented with the "VW" command. Though the user may not have direct access to cursor editing, we still strongly recommend dealing with INPUT files with text editors rather than punched cards.

The INPUT file is read by the subroutine called READX. This routine is heavily documented internally with comment lines. This internal documentation is the final authority on the EQ3NR INPUT file. What follows in this section is basically a compact restatement of the internal documentation in the latest version of EQ3NR.

Subroutine READX writes an instant echo of the INPUT file on the OUTPUT file. That is, after READX reads a line or closely related group of lines, it echoes their contents. This is particularly helpful for identifying the causes of read format errors, which most commonly occur when a line is missing or is out of the proper sequence.

The reader should be careful to note the number of lines is variable in an EQ3NR INPUT file. Whether or not some potential lines appear in a given file depends upon the contents of other lines. 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 which users need be concerned. EQ3NR establishes its own internal indexing schemes at run time. Users deal with species in terms of their names, which are alphanumeric character strings. The names are much easier to remember and are instantly recognizable; however, the names must perfectly match those on the thermodynamic data file or EQ3NR will not recognize them. When a name is not recognized, the code will write an error message and terminate activity on the current problem input.

EQ3NR input problems can be stacked on the INPUT file so that the code will read one problem, solve it, then read another, solve it, and so on, in one execution. In most cases, if an error is detected in a problem input, the code will proceed to the next problem input, if any.

A short summary of the contents of the EQ3NR INPUT file and its format is given in the table on the following page. Parameters for which default values are recommended are marked with "(*)". To take the default for a given parameter, simply leave the corresponding input field blank. The user may find it helpful to photocopy this page and keep it near a computer terminal or card punch for reference.

Following the short summary is a discussion of the INPUT file parameters. The user need not enter values for all of these. Some parameters may not appear on specific examples of INPUT files, depending on the values of other parameters. Default values are recommended for some, such as the convergence tolerance parameters TOLBT and TOLDL.

Comment lines, marked by an asterisk in column one, and analogous to comment lines in FORTRAN source codes, may appear anywhere in the INPUT file; however, the READX subroutine does not echo these lines on the OUTPUT file.

The reader should compare the discussion in this section with the INPUT file specimens in Sections 5 and 6, which follow. Section 5 presents INPUT file examples that work. Section 6 presents examples that do not work and explains why these inputs fail to function.

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Short Summary of the EQ3NR INPUT File

<u>Parameters</u>	<u>Format</u>
UTIL	(15A6)
TEMPC	(12X,E12.5)
RHO, TDSPKG, TDSPL (enter only one of TDSPKG, TDSPL)	(3(12X,E12.5))
FEP, (UREDOR(J), J = 1,2) (enter either FEP or UREDOR)	(12X,E12.5,12X,2A6)
TOLBT(*), TOLDL(*), TOLSAT(*)	(3(12X,E12.5))
ITERMX(*)	(12X,I2)
IOPT1, IOPT2, IOPT3, IOPT4, IOPT5, IOPT6, IOPT7, IOPT8, IOPT9, IOPT10	(12X,10I5)
IPRNT1, IPRNT2, IPRNT3, IPRNT4, IPRNT5, IPRNT6, IPRNT7	(12X,10I5)
IDBUG1, IDBUG2, IDBUG3, IDBUG4, IDBUG5, IDBUG6, IDBUG7	(12X,10I5)
(UEBAL(J), J = 1,2), (UACION(J), J=1,2)	(12X,2A6,12X,2A6)
NXMOD	(12X,I2)
Do N = 1, NXMOD: (UXMOD(J,N), J=1,3), JXMOD(N), KXMOD(N), XLKMOD(N)	(12X,3A6, /12X, I2, 22X, I2, 22X, E12.5)
Do the following and stop when UBASIS(1,NS) = "ENDIT." (NS is just a line counter): (UBASIS(J,NS), J = 1,3), (USPECB(J,NS), J = 1,3), CSPB(NS), JFLAGB(NS), (UPHASE(J,NS), J = 1,3)	(3X, 2A6, 3X, 2A6, 3X, E12, 3X, I2, 3X, 3A6)
Bypass the following if IOPT4 is not 2: Do the following and stop when USOLB(1,NXB) = "ENDIT." (USOLB(J,NXB), J = 1,2)	(3X, 2A6)
Do the following and stop when UMEMB(1,IKB,NXB) = "ENDIT." (UMEMB(J,IKB,NXB), XBARB(1KB,NXB), J = 1,2)	(6X, 2A6, 3X, F10.4)

(*) Default values are recommended (i.e., leave these blank on the INPUT file)

The EQ3NR INPUT file parameters are:

<u>Parameter</u>	<u>Description</u>
UTITL	Thirty lines of text that describe the input problem.
TEMPC	Temperature °C.
RHO	Aqueous solution density, g/mL.
TDSPKG	Total dissolved salts, mg/kg (enter only one of TDSPKG, TDSPI.).
TDSPL	Total dissolved salts, mg/L (enter only one of TDSPKG, TDSPL).
FEP	Default redox parameter: Log oxygen fugacity if IOPT1 = 0 . Eh if IOPT1 = -1 . pe ⁻ if IOPT1 = -2 .
UREDOR	Name of an auxiliary master species that defines the redox couple that indirectly specifies the default log oxygen fugacity (IOPT2 must be 1; enter only one of FEP, UREDOR).
TOLBT	Convergence tolerance on residual functions (default value of 1.E-10 is recommended).
TOLDL	Convergence tolerance on correction terms (default value of 1.E-10 is recommended).
TOLSAT	Saturation tolerance (this only determines whether or not a mineral is listed as "saturated" on the OUTPUT file. TOLSAT does not affect Newton-Raphson iteration. Its default value of 0.5. Values anywhere in the range 0.1-1.0 would not be unreasonable.
ITERMX	Upper limit on the number of Newton-Raphson iterations (default value of 30 is recommended).
IOPT1	Option switch for default redox coupling: = 0 log oxygen fugacity is specified in FEP. = -1 Eh is specified in FEP. = -2 pe ⁻ is specified in FEP. = 1 An aqueous redox couple identified by UREDOR indirectly constrains default oxygen fugacity. = -3 A heterogeneous redox reaction indirectly constrains the default oxygen fugacity. It is identified by the UPHASE parameter on a USPECB line for O2(G); otherwise, no such line usually appears on the INPUT file.

EQ3NR INPUT file parameters (continued)

<u>Parameter</u>	<u>Description</u>
IOPT2	Control switch for automatic basis switching: = -1 Turns it off. = 0 Allows the code to turn it on. = 1 Turns it on.
IOPT3	Control switch for writing a PICKUP file for input to EQ6: = -1 PICKUP file is not generated. = 0 PICKUP file is generated.
IOPT4	Control 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	Control switch, not currently used.
IOPT6	Control switch, not currently used.
IOPT7	Control switch, not currently used.
IOPT8	Control switch for convergence criteria: = -1 Only BETAMX is tested. = 0 Both BETAMX and DELMAX are tested.
IOPT9	Control switch, not currently used.
IPRNT1	Print control switch: = 0 No function. = 1 Lists the species being loaded into memory.
IPRNT2	Print control switch: = 0 No function. = 1 Lists all reactions and log K values. (CAUTION: This can be a lengthy item.)
IPRNT3	Print control switch: = -1 Aqueous species properties are printed in the order the species were read from the supporting data file. = 0 Aqueous species properties are printed in order of decreasing concentration.

EQ3NR INPUT file parameters (continued)

<u>Parameter</u>	<u>Description</u>
IPPNT4	Print control switch: <ul style="list-style-type: none">= -3 Aqueous species properties are not printed.= -2 Only aqueous species with concentrations no less than 1×10^{-20} are printed.= -1 Only aqueous species with concentrations no less than 1×10^{-12} are printed.= 0 All aqueous species are printed.
IPRNT5	Print control switch, not currently used.
IPRNT6	Print control switch, not currently used.
IPRNT7	Print control switch: <ul style="list-style-type: none">= -1 Saturation indices and affinities of minerals are not printed.= 0 Saturation indices and affinities of minerals are printed only if the affinities are no less than -10.kcal.= 1 Saturation indices and affinities of all minerals are printed.
IDBUG1	Debugging print switch: <ul style="list-style-type: none">= 0 No function.= 1 Prints some informational messages.= 2 Prints more informational messages.
IDBUG2	Debugging print switch: <ul style="list-style-type: none">= 0 No function.= 1 Prints some information when reading the DATA1 file.= 2 Prints more information when reading the DATA1 file.
IDBUG3	Debugging print switch, not currently used.
IDBUG4	Debugging print switch: <ul style="list-style-type: none">= 0 No function.= 1 Prints extensive detail of Newton-Raphson iteration.
IDBUG5	Debugging print switch: <ul style="list-style-type: none">= 0 No function.= 1 Prints calculated stoichiometric equivalence factors for oxygen (O^{2-}) and hydrogen (H^+).= 2 Prints calculated stoichiometric equivalence factors for all aqueous master species.

EQ3NR INPUT file parameters (continued)

<u>Parameter</u>	<u>Description</u>
IDBUG6	Debugging print switch: = 0 No function. = 1 Prints details of the calculation of the stoichiometric equivalence factors.
IDBUG7	Debugging print switch: = 0 No function. = 1 Writes aqueous reactions on the file RLIST before and after basis switching
UEBAL	Name of ionic species for electrical balancing. If UEBAL is "PICK1.", the code picks a species. If UEBAL is blank, electrical balancing is not performed. If UEBAL is not recognized, the code selects a species.
UACION	Name of an aqueous species (Na^+ or Cl^-) that defines the equivalent stoichiometric ionic strength. If UACION is "PICK1.", the code picks a species. If UACION is blank, the equivalent stoichiometric ionic strength approach to estimating the activity of water is disabled and that variable is taken as unity.
NXMOD	Number of suppressed/alterd species/reaction pairs.
UXMOD	Name of a species to be suppressed or a species whose corresponding equilibrium constant is to be modified.
JXMOD	Flag identifying the type of species affected by an alter/suppress option: = 0 Aqueous species/reaction. = 1 Mineral. = 2 Gas. = 3 Solid solution.
KXMOD	Flag identifying the type of alter/suppress option: = -1 Species is suppressed. = 0 log K is replaced by XLKMOD. = 1 log K is augmented by XLKMOD. = 2 Same as KXMOD = 1, but XLKMOD is in kcal/mole.
XLKMOD	Corresponding equilibrium constant alteration function.
UBASIS	The name of an aqueous species that is to be basis switched with this master species.

EQ3NR INPUT file parameters (continued)

<u>Parameter</u>	<u>Description</u>
USPECB	The name of an aqueous master species (first twelve letters); USPECB names are matched with those in the USPEC array.
JFLAGB	Option switch that describes the input constraint (governing equation) that applies to this master species. The JFLAGB values are unpacked into the JFLAG array (see following table of JFLAG options).
CSPB	A floating point datum whose meaning is determined by the corresponding JFLAGB value. The CSPB values are unpacked into the CSP array.
UPHASE	The name of a mineral, gas, or solid-solution species, if any, that defines a phase equilibrium (solubility) constraint.
USOLB	Name of a solid solution for which a composition is entered; USOLB names are matched up with those in the USOLX array.
XBARB	The mole fraction of a solid solution end-member component (defined by UMEMB below). The XBARB values are unpacked into the XBAR array.
UMEMB	Name of an end-member component of the solid-solution defined by USOLB.

JFLAG Options
(PHOTOCOPY THIS PAGE AND KEEP NEAR THE COMPUTER TERMINAL)

<u>JFLAG</u>	<u>CSP</u>	<u>UPHASE</u>
0	Total molal concentration.	
1	Total molar concentration.	
2	Total concentration, mg/L.	
3	Total concentration, mg/kg.	
4	Free molal concentration.	
5	Free molar concentration.	
6	Free concentration, mg/L.	
7	Free concentration, mg/kg.	
8	Free concentration, cm ³ (STP)/cm.	
10	Titration alkalinity, eq/kg (*).	
11	Titration alkalinity, eq/L (*).	
12	Carbonate alkalinity, eq/kg (*).	
13	Carbonate alkalinity, eq/L (*).	
16	Log activity (molal scale) (**).	
19		Name of a mineral of fixed composition for which phase (solubility) equilibrium is required.
20		The first twelve letters of a solid solution and the first six letters of an end-member component for which phase (solubility) equilibrium is required.
21	Log fugacity of the gas defined by UPHASE.	Name of a gas for which phase (solubility) equilibrium is required.
27	Homogeneous aqueous equilibrium. This species and its complexes are not counted in the mass balance of any other master species (compare JFLAG = 30, below).	
30	"Eliminated" species. This species is effectively removed from the master species set. It and its complexes are treated as "complexes" of the corresponding strict basis master species. An "eliminated" species is <u>not</u> eliminated from the model.	

(*) Applies only to HCO₃⁻ or CO₃²⁻.

(**) Method for entering pH (-pH = log a_H⁺).

In certain circumstances, the user may wish to calculate the concentration of one valence form of an element by assuming equilibrium with another valence form. The master species corresponding to the latter must be in the strict basis set at the time of Newton-Raphson iteration. If it is not in that set when read from the data file, it can be entered into it by basis switching during EQUINR execution.

If a strict basis master species is constrained by mass balance (i.e., a total concentration), then setting the JFLAG of any corresponding auxiliary master species to 30 counts it and all its derivative species in that strict basis species' mass balance. This effectively removes the auxiliary master species from the master set. Setting JFLAG to any legal value other than 30 retains the auxiliary basis variable in the master set.

The condition JFLAG equal to 27 works differently. In this case, the species effectively remains in the master set. It and its complexes are not counted in the mass balance of the corresponding strict basis species. Its total concentration is then constrained only by the relevant equilibria. This can be somewhat dangerous, because that total concentration could be very large (see example in Section 6.3).

If there are no lines on the INPUT file for an auxiliary aqueous master species, its JFLAG value defaults to 30, unless it is $O_2(aq)$, or $H_2(aq)$, in which case it defaults to 27. A line is not entered for $H_2O(l)$, and a line is normally entered for $O_2(g)$ only when IOPT1 has a value of -3.

If a basis switch is executed between a strict master species and an auxiliary master species, their INPUT file properties follow them. If, however, a master species is exchanged with a nonmaster species, the INPUT file properties then belong to the new master species. Concentration parameters are recomputed to satisfy changes in stoichiometry, if necessary.

For example, if $(UO_2)_3(OH)_7$ is switched with the master species UO_2^{2+} , the corresponding INPUT file concentration, if it were 9×10^{-8} molal, would be recomputed as 3×10^{-8} molal to preserve the sense of the original input parameter.

5. SAMPLE PROBLEMS THAT WORK: INPUTS AND OUTPUTS

5.1. INTRODUCTION

This section presents the INPUT and OUTPUT files for four speciation-solubility modeling problems that were successfully executed by EQ3NR. The section following this presents three examples where execution failed because the model inputs represented ill-posed combinations. Each example begins with a short discussion. The INPUT file and OUTPUT files are then given as separate figures. The reader is encouraged to compare the OUTPUT file examples presented here with the INPUT file description presented in Section 4. Full output files are given only for the first two examples. Each OUTPUT file begins with an "instant" echo of the INPUT file. The PICKUP file for the first example in this section is shown and discussed in Section 7.

5.2. SEA WATER TEST CASE, WITH ONLY MAJOR CATIONS AND ANIONS

The first sample problem is the sea water test case from Nordstrom et al. (1979b), but only the major cations and anions are included. This simplified test case is a classic example in geochemistry (Garrels and Mackenzie, 1967; Garrels and Christ, 1965). The problem required 2.23 seconds of machine time (1.77 seconds for CPU, to run on a CDC 7600 computer and four file iterations to solve.

The INPUT file is shown in Figure 5. The OUTPUT file is given in its entirety in Figure 6. Note that the model constraints are printed three times. The first printout of the constraints is part of the instant echo that is written when EQ3NR is reading the INPUT file. The second printout, headed by "----- INPUT CONSTRAINTS -----", is intended to be a permanent record of the user specification on the INPUT file (the instant echo is not normally kept as part of a permanent record). The third printout, headed by "----- MODIFIED INPUT CONSTRAINTS -----", lists the model inputs as they have been modified by the program before starting the Newton-Raphson iteration. The modified constraints may differ from the originals in several ways. They include all conversions of concentration units to the molal scale, all defaults provided by the program, and the effects of basis switching. Users

Figure 5. Input, seawater example.

input file name= iswmaj created= 07/24/82 creator= t j walery

sea water test case, major components only this is a recalculation of the classic chemical model of garrels and thompson (1962) the analytical data used here are taken from table iii of nordstrom et al (1979), who discuss the application of various computer codes to this benchmark problem.

in this run, eq3nr calculates the electrical imbalance of the sea water analysis. such imbalance results from errors in the chemical analysis of individual components and from the fact that any such set of analysis is always more or less incomplete (in principle including trace elements in the model should tend to minimize calculated electrical imbalance). eq3nr could be set to force electrical balance by adjusting the concentration of a selected component, say cl^- , by setting "uebc1= cl-" below. it is not necessary to do this to initialize eq6 calculations.

the mineral pd-oxyannite (proton-deficient oxyannite) is suppressed. it is a hypothetical biotite end-member and does not exist as a pure phase.

references

nordstrom, d.k., et al. 1979. a comparison of computerized chemical models for equilibrium calculations in aqueous systems. p. 857-992 in jenne, e.a., ed., chemical modeling in aqueous systems, ocs symposium series 93, american chemical society, washington, d.c.

garrels, r.m., and thompson, m.e. 1962. a chemical model for sea water at 25 c and one atmosphere total pressure. amer. jour. sci. 260, 57-66.

tempc=	25.									
rho=	1.02336	tdspkg=	0.	tdspl=	0.					
fep=	0.500	uredox=								
loibt=	0.	loldl=	0.	lolsat=	0.					
itermx=	0									
iopt1-10=	-1	0	0	0	0	0	0	0	0	0

Figure 5. Input, seawater example (continued).

```

iprnt1-10= 0 0 0 0 0 0 0
idbug1-10= 0 0 0 0 0 0 0
ueba:=
          uacion= cl-
nxmod= 1
species= pd-oxyannite
type= 1
          option= -1
          xlkmod= 0.
          na+ 10768. 3
          k+ 399.1 5
          ca++ 412.3 3
          mg++ 1291.8 3
          h+ -8.22 16
          hco3- .002322 10
          cl- 19353. 3
          so4-- 2712. 3
          co3-- 30
hco3-
endit.

```


Figure 6. Output, seawater example (continued).

```

      1  2  3  4  5  6  7  8  9 10
iop11-10= -1  0  0  0  0  0  0  0  0  0
ipr11-10=  0  0  0  0  0  0  0  0  0  0
idbug1-10=  0  0  0  0  0  0  0  0  0  0
uebal=
          uacion= cl-
nxmod= 1
species= pd-oxyannite
type= 1
option= -1
xlkmod= 0.
run master data file csp jflag uphase
species master species
      na+ .10768e+05 3
      k+ .39910e+03 3
      ca++ .41230e+03 3
      mg++ .12918e+04 3
      h+ -.82200e+01 16
      hco3- .23220e-02 10
      cl- .19353e+05 3
      so4-- .27120e+04 3
hco3- co3-- 0. 30
endit.

```

----- the input file has been read -----

----- alter/suppress species pd-oxyannite was not among the loaded minerals -----

----- file data1 has been successfully read -----

Figure 6. Output, seawater example (continued).

```
eeee  qqq  33333  n  n  rrrr
e     q  q      3  nn  n  r  r
eeee  q  q      33  n  n  n  rrrr
e     q  q  q      3  n  nn  r  r
eeee  qqq  3333  n  n  r  r          3230 version
      q
```

input file name= iswmaj created= 07/24/82 creator= t.j. wolery

sea water test case, major components only. this is a recalculation of the classic chemical model of garrels and thompson (1962). the analytical data used here are taken from table iii of nordstrom et al. (1979), who discuss the application of various computer codes to this benchmark problem.

in this run, eq3nr calculates the electrical imbalance of the sea water analysis. such imbalance results from errors in the chemical analysis of individual components and from the fact that any such set of analyses is always more or less incomplete (in principle including trace elements in the model should tend to minimize calculated electrical imbalance). eq3nr could be set to force electrical balance by adjusting the concentration of a selected component, say cl-, by setting "uebal= ci-" below. it is not necessary to do this to initialize eq6 calculations.

the mineral pd-oxyannite (proton-deficient oxyannite) is suppressed. it is a hypothetical biotite end-member and does not exist as a pure phase.

references

nordstrom, d.k., et al. 1979. a comparison of computerized chemical models for equilibrium calculations in aqueous systems. p. 857-892 in jenne, e.a., ed., chemical modeling in aqueous systems, acs symposium series 93, american chemical society, washington, d.c.

Figure 6. Output, seawater example (continued).

garrels, r.m., and thompson, m.e. 1962. a chemical model for sea water at
25 c and one atmosphere total pressure. amer. jour. sci. 260, 57-66.

data file set deqpk9
supporting data for programs eq3 and eq6
1 atm.-steam saturation curve data
last revised 11 february 1983

temperature= 25.00 degrees celsius
pressure= 1.0134 bars

29 elements are in the data base
40 elements can be loaded into memory
9 elements are active in this problem

285 aqueous species are in the data base
74 aqueous species were loaded into memory
300 aqueous species can be loaded into memory
32 aqueous species are active in this problem

255 aqueous reactions are in the data base
44 aqueous reactions were loaded into memory
259 aqueous reactions can be loaded into memory

229 minerals are in the data base
18 minerals were loaded into memory
275 minerals can be loaded into memory
15 minerals are active in this problem

7 solid solutions are in the data base
20 solid solutions can be loaded into memory

Figure 6. Output, seawater example (continued).

8 gases are in the data base
7 gases were loaded into memory
15 gases can be loaded into memory
7 gases are active in this problem

iopt1 = -1 (redox option switch)
iopt2 = 0 (automatic basis switching switch)
iopt3 = 0 (interfacing output control switch)
iopt4 = 0 (turn-on solid solutions switch)
iopt5 = 0 (pre-iter. optimization switch)
iopt6 = 0 (not currently used)
iopt7 = 0 (not currently used)
iopt8 = 0 (conv. test criteria switch)
iopt9 = 0 (not currently used)
iopt10 = 0 (not currently used)

iprnt1 = 0 (list loading of species)
iprnt2 = 0 (list reactions and log k values)
iprnt3 = 0 (aqueous species print order control)
iprnt4 = 0 (aqueous species print cut-off control)
iprnt5 = 0 (mass balance percentages print control)
iprnt6 = 0 (not currently used)
iprnt7 = 0 (mineral affinity print control)

idbug1 = 0 (print info. messages switch)
idbug2 = 0 (print data read info. switch)
idbug3 = 0 (not currently used)
idbug4 = 0 (print newton-raphson iterations switch)
idbug5 = 0 (list stoichiometric equivalences)
idbug6 = 0 (controls idbug5 level of detail)
idbug7 = 0 (write reactions on file rlist switch)

Figure 6. Output, seawater example (continued).

solution density = 1.02336 g/ml

total dissolved salts = 0.00 mg/kg solution

total dissolved salts = 0.00 mg/l

tolbt = .10000e-09 (convergence tolerance on residual functions)

tolcl = .10000e-09 (convergence tolerance on correction terms)

tolst = .50000e+00 (phase saturation tolerance, does not affect convergence)

----- input constraints -----

species	csp	jflag	type of input	uphase	basis species
na+	.10768e+05	3	tot conc. mg/kg		
k+	.39910e+03	3	tot conc. mg/kg		
ca++	.41230e+03	3	tot conc. mg/kg		
mg++	.12918e+04	3	tot conc. mg/kg		
h+	-.82200e+01	16	log activity		
hco3-	.23220e-02	10	tit alk. eq/kg h2o		co3--
cl-	.19353e+05	3	tot conc. mg/kg		
so4--	.27120e+04	3	tot conc. mg/kg		
co3--	0.	30	eliminated species		hco3-

switching co3--

from the basis for hco3-

1.000 hco3-
 ==
 1.000 h+
 + 1.000 co3--

log k = -10.3281

Figure 6. Output, seawater example (continued).

```

1.000 co3--
+ 1.000 h+
==
1.000 hco3-
log k = 10.3281

```

----- inactive aqueous species -----

```

ch4(aq)      clo4-      kcl      kco3-
koh          mgcl+

```

----- modified input constraints -----

species	csp	jflag	type of input	uphase
na+	.46838e+00	0	tot conc. molal	
k+	.10208e-01	0	tot conc. molal	
ca++	.10287e-01	0	tot conc. molal	
mg++	.53150e-01	0	tot conc. molal	
h+	-.82200e+01	16	log activity	
hco3-	.23220e-02	10	tit alk. eq/kg h2o	
cl-	.54588e+00	0	tot conc. molal	
so4--	.28233e-01	0	tot conc. molal	
o2(aq)	0.	27	dependent species	
h2(aq)	0.	27	dependent species	
ch4(aq)			not present in the model	
hs-	0.	30	eliminated species	
co3--	0.	30	eliminated species	
clo4-			not present in the model	
oh-	0.	30	eliminated species	

the ion that defines equiv. stoich. ionic strength is cl-

Figure 6. Output, seawater example (continued).

iter = 0	delmax = 0.	del() = 0.	beta(so4--) = .981e+00	delfnc = 0.
iter = 1	delmax = .202e+00	del(so4--) = -.506e-01	beta(so4--) = .752e+00	delfnc = 0.
iter = 2	delmax = .176e+00	del(so4--) = -.176e+00	beta(so4--) = .145e+00	delfnc = .128e+00
iter = 3	delmax = .540e-01	del(so4--) = -.540e-01	beta(so4--) = .903e-02	delfnc = .694e+00
iter = 4	delmax = .386e-02	del(so4--) = -.386e-02	beta(so4--) = .449e-04	delfnc = .928e+00
iter = 5	delmax = .194e-04	del(so4--) = -.194e-04	beta(o2(g)) = -.544e-07	delfnc = .995e+00
iter = 6	delmax = .191e-07	del(so4--) = -.191e-07	beta(o2(g)) = -.501e-09	delfnc = .999e+00
iter = 7	delmax = .172e-09	del(so4--) = -.172e-09	beta(o2(g)) = -.477e-11	delfnc = .991e+00
iter = 8	delmax = .158e-11	del(so4--) = -.158e-11	beta(ca++) = .432e-13	delfnc = .991e+00

newton-raphson iteration converged in 8 steps

----- summary of the aqueous phase -----

----- elemental composition of the aqueous phase -----

element	mg/l	mg/kg	moles/kg
o	910814.3809	890023.4335	.5562855057e+02
no	11019.4302	10767.8923	.4683775555e+00
k	408.4261	399.1031	.1020768326e-01
ca	421.9313	412.3000	.1028692615e-01
mg	1321.9764	1291.8000	.5314955770e-01
h	114511.4884	111897.5614	.1110204994e+03
c	25.8627	25.2723	.2104098918e-02
cl	19805.0861	19353.0000	.5458776408e+00
s	926.2924	905.1481	.2823294260e-01

Figure 6. Output, seawater example (continued).

----- elemental composition on strict basis species -----

species	mg/l	mg/kg	moles/kg
h2o	1025558.5255	1002148.3403	.5562855067e+02
na+	11019.5405	10768.0000	.4683775555e+00
k+	408.4230	399.1000	.1020768326e-01
ca++	421.9313	412.3000	.1028692615e-01
mg++	1321.9764	1291.8000	.5314955770e-01
h+	114522.8498	111908.6634	.1110204994e+03
co3--	129.2144	126.2649	.2104098918e-02
cl-	19805.0861	19353.0000	.5458776408e+00
so4--	2775.3523	2712.0000	.2823294260e-01

----- equivalent composition of the aqueous phase -----

species	moles/kg h2o
h2o	.5562855067e+02
na+	.4683775555e+00
k+	.1020768326e-01
ca++	.1028692615e-01
mg++	.5314955770e-01
h+	.1110190123e+03
hco3-	.2104098918e-02
cl-	.5458776408e+00
so4--	.2823294260e-01

ionic strength = .6408087437851

equiv. stoich. ionic strength (cl-) = .5458776408202

ph = 8.22000

Figure 6. Output, seawater example (continued).

activity of water = 98203
 log activity of water = -.00788
 titration alkalinity = .23220e-02 eq/kg h2o

----- electrical balance totals -----

equiv/kg

cation subtotal .5711811338e+00
 anion subtotal -.5703884436e+00
 charge imbalance .7926901654e-03

this is .14 per cent of the cation subtotal
 and -.14 per cent of the anion subtotal

----- activity ratios of ions -----

log (act(no+) / act(h+)xx 1)	7.009
log (act(k+) / act(h+)xx 1)	6.0199
log (act(ca++) / act(h+)xx 2)	13.7903
log (act(mg++) / act(h+)xx 2)	14.6061
log (act(co3--) x act(h+)xx 2)	-21.5238
log (act(cl-) x act(h+)xx 1)	-8.6945
log (act(so4--) x act(h+)xx 2)	-19.0427
log (act(o2(aq)))	-19.3289
log (act(h2(aq)))	-36.4563
log (act(hs-) x act(h+)xx 1)	-118.7332
log (act(hco3-) x act(h+)xx 1)	-11.1957
log (act(oh-) x act(h+)xx 1)	-13.9953

Figure 6. Output, seawater example (continued).

----- distribution of aqueous species -----

species	molar conc	log conc	log g	activity	log act
cl-	5335e+00	-2.729	-20.16	.3353e+00	-4.745
na+	4501e+00	-3.467	-17.74	.3026e+00	-5.191
mg++	.4623e-01	-1.3346	-4.994	.1466e-01	-1.8339
so4--	.1465e-01	-1.8341	-7.686	.2496e-02	-2.6027
nacl	.1241e-01	-1.9062	0.0000	.1241e-01	-1.9062
k+	.1034e-01	-1.9985	-2.2016	.6308e-02	-2.2001
ca++	.9053e-02	-2.0437	-6.065	.2240e-02	-2.6497
mgso4	.6171e-02	-2.1891	0.0000	.6471e-02	-2.1891
na2so4-	.5793e-02	-2.2371	-1.1651	.3961e-02	-2.4022
hco3-	.1530e-02	-2.8152	-1.1605	.1058e-02	-2.9757
caso4	.1145e-02	-2.9410	0.0000	.1145e-02	-2.9410
mghco3+	.2813e-03	-3.5508	-1.1724	.1891e-03	-3.7233
kso4-	.1720e-03	-3.7644	-1.1860	.1121e-03	-3.9504
mgco3	.1158e-03	-3.9365	0.0000	.1158e-03	-3.9365
cahco3+	.5898e-04	-4.2293	-1.1460	.4215e-04	-4.3752
cc3--	.4335e-04	-4.3630	-1.7207	.8246e-05	-5.0832
na2co3--	.3296e-04	-4.4820	-1.1605	.2278e-04	-4.6425
caco3	.2916e-04	-4.5352	0.0000	.2916e-04	-4.5352
h2co3	.1212e-04	-4.9165	.0683	.1418e-04	-4.8482
mg(oh)+	.5975e-05	-5.2236	-1.1724	.4017e-05	-5.3961
oh-	.2575e-05	-5.5892	-1.1860	.1678e-05	-5.7753
ca(oh)+	.1403e-06	-6.8530	-1.1724	.9431e-07	-7.0255
naoh	.1013e-06	-6.9944	0.0000	.1013e-06	-6.9944
h+	.7496e-08	-8.1251	-1.0949	.6076e-08	-8.2200
hso4-	.2263e-08	-8.6452	-1.1724	.1522e-08	-8.8177
hcl	.1484e-14	-14.8284	0.0000	.1484e-14	-14.8284
o2(aq)	4006e-19	-19.3973	.0683	.4689e-19	-19.3289
h2(aq)	.2988e-36	-36.5246	.0683	.3497e-36	-36.4563
hs-	.4709-110	-110.3271	-1.1860	3068-110	-110.5132
h2s(aq)	.1757-111	-111.7526	0.0000	.1768-111	-111.7526
s--	.1653-112	-112.7818	-1.6763	.3467-119	-119.4601

Figure 6. Output, seawater example (continued).

----- major aqueous species contributing to mass balances -----

aqueous species accounting for 99% or more of na+

species	molar conc	per cent
na+	.4501e+00	96.11
nacl	.1241e-01	2.65
naoc4-	.5793e-02	1.24

subtotal		99.99

aqueous species accounting for 99% or more of k+

species	molar conc	per cent
k+	.1004e-01	98.31
koc4-	.1720e-03	1.69

subtotal		100.00

aqueous species accounting for 99% or more of ca++

species	molar conc	per cent
ca++	.9053e-02	88.01
caso4	.1145e-02	11.14

subtotal		99.14

Figure 6. Output, seawater example (continued).

aqueous species accounting for 99% or more of mg++

species	molar conc	per cent
mg++	.4628e-01	87.07
mgso4	.6471e-02	12.17

subtotal		99.24

aqueous species accounting for 99% or more of hco3-

species	molar conc	per cent
hco3-	.1530e-02	72.74
mg hco3+	.2813e-02	13.37
mgco3	.1158e-03	5.50
ca hco3+	.5898e-04	2.80
co3--	.4335e-04	2.06
na co3-	.3296e-04	1.57
co co3	.2916e-04	1.39

subtotal		99.42

aqueous species accounting for 99% or more of cl-

species	molar conc	per cent
cl-	.5335e+00	97.73
nacl	.1241e-01	2.27

subtotal		100.00

Figure 6. Output, seawater example (continued).

aqueous species accounting for 99% or more of so4--

species	molar conc	per cent
so4--	.1465e-01	51.90
mgso4	.6471e-02	22.92
na2so4-	.5793e-02	20.52
caso4	.1145e-02	4.06

subtotal		99.39

----- summary of aqueous redox reactions -----

couple	eh. volts	pe-	log fo2	ah. kcal
default	.500	.8452e+01	-16.430	11.531
o2(aq) /h2o	.500	.8452e+01	-16.430	11.531
h2(aq) /h2o	.500	.8452e+01	-16.430	11.531
hs- /so4--	.500	.8452e+01	-16.430	11.531

----- summary of aqueous non-equilibrium non-redox reactions -----

couple	affinity, kcal
none	

Figure 6. Output, seawater example (continued).

----- summary of stoichiometric mineral saturation states -----

(minerals with affinities ≥ -10 kcal are not listed)

mineral	log q/k	aff. kcal	state	mineral	log q/k	aff. kcal	state
brucite	-1.84E	-2.522		halite	-2.603	-3.551	
sylvite	-3.570	-4.870		calcite	.791	1.080	ssald
magnesite	.990	1.351	ssald	dolomite	3.410	4.652	ssald
hydromagnesite	-3.297	-4.498		anhydrite	-.987	-1.347	
gypsum	-.418	-.570		arlinite	-1.943	-2.651	
huntite	2.029	2.768	ssald	aragonite	.626	.855	ssald
disordered d	1.866	2.545	ssald	ordered dolo	3.410	4.652	ssald
nesquehonite	-1.732	-2.363					

0 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

Figure 6. Output, seawater example (continued).

----- summary of gases -----

gas	fugacity	log fugacity
co2(g)	.443321e-03	-3.35328
o2(g)	.371593e-16	-16.42993
s2(g)	.352013-180	-180.45344
ch4(g)	.152242-113	-113.81747
h2(g)	.452575e-33	-33.34431
h2s(g)	.179327-110	-110.74635
steam	.307485e-01	-1.51218

----- end of output -----
----- pickup file successfully written -----
----- reading the input file -----
----- end of input file -----

should make a point to examine this part of the OUTPUT file to ensure that the model they obtain is the model they want.

The listing headed by "----- INACTIVE AQUEOUS SPECIES -----" is also important. It lists those aqueous species that are on the data file but do not appear in the model being computed in the current run either because corresponding data on the DATA0 file are lacking or because of user-specified suppression on the INPUT file. The "----- DISTRIBUTION OF AQUEOUS SPECIES -----" heading normally lists the aqueous solute species in decreasing order of concentration, however, it is possible to provide lower limit cutoff values for this listing (see Section 4).

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 (refer to any aqueous geochemistry text, such as Berner, 1971).

The redox reaction summary, (headed by "----- SUMMARY OF AQUEOUS REDOX REACTIONS -----"), for this example indicates that all redox couples are in mutual equilibrium. This is not a scientific conclusion about the chemistry of sea water, but rather an example showing that the output of a model must be consistent with its input. The input constraints for this run assumed this equilibrium. Compare this with the case in Section 5.5, where redox equilibrium is treated in the model.

In the model, PD-oxyannite ($KFe_3AlSi_3O_{12}H_{-1}$, a hypothetical biotite end member) is suppressed. This is merely for illustrative purposes. Suppression of minerals, gases, and solid solutions has meaning only for EQ6, but has no meaning for EQ3NR. This information transmitted to EQ6 via the PICKUP file (see Section 7).

5.3. EXAMPLE USING MINERAL SOLUBILITY CONSTRAINTS

In this example we modify the sea water test case, dropping some trace components while constraining three others, aluminum, iron, and fluoride, to satisfy mineral solubility equilibria for gibbsite $[Al(OH)_3]$, Na-nontronite $[Na_{0.33}(Fe_2)(Al_{0.33}Si_{3.67})(OH)_2]$, and fluorite (CaF_2). To make the problem a bit more interesting, we also altered the log K values for $NaSO_4^-$ and Na-nontronite. The INPUT file is shown in Figure 7. This run required 4.51 seconds of CDC 7600 machine time (4.02 seconds for CPU) and eight iterations.

Figure 7. Input, modified seawater example (continued).

```

iprnt1-10= 0 0 0 0 0 0 0
idbug1-10= 0 0 0 0 0 0 0
uebal=
nzmmod= 3
species= pd-oxyannite
type= 1 option= -1 xikmod= 0.
species= ms04-
type= 0 option= 1 xikmod= 0.1
species= na-nontronite
type= 1 option= 1 xikmod= 2.0
na+ 10765 3
k+ 399.1 3
ca++ 412.3 3
mg++ 1291.3 3
al+++ 19 gibbsite
si2(aq) 4.28 3
n+ -8.22 16
hco3- 002322 10
cl- 19353. 3
so4-- 2712. 3
f- 19 fluorite
fe++ 19 na-nontronite
hpo4-- 0.061 3
o2(aq) 30
h2(aq) 27
ch4(aq) 27
hs- 27
hco3- co3-- 30
endit

```

The OUTPUT file is given in its entirety in Figure 8. In the mineral saturation state listing on the OUTPUT file, gibbsite, Na-nontronite, and fluorite are exactly saturated in accord with the input constraints while many aluminum-bearing minerals, other than gibbsite, are supersaturated. Substituting one of these minerals for gibbsite in the equilibrium solubility constraint on dissolved aluminum would reduce the number of supersaturated minerals.

5.4. EXAMPLE CALCULATING pH FROM ELECTRICAL BALANCE

This short example illustrates the use of EQ3NR to calculate the pH of the solution from the electrical balance constraint. The INPUT file is shown in Figure 9. The aqueous solution in this example is a mixture of water and four salts and is assumed to be open to the atmosphere; thus, exchange of carbon dioxide between air and the solution is taken into account. This run required 1.70 seconds of CDC 7600 machine time (1.09 seconds for CPU) and nine iterations.

Parts of the OUTPUT file are shown in Figures 10A and 10B. The calculated pH is 8.11546 (Fig. 10A). When this problem was run with carbonate constrained to match the amount resulting from dissolution of the NaHCO_3 salt (ignoring carbon dioxide exchange with air), the pH was calculated to be 7.72770; therefore, if one were to produce the designated solution in the laboratory, we would expect the pH to rise from approximately 7.60 to approximately 7.72 as a result of a slight degassing of carbon dioxide.

We see in Figure 10B that the solution is supersaturated with respect to two calcium carbonate phases (calcite and aragonite) and three calcium phosphate minerals (whitlockite, hydroxyapatite, and $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$). To find the pH that would result from subsequent precipitation of such phases, we would have to use the EQ6 code (Wolery, 1983a) and enter the solution composition via the PICKUP file (Section 7).

5.5 EXAMPLE OF REDOX DISEQUILIBRIUM: RIVER WATER TEST CASE

This example is the river water test case of Nordstrom et al. (1979b). The INPUT file is shown in Figure 11. This model tests for redox equilibrium among several redox couples (see Section 2.3.5). Disequilibrium is apparent

Figure 8. Output, modified seawater example.

----- reading the input file -----

input file name: isw3eq created: 07/24/82 creator: l.j. wolery

sea water test case of nordstrom et al. (1979, table iii), modified by dropping a few trace components, and substituting equilibrium constraints for concentrations for three of the remaining components. To make this example more interesting, the log k values for no_3^- dissociation and no_2^- nontronite dissolution are increased 0.1 and 2.0 units, respectively, from the values on the thermodynamic data file.

references

nordstrom, d.k., et al. 1979. a comparison of computerized chemical models for equilibrium calculations in aqueous systems. p. 857-892 in jenne, e.a., ed., chemical modeling in aqueous systems, acs symposium series 93, american chemical society, washington, d.c.

tempc=	.25000e+02		
rho=	.10234e+01	tdspkg= 0.	tdspl= 0.
fep=	.50000e+00	uredox=	
tolbt=	0.	toldl= 0.	tolst= 0.
itermx=	0.		

Figure 8. Output, modified seawater example.

----- reading the input file -----

input file name: isw3eq created: 07/24/82 creator: l.j. walery

sea water test case of nordstrom et al. (1979, table iii), modified by dropping a few trace components, and substituting equilibrium constraints for concentrations for three of the remaining components. To make this example more interesting, the log K values for no_3^- dissociation and no_2^- nontronite dissolution are increased 0.1 and 2.0 units, respectively, from the values on the thermodynamic data file.

references

nordstrom, d.k., et al. 1979. a comparison of computerized chemical models for equilibrium calculations in aqueous systems. p. 857-892 in jenne, e.o., ed., chemical modeling in aqueous systems, acs symposium series 93, american chemical society, washington, d.c.

tempc=	.25000e+02		
rho=	.10234e+01	tdspkg= 0.	tdspl= 0.
fep=	.50000e+00	uredox=	
tolbt=	0.	toldl= 0.	tolst= 0.
itermx=	0		

Figure 8. Output, modified seawater example.

----- reading the input file -----

input file name: isw3eq created: 07/24/82 creator: l.j. walery

sea water test case of nordstrom et al. (1979, table iii), modified by dropping a few trace components, and substituting equilibrium constraints for concentrations for three of the remaining components. To make this example more interesting, the log k values for na_2so_4 dissociation and na -nontronite dissolution are increased 0.1 and 2.0 units, respectively, from the values on the thermodynamic data file.

82

references

nordstrom, d.k., et al. 1979. a comparison of computerized chemical models for equilibrium calculations in aqueous systems. p. 857-892 in jenne, e.a., ed., chemical modeling in aqueous systems, acs symposium series 93, american chemical society, washington, d.c.

tempc=	.25000e+02		
rho=	.10234e+01	tdspkg= 0.	tdspl= 0.
fep=	.50000e+00	uredox=	
tolbt=	0.	tolcl= 0.	tolcat= 0.
itermx=	0		

Figure 8. Output, modified seawater example (continued).

```

      1   2   3   4   5   6   7   8   9  10
iop11-10= -1   0   0   0   0   0   0   0   0   0
iprnt1-10=  0   0   0   0   0   0   0   0   0   0
idbug1-10=  0   0   0   0   0   0   0   0   0   0
uebal=
nxmod= 3
species= pd-oxyannite
  type= 1
species= naso4-
  type= 0
species= na-nontronite
  type= 1
run master      data file      csp      jflag      uphase
species          master species
na+              .10768e+05      3
k+               .39910e+03      3
ca++             .41230e+03      3
mg++             .12918e+04      3
al+++           0.          19  gibbsite
sio2(aq)         .42800e+01      3
h+              -.82200e+01     16
hco3-           .23220e-02     10
cl-             19353e+05      3
so4--           .27120e+04      3
f-              0.          19  fluorite
fe++            0.          19  na-nontronite
hpo4--          .61000e-01      3
o2(aq)          0.          30
h2(aq)          0.          27
ch4(aq)         0.          27
hs-             0.          27
hco3-           co3--      0.          30
endit.

```

----- the input file has been read -----

Figure 8. Output, modified seawater example (continued).

```

1.000 na34-
==
log k = -.7197
1.000 na+
+ 1.000 so4--

```

log k of the above reaction was changed to -6197

```

1.000 na-nontronite
+ 7.320 h+
==
log k = -15.9492
4.660 h2o
+ .330 na+
+ .330 al+++
+ 3.670 sio2(aq)
+ 2.000 fe+++

```

log k of the above reaction was changed to -13.3432

pd-cyanite has been user-suppressed

----- file data1 has been successfully read -----

```

eeee qqr 33333 n n rrrr
e q q 3 nn n r r
eeee q q 33 n n n rrrr
e q q q 3 n nn r r
eeee qqq 3333 n n r r
q

```

3230 version

Figure 8. Output, modified seawater example (continued).

input file name: isw3eq .created: 07/24/82 creator: t j. wclery

sea water test case of nordstrom et al. (1979, table iii), modified by dropping a few trace components, and substituting equilibrium constraints for concentrations for three of the remaining components. To make this example more interesting, the $\log K$ values for naSO_4^- dissociation and na-natronite dissolution are increased 0.1 and 2.0 units, respectively, from the values on the thermodynamic data file.

references

nordstrom, d.k., et al. 1979. a comparison of computerized chemical models for equilibrium calculations in aqueous systems. p. 857-892 in jenne, e.a., ed., chemical modeling in aqueous systems, acs symposium series 93, american chemical society, washington, d.c.

data file set deqpak9
supporting data to programs eq3 and eq6
1 atm.-steam saturation curve data
last revised 11 february 1983

Figure 8. Output, modified seawater example (continued).

temperature= 25.00 degrees celsius
pressure= 1.0134 bars

29 elements are in the data base
40 elements can be loaded into memory
14 elements are active in this problem

285 aqueous species are in the data base
133 aqueous species were loaded into memory
300 aqueous species can be loaded into memory
93 aqueous species are active in this problem

255 aqueous reactions are in the data base
103 aqueous reactions were loaded into memory
259 aqueous reactions can be loaded into memory

229 minerals are in the data base
144 minerals were loaded into memory
275 minerals can be loaded into memory
138 minerals are active in this problem

7 solid solutions are in the data base
20 solid solutions can be loaded into memory

8 gases are in the data base
7 gases were loaded into memory
15 gases can be loaded into memory
7 gases are active in this problem

Figure 8. Output, modified seawater example (continued).

iop11 = -1 (redox option switch)
iop12 = 1 (automatic basis switching switch)
iop13 = 0 (interfacing output control switch)
iop14 = 0 (turn-on solid solutions switch)
iop15 = C (pre-iter. optimization switch)
iop16 = 0 (not currently used)
iop17 = 0 (not currently used)
iop18 = 0 (conv. test criteria switch)
iop19 = 0 (not currently used)
iop110 = 0 (not currently used)

iprint1 = 0 (list loading of species)
iprint2 = 0 (list reactions and log k values)
iprint3 = 0 (aqueous species print order control)
iprint4 = 0 (aqueous species print cut-off control)
iprint5 = 0 (mass balance percentages print control)
iprint6 = 0 (not currently used)
iprint7 = 0 (mineral affinity print control)

idbug1 = 0 (print info. messages switch)
idbug2 = 0 (print data read info. switch)
idbug3 = 0 (not currently used)
idbug4 = 0 (print newton-raphson iterations switch)
idbug5 = 0 (list stoichiometric equivalences)
idbug6 = 0 (controls idbug5 level of detail)
idbug7 = 0 (write reactions on file rlist switch)

solution density = 1.02336 g/ml

total dissolved salts = 0.00 mg/kg solution
total dissolved salts = 0.00 mg/l

Figure 8. Output, modified seawater example (continued).

tolbl = .10000e-09 (convergence tolerance on residual functions)
 toldl = .10000e-09 (convergence tolerance on correction terms)
 tolsl = .50000e+00 (phase saturation tolerance, does not affect convergence)

----- input constraints -----

species	csp	jflag	type of input	uphase	basis species
na+	.10768e+05	3	tot conc. mg/kg		
k+	.39910e+03	3	tot conc. mg/kg		
ca++	.41230e+03	3	tot conc. mg/kg		
mg++	.12918e+04	3	tot conc. mg/kg		
al+++	0.	19	min equil	gibbsite	
	1.000		gibbsite		
	+ 3.000		h+		
	==		log k =	7.9603	
	3.000		h2o		
	+ 1.000		al+++		
sio2(aq)	.42800e+01	3	tot conc. mg/kg		
h+	-.82200e+01	16	log activity		
hco3-	.23220e-02	10	tit alk. eq/kg h2o		co3--
cl-	.19353e+05	3	tot conc. mg/kg		
so4--	.27120e+04	3	tot conc. mg/kg		
f-	0.	19	min equil	fluorite	
	1.000		fluorite		
	==		log k =	-10.9589	
	1.000		ca++		
	+ 2.000		f-		
fe++	0.	19	min equil	na-nontronite	

Figure 8. Output, modified seawater example (continued).

```

1.000 na-nontronite
+ 7.320 h+
== log k = -13.8482
4.660 h2o
+ .330 na+
+ .330 al+++
+ 3.670 sio2(aq)
+ 2.000 fe+++
hpo4-- .61000e-01 ? tot conc. mg/kg
o2(aq) 0. 30 eliminated species
h2(aq) 0. 27 dependent species
ch4(aq) 0. 27 dependent species
hs- 0. 27 dependent species
co3-- 0. 30 eliminated species hco3-

```

switching co3--

from the basis for hco3-

```

1.000 hco3-
== log k = -10.3281
1.000 h+
+ 1.000 co3--

1.000 co3--
+ 1.000 h+
== log k = 10.3281
1.000 hco3-

```

----- inactive aqueous species -----

```

ch4(aq)          clo4-          kcl          kco3-
fecl+           fecl2         fecl3-       fecl4--
fe(so4)2-       koh           mgcl+

```

Figure 8. Output, modified seawater example (continued).

```

----- modified input constraints -----
species      csp      jflag  type of input      uphase

na+          .46838e+00  0      tot conc. molal
k+           .10208e-01  0      tot conc. molal
ca++        .10287e-01  0      tot conc. molal
mg++        .53150e-01  0      tot conc. molal
al+++       0.          19     min equil          gibbsite

      1.000 gibbsite
      + 3.000 h+
      ==
      3.000 h2o
      + 1.000 al+++
sio2(aq)    .71234e-04  0      tot conc. molal
h+          -.82200e+01  16     log activity
hco3-       .23220e-02  10     tit alk. eq/kg h2o
cl-         .54588e+00  0      tot conc. molal
so4--       .28233e-01  0      tot conc. molal
f-          0.          19     min equil          fluorite

      1.000 fluorite
      ==
      1.000 ca++
      + 2.000 f-
fe++       0.          19     min equil          na-nontronite

      1.000 na-nontronite
      + 5.320 h+
      ==
      3.660 h2o
      + .330 na+
      + .330 al+++
      + 3.670 sio2(aq)
      + 2.000 fe++

```

log k = 7.9603

log k = -10.9589

log k = -29.3778

Figure 8. Output, modified seawater example (continued).

```

+ .500 o2(g)
hpo4--      .63556e-06   0   tot conc. molal
o2(aq)      0.         27   dependent species
h2(oq)      0.         27   dependent species
ch4(oq)     0.         27   dependent species
hs-         0.         27   dependent species
fe+++      0.         30   eliminated species
h2po4-     0.         30   eliminated species
co3--      0.         30   eliminated species
cl-         0.         30   not present in the model
oh-        0.         30   eliminated species

```

the ion that defines equiv. stoich. ionic strength is cl-

16

```

iter = 0   delmax = 0.         del(      ) = 0.         beta(hpo4--) = .402e+01   del fnc = 0.
iter = 1   delmax = .363e+00   del(hpo4--) = -.908e-01   beta(hpo4--) = .311e+01   del fnc = 0.
iter = 2   delmax = .343e+00   del(hpo4--) = -.856e-01   beta(hpo4--) = .240e+01   del fnc = .565e-01
iter = 3   delmax = .319e+00   del(hpo4--) = -.797e-01   beta(hpo4--) = .185e+01   del fnc = .691e-01
iter = 4   delmax = .293e+00   del(hpo4--) = -.293e+00   beta(hpo4--) = .503e+00   del fnc = .226e-01
iter = 5   delmax = .148e+00   del(hpo4--) = -.148e+00   beta(hpo4--) = .772e-01   del fnc = .494e+00
iter = 6   delmax = .312e-01   del(hpo4--) = -.312e-01   beta(hpo4--) = .274e-02   del fnc = .789e+00
iter = 7   delmax = .119e-02   del(hpo4--) = -.119e-02   beta(hpo4--) = .408e-05   del fnc = .962e+00
iter = 8   delmax = .177e-05   del(hpo4--) = -.177e-05   beta(hpo4--) = .318e-08   del fnc = .999e+00
iter = 9   delmax = .277e-08   del(f-      ) = -.277e-08   beta(hpo4--) = .296e-10   del fnc = .998e+00
iter = 10  delmax = .258e-10   del(f-      ) = -.258e-10   beta(o2(g) ) = -.455e-12   del fnc = .991e+00

```

newton-raphson iteration converged in 10 steps

Figure 8. Output, modified seawater example (continued).

----- summary of the aqueous phase -----

----- elemental composition of the aqueous phase -----

element	mg/l	mg/kg	moles/kg
c	910816.7140	890025.7133	.5562869316e+02
na	11019.4302	10767.8923	.4683775555e+00
k	408.4261	399.1031	.1020768326e-01
ca	421.9313	412.3000	.1028692615e-01
mg	1321.9764	1291.8000	.5314955770e-01
al	.0045	.0044	.1638910844e-06
si	2.0474	2.0006	.7123360628e-04
h	114511.4992	111897.5725	.1110205105e+03
c	25.8142	25.2255	.2100199501e-02
cl	19805.0861	19353.0000	.5458776408e+00
s	926.2924	905.1481	.2823294260e-01
i	4.0682	3.9753	.2092434829e-03
fe	.0000	.0000	.4846993972e-15
p	.0201	.0197	.6355556945e-06

----- elemental composition as strict basis species -----

species	mg/l	mg/kg	moles/kg
h2o	1025561.1525	1002150.9073	.5562869316e+02
na+	11019.5405	10768.0000	.4683775555e+00
k+	408.4230	399.1000	.1020768326e-01
ca++	421.9313	412.3000	.1028692615e-01
mg++	1321.9764	1291.8000	.5314955770e-01
al+++	.0045	.0044	.1638910844e-06
sio2(o)	4.3800	4.2800	.7123360628e-04

Figure 8. Output, modified seawater example (continued).

h+	114522.8612	111908.6746	.1110205105e+03
co3--	128.9750	126.0309	.2100199501e-02
cl-	19805.0861	19353.0000	.5458776408e+00
so4--	2775.3523	2712.0000	.2823294260e-01
f-	4.0681	3.9752	.2092434829e-03
fe++	.0000	.0000	.4846993972e-15
hpo4--	.0624	.0610	.6355556945e-06

----- equivalent composition of the aqueous phase -----

species	moles/kg h2o
h2o	.5562869316e+02
na+	.4683775555e+00
k+	.1020768326e-01
ca++	.1028692615e-01
mg++	.5314955770e-01
al+++	.1638910844e-06
sio2(aq)	.7123360628e-04
h+	.1110190238e+03
hco3-	.2100199501e-02
cl-	.5458776408e+00
so4--	.2823294260e-01
f-	.2092434829e-03
fe++	.4846993972e-15
hpo4--	.6355556945e-06

ionic strength = .6414642840581
 equiv. stoich. ionic strength (cl-) = .5458776408202

ph = 8.22000

activity of water = .98203
 log activity of water = -.00788

titration alkalinity = .23220e-02 eq/kg h2o

Figure 8. Output, modified seawater example (continued).

----- electrical balance totals -----

	equiv/kg
cation subtotal	5.14432565e+00
anion subtotal	-5.208607008e+00
charge imbalance	5825556966e-03

this is .10 per cent of the cation subtotal
and -.10 per cent of the anion subtotal

----- activity ratios of ions -----

log (act(na+) / act(h+)xx 1)	7.7018
log (act(k+)) / act(h+)xx 1)	6.0195
log (act(ca++)) / act(h+)xx 2)	13.7879
log (act(mg++)) / act(h+)xx 2)	14.6028
log (act(al+++) / act(h+)xx 3)	7.9839
log (act(sio2(aq)))	-4.1743
log (act(co3--) x act(h+)xx 2)	-21.5239
log (act(cl-) x act(h+)xx 1)	-8.6946
log (act(so4--) x act(h+)xx 2)	-19.0234
log (act(f-) x act(h+)xx 1)	-12.3734
log (act(fe++)) / act(h+)xx 2)	-5.4954
log (act(hpo4--) x act(h+)xx 2)	-24.1346
log (act(o2(aq)))	-19.3289
log (act(h2(oq)))	-36.4563
log (act(hs-) x act(h+)xx 1)	-118.7138
log (act(fe+++) / act(h+)xx 3)	-1.8341
log (act(h2po4-) x act(h+)xx 1)	-16.9294
log (act(hco3-) x act(h+)xx 1)	-11.1958
log (act(oh-) x act(h+)xx 1)	-13.1953

Figure 8. Output, modified seawater example (continued).

----- distribution of aqueous species -----

species	molar conc	log conc	log g	activity	log act
cl-	.5334e+00	-.2729	-.2017	.3353e+00	-.4746
na+	.4511e+00	-.3457	-.1725	.3032e+00	-.5182
mg++	.4594e-01	-1.3378	-.4993	.1455e-01	-1.8372
so4--	.1533e-01	-1.8146	-.7688	.2610e-02	-2.5834
nacl	.1243e-01	-1.9054	0.0000	.1243e-01	-1.9054
k+	.1003e-01	-1.9988	-.2017	.6303e-02	-2.2005
ca++	.9005e-02	-2.0455	-.6066	.2228e-02	-2.6521
mgso4	.6715e-02	-2.1729	0.0000	.6715e-02	-2.1729
na2so4-	.4822e-02	-2.3168	-.1651	.3297e-02	-2.4819
hco3-	.1530e-02	-2.8153	-.1605	.1057e-02	-2.9758
caso4	.1191e-02	-2.9241	0.0000	.1191e-02	-2.9241
mghco3+	.2791e-03	-3.5542	-.1725	.1877e-03	-3.7266
kso4-	.1797e-03	-3.7453	-.1861	.1171e-03	-3.9314
mgco3	.1149e-03	-3.9398	0.0000	.1149e-03	-3.9398
f-	.1078e-03	-3.9673	-.1861	.7024e-04	-4.1534
mgf+	.9557e-04	-4.0197	-.1725	.6424e-04	-4.1922
sio2(aq)	.6695e-04	-4.1743	0.0000	.6695e-04	-4.1743
cahco3+	.5864e-04	-4.2318	-.1460	.4190e-04	-4.3778
co3--	.4335e-04	-4.3630	-.7209	.8244e-05	-5.0839
na2co3-	.3302e-04	-4.4812	-.1605	.2282e-04	-4.6417
caco3	.2899e-04	-4.5377	0.0000	.2899e-04	-4.5377
h2co3	.1211e-04	-4.9167	.0684	.1418e-04	-4.8483
mg(oh)+	.5931e-05	-5.2268	-.1725	.3987e-05	-5.3993
h3sio4-	.4286e-05	-5.3680	-.1725	.2881e-05	-5.5404
caf+	.3019e-05	-5.5202	-.1725	.2029e-05	-5.6927
naf	.2845e-05	-5.5459	0.0000	.2845e-05	-5.5459
oh-	.2575e-05	-5.5892	-.1861	.1678e-05	-5.7753
mghpo4	.2390e-06	-6.6217	0.0000	.2390e-06	-6.6217
al(oh)4-	.1639e-06	-6.7854	-.1725	.1102e-06	-6.9579
ca(oh)+	.1395e-06	-6.8554	-.1725	.9378e-07	-7.0279
nahpo4-	.1294e-06	-6.8879	-.1725	.8702e-07	-7.0604
hpo4--	.1186e-06	-6.9258	-.7688	.2020e-07	-7.6946
naoh	.1015e-06	-6.9935	0.0000	.1015e-06	-6.9935
mgpo4-	.1009e-06	-6.9961	-.1725	.5783e-07	-7.1686

Figure 8. Output, modified seawater example (continued).

species	molar conc	log conc	log g	activity	log act
cahpo4	.2555e-07	-7.5927	0.0000	.2555e-07	-7.5927
capo4-	.1557e-07	-7.8076	-.1725	.1047e-07	-7.9801
h+	.7496e-08	-8.1252	-.0948	.6026e-08	-8.2200
h2po4-	.2905e-08	-8.5369	-.1725	.1953e-08	-8.7094
hso4-	.2367e-08	-8.6258	-.1725	.1591e-08	-8.7983
khpo4-	.2103e-08	-8.6772	-.1725	.1414e-08	-8.8497
mgh2po4+	.1393e-08	-8.8560	-.1725	.9365e-09	-9.0285
hf	.6240e-09	-9.2048	0.0000	.6240e-09	-9.2048
po4---	.9236e-10	-10.0345	-1.7626	.1595e-11	-11.7971
al12+	.5993e-12	-12.2223	-.1725	.4029e-12	-12.3948
al13	.3564e-12	-12.4481	0.0000	.3564e-12	-12.4481
al(oh)++	.2616e-12	-12.5823	-.6066	.6473e-13	-13.1889
hf2-	.2050e-12	-12.6862	-.1725	.1385e-12	-12.8587
al1++	.6867e-13	-13.1633	-.6785	.1440e-13	-13.8417
al14-	.9357e-14	-14.0288	-.1725	.6290e-14	-14.2513
h3po4	.1665e-14	-14.7786	0.0000	.1665e-14	-14.7786
hcl	.1484e-14	-14.8285	0.0000	.1484e-14	-14.8285
fe(oh)4-	.4756e-15	-15.3228	-.1725	.3197e-15	-15.4952
al1++	.2443e-15	-15.6121	-1.0640	.2108e-16	-16.6761
al15--	.1929e-15	-15.7147	-.7688	.3285e-16	-16.4835
al3o4+	.9561e-16	-16.0675	-.1725	.5755e-16	-16.2400
p2o7----	.5952e-16	-16.2224	-3.1540	.4203e-19	-19.3764
alhpo4+	.3988e-16	-16.3992	-.1725	.2681e-16	-16.5717
hp2o7----	.3762e-16	-16.4246	-1.7626	.6498e-18	-18.1872
fe(oh)2+	.9074e-17	-17.0422	-.1725	.6100e-17	-17.2147
h212	.1047e-17	-17.9799	0.0000	.1047e-17	-17.9799
h2p2o7--	.1166e-18	-18.9334	-.7608	.1985e-19	-19.7022
al16---	.7301e-19	-19.1366	-1.7626	.1261e-20	-20.8992
o2(aq)	.4006e-19	-19.3973	.0684	.4689e-19	-19.3289
fe(oh)++	.1996e-19	-19.6999	-.7688	.3399e-20	-20.4687
fe++	.4690e-21	-21.3288	-.6066	.1160e-21	-21.9354
alh2po4++	.3916e-21	-21.4071	-.6785	.8212e-22	-22.0856
fe(oh)+	.1454e-21	-21.8373	-.1725	.9777e-22	-22.0098
fesO4	.5358e-22	-22.2710	0.0000	.5358e-22	-22.2710

Figure 8. Output, modified seawater example (continued).

fehpo4+	.1787e-23	-23.7478	-.1725	.1201e-23	-23.9203
fef2+	.1346e-23	-23.8709	-.1725	.9049e-24	-24.0434
fef++	.1069e-23	-23.9709	-.6785	.2242e-24	-24.6493
fef+	.3394e-24	-24.4693	-.1725	.2282e-24	-24.6417
fec1++	.1503e-24	-24.8231	-.7688	.2560e-25	-25.5918
feso4+	.1026e-24	-24.9890	-.1725	.6895e-25	-25.1615
fef3	.7319e-25	-25.1356	0.0000	.7319e-25	-25.1356
fe+++	.3714e-25	-25.4301	-1.0640	.3205e-26	-26.4941
h3p2o7-	.2834e-25	-25.5475	-.1725	.905e-25	-25.7200
fehpo4	.9314e-26	-26.0309	0.0000	.9314e-26	-26.0309
fepo4-	.7116e-26	-26.1478	-.1725	.4783e-26	-26.3203
fec12+	.2384e-26	-26.6227	-.1725	.1602e-26	-26.7952
fec13	.1630e-26	-26.7879	0.0000	.1630e-26	-26.7879
feh2po4+	.1688e-27	-27.7727	-.1725	.1135e-27	-27.9452
fec14-	.1008e-28	-28.9965	-.1725	.6776e-29	-29.1690
fe(oh)3-	.8535e-29	-29.0687	-.1725	.5739e-29	-29.2412
feh2po4++	.8216e-30	-30.0854	-.6785	.1723e-30	-30.7638
si16--	.9683e-31	-31.0140	-.7688	.1649e-31	-31.7828
h4p2o7	.6914e-33	-33.1603	0.0000	.6914e-33	-33.1603
(feoh++)2	.5624e-36	-36.2499	-3.1540	.3945e-39	-39.4039
h2(aq)	.2987e-36	-36.5247	.0684	.3497e-36	-36.4563
hs-	.4924-110	-110.3077	-.1861	.3208-110	-110.4938
h2s(aq)	.1848-111	-111.7332	0.0000	.1848-111	-111.7332
s--	.1729-118	-118.7623	-.6785	.3625-119	-119.4408

----- major aqueous species contributing to mass balances -----

aqueous species accounting for 99% or more of na+

species	molar conc	per cent
na+	.4511e+00	96.31
nacl	.1243e-01	2.65
na2so4-	.4822e-02	1.03

subtotal		99.99

Figure 8. Output, modified seawater example (continued).

aqueous species accounting for 99% or more of k+

species	molar conc	per cent
k+	.1003e-01	98.24
kso4-	.1797e-03	1.76

subtotal		100.00

aqueous species accounting for 99% or more of ca++

species	molar conc	per cent
ca++	.9005e-02	87.54
caso4	.1191e-02	11.58

subtotal		99.12

aqueous species accounting for 99% or more of mg++

species	molar conc	per cent
mg++	.4594e-01	86.43
mgso4	.6715e-02	12.63

subtotal		99.07

Figure 8. Output, modified seawater example (continued).

aqueous species accounting for 99% or more of al+++

species	molar conc	per cent
al(oh)4-	1639e-06	100.00

subtotal		100.00

aqueous species accounting for 99% or more of sio2(aq)

species	molar conc	per cent
sio2(aq)	.6695e-04	93.98
h3sio4-	.4286e-05	6.07

subtotal		100.00

aqueous species accounting for 99% or more of ncu3-

species	molar conc	per cent
hco3-	.1530e-02	72.85
mghco3+	.2791e-03	13.29
mgco3	.1149e-03	5.47
cahco3+	.5864e-04	2.79
co3--	.4335e-04	2.06
na2co3	.3307e-04	1.57
ca2co3	.2899e-04	1.38

subtotal		99.42

Figure 8. Output, modified seawater example (continued).

aqueous species accounting for 99% or more of cl--

species	molal conc	per cent
cl--	.5334e+00	97.72
nacl	.1243e-01	2.28

subtotal		100.00

aqueous species accounting for 99% or more of so4--

species	molal conc	per cent
so4--	.1533e-01	54.28
mgso4	.6715e-02	23.79
na2so4	.4822e-02	17.08
caso4	.1191e-02	4.22

subtotal		99.36

aqueous species accounting for 99% or more of i-

species	molal conc	per cent
i-	.1078e-03	51.52
mgf+	.9557e-04	45.67
caf+	.3019e-05	1.44
naf	.2845e-05	1.36

subtotal		100.00

Figure 8. Output, modified seawater: example (continued).

aqueous species accounting for 99% or more of fe++

species	molal conc	per cent
fe(oh)4-	.4756e-15	98.12
fe(oh)2+	.9074e-17	1.87

subtotal		100.00

aqueous species accounting for 99% or more of hpo4--

species	molal conc	per cent
mghpo4	.2390e-06	37.60
nahpo4-	.1294e-06	20.37
hpo4--	.1186e-06	18.67
mgpo4-	.1009e-06	15.38
cahpo4	.2555e-07	4.02
capo4-	.1557e-07	2.45
h2po4-	.2905e-08	.46

subtotal		99.44

----- summary of aqueous redox reactions -----

couple	eh, volts	pe-	log fo2	gh, kcal
default	.500	.8452e+01	-16.430	11.531
o2(aq) /h2o	.500	.8452e+01	-16.430	11.531
h2(aq) /h2o	.500	.8452e+01	-16.430	11.531
hs- /so4--	.500	.8452e+01	-16.430	11.531
fe+++ /fe++	.500	.8452e+01	-16.430	11.531

Figure 8. Output, modified seawater example (continued).

----- summary of aqueous non-equilibrium non-redox reactions -----

couple affinity, kcal

none

----- summary of stoichiometric mineral saturation states -----

(minerals with affinities .11. -10 kcal are not listed)

mineral	log q/k	aff. kcal	state	mineral	log q/k	aff. kcal	state
antigorite	74.420	101.529	ssald	phengite	3.921	5.349	ssald
corundum	-5.440	-7.421		hematite	.630	.860	ssald
dehydrated a	-4.667	-6.367		brucite	-1.852	-2.526	
gibbsite	-.000	-.000	sald	halite	-2.602	-3.550	
sylvite	-3.570	-4.871		calcite	.789	1.076	ssald
magnesite	.987	1.346	ssald	dolomite	3.404	4.644	ssald
hydromagnesi	-3.314	-4.521		anhydrite	-.070	-1.323	
gypsum	-.401	-.547		quartz	-.175	-.239	sald
maximum micr	1.382	1.885	ssald	low albite	.050	.068	sald
anorthite	-5.687	-7.758		sepiolite	2.275	3.104	ssald
14a-omesite	4.075	6.310	ssald	nepheline	-2.638	-3.599	
analcime	.034	.046	sald	kaolinite	.151	.206	sald
chrysolite	3.872	5.282	ssald	pyrophyllite	-1.821	-2.484	
talc	5.517	7.527	ssald	na-beidellit	-.589	-.804	
muscovite	2.837	3.870	ssald	illite	1.173	1.600	ssald
artinite	-1.950	-2.660		tremolite	5.461	7.451	ssald
enstatite	-1.048	-1.430		diopside	-.943	-1.287	
wollastonite	-4.018	-5.482		zoisite	-5.010	-6.835	
kyanite	-4.525	-6.174		forsterite	-3.131	-4.271	
prehnite	-2.304	-3.143		huntite	2.016	2.750	ssald
amorphous si	-1.461	-1.993		phlogopite	7.019	9.576	ssald
k-feldspar	1.382	1.885	ssald	high sanidin	.183	.249	sald

Figure 8. Output, modified seawater example (continued).

high albite	-1.269	-1.731		k-beidellite	-.815	-1.111	
ca-beidellite	-.797	-1.087		mg-beidellite	-.644	-.879	
h-beidellite	-2.111	-2.881		aragonite	.624	.851	ssald
na-saponite	6.748	9.207	ssald	k-saponite	6.523	8.899	ssald
clinozoisite	-4.965	-6.774		paragonite	.608	.830	ssald
diaspore	-.784	-1.069		ca-saponite	6.541	8.924	ssald
boehmite	-1.628	-2.221		chalcedony	.446	-.609	
mg-saponite	6.694	9.132	ssald	7a-clinoclho	4.426	6.038	ssald
andalusite	-4.800	-6.549		h-saponite	5.237	7.144	ssald
14j-clinocl	7.799	10.641	ssald	anthophyllit	.974	1.329	ssald
monticellite	-5.551	-7.573		na-nontronit	-.000	-.000	sald
k-nontronite	1.775	2.421	ssald	albite	.050	.068	sald
ordered epid	-1.930	-2.633		andradite	-3.359	-4.596	
ca-nontronit	1.793	2.446	ssald	mg-nontronit	1.945	2.654	ssald
h-nontronite	.479	.654	ssald	crystalbite	-.725	-.990	
disordered d	1.860	2.537	ssald	ordered dolo	3.404	4.644	ssald
nesquehonite	-1.736	-2.368		epidote	-1.930	-2.633	
wairakite	-5.547	-7.568		laumontite	-1.151	-1.571	
margarite	-4.859	-6.628		fluorite	.000	.000	sald
sillimanite	-5.159	-7.039		kalsilite	-1.444	-1.970	
jadeite	-1.400	-1.910		mgf2(c)	-1.965	-2.681	
hydroxyapatite	8.051	10.984	ssald	fluorapatite	17.607	24.021	ssald
berlinite	31.340	42.757	ssald	whitlockite	2.995	4.086	ssald
cahpo4.2h2o	-3.805	-5.191		pseudowollas	-4.409	-6.015	
cas12o5.2h2o	-4.545	-6.201		leonhardite	4.013	5.474	ssald
lawsonite	-1.334	-1.820		tridymite	-.341	-.465	sald

10 approx. saturated pure minerals

0 approx. saturated end-members of specified solid solutions

0 saturated end-members of hypothetical solid solutions

38 supersaturated pure minerals

0 supersald. end-members of specified solid solutions

0 supersald. hypothetical solid solution phases

Figure 8. Output, modified seawater example (continued).

----- summary of gases -----

gas	fugacity	log fugacity
co2(g)	.443191e-03	-3.35341
o2(g)	.371593e-16	-16.42993
s2(g)	.384831-180	-180.41473
ch4(g)	.152197-113	-113.81759
h2(g)	.452575e-33	-33.34431
h2s(g)	.187500-110	-110.72700
steam	.307485e-01	-1.51218

----- end of output -----

----- pickup file successfully written -----

----- reading the input file -----

----- end of input file -----

Figure 9. Input, pH calculation example (continued).

```

iprnt1-10= 0 0 0 0 0 0 0
idbug1-10= 0 0 0 0 0 0 0
  uebal= h+          uacion= cl-
  nxmod= 1
  species= pd-oxyannite
  type= 1          option= -1      x1kmod= 0.
                na+          0.013  0
                ca++         0.010  0
                h+           -7.0   16
                hco3-         -3.5  21  co2(g)
                hpo4--        0.001  0
                cl-           0.030  0
hco3-          co3--          30
endit.

```

Figure 10a. Partial output, pH calculation example.

----- modified input constraints -----

species	csp	jflag	type of input	uphase
na+	.13000e-01	0	tot conc, molal	
ca++	.10000e-01	0	tot conc, molal	
h+	-.70000e+01	16	log activity	
hco3-	-.35000e+01	21	gas equil	co2(g)
	1.000		co2(g)	
	+ 1.000		h2o	
	==		log k =	-7.8345
	1.000		h+	
	+ 1.000		hco3-	
cl-	.30000e-01	0	tot conc, molal	
hpo4--	.10000e-02	0	tot conc, molal	
o2(aq)	0.	27	dependent species	
h2(aq)	0.	27	dependent species	
ch4(aq)			not present in the model	
h2po4-	0.	30	eliminated species	
co3--	0.	30	eliminated species	
clo4-			not present in the model	
oh-	0.	30	eliminated species	

the ion that defines equiv. stoich. ionic strength is cl-

electrical balance will be achieved by adjusting the concentration of h+

iter = 0	delmax = 0.	del() = 0.	beta(hpo4--)	= .169e+01	delfnc = 0.
iter = 1	delmax = .834e+00	del(h+) = -.208e+00	beta(hpo4--)	= .136e+01	delfnc = 0.
iter = 2	delmax = .895e+00	del(h+) = -.224e+00	beta(hpo4--)	= .109e+01	delfnc = -.734e-01
iter = 3	delmax = .832e+00	del(h+) = -.208e+00	beta(hpo4--)	= .866e+00	delfnc = .704e-01
iter = 4	delmax = .617e+00	del(h+) = -.617e+00	beta(hpo4--)	= .358e+00	delfnc = .259e+00

Figure 10a. Partial output, pH calculation example (continued).

iter = 5	delmax = .107e+00	del(hco3-) = -.107e+00	beta(hpo4--) = .499e-01	delfnc = .826e+00
iter = 6	delmax = .220e-01	del(hco3-) = -.220e-01	beta(hpo4--) = .136e-02	delfnc = .795e+00
iter = 7	delmax = .764e-03	del(hco3-) = -.764e-03	beta(hpo4--) = .111e-05	delfnc = .965e+00
iter = 8	delmax = .858e-06	del(hco3-) = -.858e-06	beta(hco3-) = -.115e-09	delfnc = .999e+00
iter = 9	delmax = .101e-09	del(h+) = -.101e-09	beta(ca++) = .222e-13	delfnc = .100e+01
iter = 10	delmax = .342e-13	del(hco3-) = .342e-13	beta(hco3-) = .284e-13	delfnc = .100e+01

newton-raphson iteration converged in 10 steps

----- summary of the aqueous phase -----

----- elemental composition of the aqueous phase -----

element	mg/l	mg/kg	moles/kg
o	888227.1999	888227.1999	.5551628185e+02
na	298.8670	298.8670	.1300000000e-01
ca	400.8000	400.8000	.1000000000e-01
h	111897.3153	111897.3153	.1110202553e+03
c	9.9453	9.9453	.8280129294e-03
cl	1063.5900	1063.5900	.3000000000e-01
p	30.9738	30.9738	.1000000000e-02

Figure 10a. Partial output, pH calculation example (continued).

----- elemental composition as strict basis species -----

species	mg/l	mg/kg	moles/kg
h2o	1000125.8176	1000125.8176	.5551628185e+02
na+	298.8700	298.8700	.1300000000e-01
ca++	400.8000	400.8000	.1000000000e-01
h+	111908.4173	111908.4173	.1110202553e+03
co3--	49.6882	49.6882	.8280129294e-03
cl-	1063.5900	1063.5900	.3000000000e-01
hpo4--	95.9790	95.9790	.1000000000e-02

----- equivalent composition of the aqueous phase -----

species	moles/kg h2o
h2o	.5551628185e+02
na+	.1300000000e-01
ca++	.1000000000e-01
h+	.1110195412e+03
hco3-	.8280129294e-03
cl-	.3000000000e-01
hpo4--	.1000000000e-02

ionic strength = .0412723908305
 equiv. stolch. ionic strength (cl-) = .0300000000000

ph = 8.11546

activity of water = .99897
 log activity of water = -.00045

titration alkalinity = .85536e-03 eq/kg h2o

Figure 10a. Partial output, pH calculation example (continued).

----- electrical balance totals -----

	equiv/kg
cation subtotal	.3161402929e-01
anion subtotal	-.3161402929e-01
charge imbalance	.1110223025e-15

this is .00 per cent of the cation subtotal
and -.00 per cent of the anion subtotal

----- electrical balancing on h+ -----

log activity

input	-7.0000
final	-8.1155
adj	-1.1155

----- activity ratios of ions -----

log (act(na+) / act(h+)xx 1)	6.1473
log (act(co++)) / act(h+)xx 2)	13.9060
log (act(co3--) x act(h+)xx 2)	-21.6630
log (act(cl-) x act(h+)xx 1)	-9.7233
log (act(hpo4--) x act(h+)xx 2)	-20.0213
log (act(o2(aq)))	-3.5990
log (act(h2(aq)))	-44.3138
log (act(h2po4-) x act(h+)xx 1)	-12.8161
log (act(hco3-) x act(h+)xx 1)	-11.3349
log (act(oh-) x act(h+)xx 1)	-13.9878

Figure 10b. Partial output, pH calculation example.

----- summary of stoichiometric mineral saturation states -----

(minerals with affinities .11. -10 kcal are not listed)

mineral	log q/k	aff. kcal	state	mineral	log q/k	aff. kcal	state
halite	-5.185	-7.074		calcite	.768	1.048	ssald
aragonite	.603	.822	ssald	hydroxyapatite	20.989	28.635	ssald
whitlockite	11.576	15.793	ssald	cahpo4.2h2o	.441	.602	ssald

0 approx. saturated pure minerals
 0 approx. saturated end-members of specified solid solutions
 0 saturated end-members of hypothetical solid solutions

5 supersaturated pure minerals
 0 supersald. end-members of specified solid solutions
 0 supersald. hypothetical solid solution phases

----- summary of gases -----

gas	fugacity	log fugacity
co2(g)	.316228e-03	-3.50000
o2(g)	.199526e+00	-.70000
ch4(g)	.389768-145	-145.40919
h2(g)	.628279e-41	-41.20185
steam	.312790e-01	-1.50475

Figure 11. Input, river water test case (continued).

```

iprn11-10= 0 0 0 0 0 0 0
idbug1-10= 0 0 0 0 0 0 0
uehal=
nxmod= 1
species= pd-oxyannite
type= 1
uacion= cl-
option= -1
xlkmod= 0.

na+ 12. 2
k+ 1.4 2
ca++ 12.2 2
mg++ 7.5 2
sio2(aq) 1.3 2
hco3- .001232 11
cl- 9.9 2
so4-- 7.7 2
f- 0.10 2
hpo4-- 0.21223 2
no3- 0.898 2
nh4+ 0.144 2
fe++ 0.015 2
fe+++ 0.0007 2
mn++ 0.0044 2
al+++ 0.005 2
zn++ 0.00049 2
hg++ 0.00001 2
pb++ 0.00003 2
cu+ 0.0005 2
ag+ 0.00004 2
as(oh)4- 0.0038 2
hs- 0.0019 2
o2(aq) 10.94 2
h+ -8.01 16
hco3- co3-- 30
endit.

```

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in the part of the OUTPUT file given in figure 12. Partial equilibrium exists in the model among $\text{H}_2(\text{aq})/\text{H}_2\text{O}$, $\text{Hg}_2^{2+}/\text{Hg}^{2+}$, $\text{As}(\text{OH})_4^-/\text{As}(\text{O})_4^-$, and $\text{Cu}^{2+}/\text{Cu}^+$ only because these couples were constrained to fit the input default for an Eh of 0.44 volts. This run required 18.33 seconds of CDC 7600 time (17.78 seconds for CPU) and nine iterations.

6. SAMPLE PROBLEMS THAT DON'T WORK: INPUTS AND OUTPUTS

6.1. INTRODUCTION

This chapter follows the same format as the previous one. For each example, a short discussion is presented, followed by the INPUT file and the last page of the OUTPUT file. The three sample problems in this chapter, however, do not work.

6.2. VIOLATING THE APPARENT (MINERALOGIC) PHASE RULE

The so-called "apparent" or "mineralogic" phase rule was discussed in Section 2.3.4. It is a slightly more restrictive version of the phase rule of thermodynamics. To explain this rule, consider thermodynamic equilibrium constraints as the logarithmic forms of mass action expressions. If there are n such linear equations in n unknowns, the unknowns may be evaluated by solving a matrix equation. The matrix is n by n and composed of the reaction coefficients of the unknowns. If this matrix is singular, there is no solution and the system is said to be overdetermined.

Subroutine ARRSET evaluates such a matrix when generating starting estimates for aqueous species constrained by specified equilibria. Apparent phase rule violations are detected at this stage. If such an error is detected, a warning message is printed and execution of the current problem is terminated.

The following example illustrates a violation of the apparent phase rule. The INPUT file is shown in Figure 13, and the last page of the OUTPUT file (containing the diagnostic message) is given in Figure 14. This run required 1.48 seconds of CDC 7600 machine time (1.16 seconds for CPU) and no iterations were made.

Figure 12. Partial output, river water test case.

----- summary of aqueous redox reactions -----

couple	eh. volts	pe-	log fo2	ah. kcal
default	.440	.7846e+01	-24.439	10.147
o2(aq) /h2o	.773	.1378e+02	-.699	17.824
h2(aa) /h2o	.440	.7846e+01	-24.439	10.147
hs- /so4--	- .241	-.4295e+01	-73.003	-5.555
hg2++ /hg++	.440	.7846e+01	-24.439	10.147
as(oh)8-/as(oh)4-	.440	.7846e+01	-24.439	10.147
fe+++ /fe++	.197	.3513e+01	-41.769	4.544
cu++ /cu+	.440	.7846e+01	-24.439	10.147
no3- /nh4+	.318	.5662e+01	-33.174	7.323

Figure 13. Input, phase rule violation example.

input file name: iphrv created: 07/24/82 creator: l.j. wolery

example of a phase rule violation. this is the sea water test case of nordstrom et al. (1979, table iii), modified by deleting a few trace components and by substituting mineral equilibrium constraints for a few of the remaining components. there is no numerical solution to this problem, because this set of mineral equilibrium constraints violates the phase rule.

reference

nordstrom, d.k., et al. 1979. a comparison of computerized chemical models for equilibrium calculations in aqueous systems. p. 857-892 in jenne, e.o., ed., chemical modeling in aqueous systems, acs symposium series 93, american chemical society, washington, d.c.

tempc=	25.								
rho=	1.02336	ldspkg=	0.	ldspl=	0.				
fep=	0.500	uredox=							
tolbt=	0.	toldt=	0.	tolst=	0.				
itermx=	0								
iop11-10=	-1	0	0	0	0	0	0	0	0

Figure 13. Input, phase rule violation example (continued).

```

iprnl1-10= 0 0 0 0 0 0 0
idbug1-10= 0 0 0 0 0 0 0
uebal=
nxmod= 1
species= pd-oxyannite
type= 1
option= -1
xlkmod= 0.
na+ 10768. 3
k+ 399.1 3
ca++ 412.3 3
mg++ 1291.8 3
al+++ 19 gibbsite
sio2(aq) 19 quartz
h+ 19 kaolinite
hco3- .002322 10
cl- 19353. 3
so4-- 2712 3
f- 19 fluorite
fe++ 19 na-nontronite
hpo4-- 0.061 3
o2(aq) 30
h2(aq) 27
ch4(aq) 27
hs- 27
hco3-
endil. co3-- 30

```

Figure 14. Last page of output, phase rule violation.

```

          ==          log k = -10.9589
          1.000 ca++
+         2.000 f-
fe++      0.          19  min equil          na-nontronite

          1.000 na-nontronite
+         5.320 h+
          ==          log k = -31.3778
          3.660 h2o
+         .330 na+
+         .330 al+++
+         3.670 sio2(aq)
+         2.000 fe++
+         .500 o2(g)
hpo4--    .63556e-06  0  tot conc, molal
o2(aq)    0.          27  dependent species
h2(aq)    0.          27  dependent species
ch4(aq)   0.          27  dependent species
hs-       0.          27  dependent species
fe+++     0.          30  eliminated species
h2po4-    0.          30  eliminated species
co3--     0.          30  eliminated species
clo4-     0.          30  not present in the model
oh-       0.          30  eliminated species

```

the ion that defines equiv. stoich. ionic strength is cl-

----- ludatf (l-u decomp.) failed in arrset -----

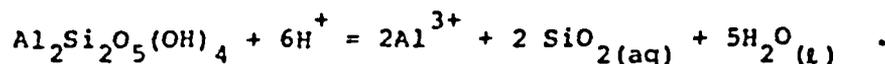
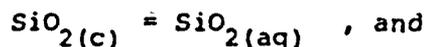
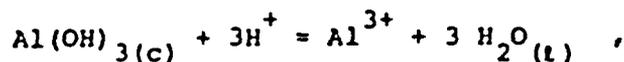
----- the speciation model appears to be singular -----

----- probable apparent phase rule violation -----

----- reading the input file -----

----- end of input file -----

In this example, Al^{3+} is constrained by gibbsite $[\text{Al}(\text{OH})_3]$ solubility, $\text{SiO}_2(\text{aq})$ by quartz, H^+ by kaolinite $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$, F^- by fluorite (CaF_2), and Fe^{2+} (including Fe^{3+}) by Na-nontronite $[\text{Na}_{0.33}(\text{Fe}_2)\text{Al}_{0.33}\text{Si}_{3.67}(\text{OH})_2]$. The problem lies with the first three of these constraints. The dissolution reactions are



Taking the signs of reactants as negative and those of products as positive, the matrix for H^+ , Al^{3+} , and $\text{SiO}_2(\text{aq})$ is

$$\begin{array}{ccc} -3 & 1 & 0 \\ 0 & 0 & 1 \\ -6 & 2 & 2 \end{array}$$

It is clear from inspection that this matrix is singular because the third row may be obtained by adding the first two and multiplying by a factor of 2. This problem could be "fixed" by either substituting an input pH value for the kaolinite equilibrium assigned to H^+ , or by entering a different kind of input, such as a total concentration, for one of Al^{3+} or $\text{SiO}_2(\text{aq})$ to substitute for the corresponding required solubility equilibrium.

6.3. UNREALISTIC SOLUBILITY EQUILIBRIUM CONSTRAINT

This example illustrates the action taken by subroutine ARRSET when it determines that the result of an equilibrium constraint or set of equilibrium constraints is grossly unrealistic. ARRSET generates the starting estimates for Newton-Raphson iteration. If the concentration estimate for an equilibrium-constrained species is large (greater than 10 molal), a warning message is printed. If the estimate is grossly large (greater than 100 molal), ARRSET not only writes this warning message, but it also terminates execution of the current problem.

The following example requires Zn^{2+} to satisfy solubility equilibrium with sphalerite (ZnS). The zinc concentration, however, would have to be grossly large, because dissolved sulfide is constrained to be in equilibrium with sulfate under relatively oxidizing conditions; hence, the amount of dissolved sulfide must be very, very low, and conversely, the amount of dissolved zinc required for equilibrium with sphalerite must be very great. This run required 1.32 seconds of CDC 7600 machine time (1.11 seconds for CPU) and no iterations were made. The INPUT file is shown in Figure 15, the last page of the OUTPUT file in Figure 16.

6.4. ELECTRICAL BALANCE CRASH

This example shows what happens when the concentration of the aqueous component required to satisfy electrical balance would have to be negative. The INPUT file is shown in Figure 17, the last page of the OUTPUT file in Figure 18. This run required 1.79 seconds of CDC 7600 machine time (1.44 seconds for CPU) and the Newton-Raphson iteration completed eight steps before stopping.

All iteration variables corresponding to aqueous species are logarithmic. The logarithmic concentration of the species required to satisfy electrical balance (Na^+) diverges toward negative infinity. Note that "DEL(Na+) = -0.200E+01" during the last several iterations: (DEL is the log concentration correction term for a given iteration; 2.0 is the usual limit on the magnitude of any such term).

In this example, the problem is not completely obvious from inspection of the input, because some of the constraints involve solubility equilibria. The corresponding total concentrations are unknown parameters to be calculated.

7. PICKUP FILE: THE EQ3NR TO EQ6 CONNECTION

EQ3NR creates a model of the state 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 model constraints on this aqueous solution are input only to EQ3NR. The user

Figure 15. Input, bad solubility equilibrium example.

input file name= ibodeq created= 07/24/82 creator= i.j. wolery

example of choosing a bad mineral solubility constraint, based partially on the sea water test case of nordstrom et al. (1979, table iii). the problem here is that the concentration of dissolved zinc required for equilibrium with sphalerite (zns(c)) is unrealistically high in sea water.

references

nordstrom, d.k., et al. 1979. a comparison of computerized chemical models for equilibrium calculations in aqueous systems. p. 857-892 in jenne, e.o., ed., chemical modeling in aqueous systems, acs symposium series 93, american chemical society, washington, d.c.

tempc=	25.									
rho=	1.02336	ldspkg=	0.	ldspl=	0.					
fep=	0.500	uredox=								
tolbt=	0.	loldl=	0.	tolosal=	0.					
itermx=	0									
iop11-10=	-1	0	0	0	0	0	0	0	0	0

Figure 15. Input, bad solubility equilibrium example (continued).

```

iprnt1-10=    0    0    0    0    0    0    0
idbug1-10=    0    0    0    0    0    0    0
  uebal=
  nxmod= 1
  species= pd-oxyannite
  type= 1
          option= -1
          xlkmod= 0.
          na+          10768.  3
          k+           399.1   3
          ca++         412.3   3
          mg++         1291.8  3
          h+           -8.22   16
          zn++          19      19  sphalerite
          hco3-         .002322 10
          cl-           19353.  3
          so4--         2712.   3
          hs-           27
          hco3-         30
          co3--
  hco3-
  endl.
  
```

Figure 16. Last page of output, bad solubility equilibrium.

species	csp	jflag	type of input	uphase
na+	.46838e+00	0	tot conc. molal	
k+	.10205e-01	0	tot conc. molal	
ca++	.10287e-01	0	tot conc. molal	
mg++	.53150e-01	0	tot conc. molal	
zn++	0.	19	min equil	sphalerite
	1.000		sphalerite	
	+ 1.000		h+	
	==			log k = -11.3587
	1.000		zn++	
	+ 1.000		hs-	
h+	-.82200e+01	16	log activity	
hco3-	.23220e-02	10	tit alk. eq/kg h2o	
cl-	.54588e+00	0	tot conc. molal	
so4--	.28233e-01	0	tot conc. molal	
o2(aq)	0.	27	dependent species	
h2(aq)	0.	27	dependent species	
ch4(aq)			not present in the model	
hs-	0.	27	dependent species	
co3--	0.	30	eliminated species	
clo4-			not present in the model	
oh-	0.	30	eliminated species	

the ion that defines equiv. stoich. ionic strength is cl-

----- zn++ has a required log concentration near 91.34 (log molal) -----

----- reconsider your choice of input constraints -----

----- reading the input file -----

----- end of input file -----

Figure 17. Input, electrical balance crash example.

input file name: ieocr created: 07/23/82 creator: l.j. wolery

example of electrical balance crash. in this case, na+ concentration is to be adjusted to satisfy electrical balance. the constraints put on this problem are such that this concentration would have to be negative. because three of these constraints involve heterogeneous equilibria, one can not be sure beforehand that there is no physically reasonable answer. note that eq3nr terminates the run after writing an appropriate diagnostic message. it does not compute a physically unreasonable answer.

tempc=	25.									
rho=	1.00	tdspkg=	0.	tdspl=	0.					
fep=	0.000	uredox=								
tolbt=	0.	tolcl=	0.	tolsof=	0.					
itermx=	0									
iopt1-10=	-1	0	0	0	0	0	0	0	0	0

Figure 17. Input, electrical balance crash example (continued).

```

iprnt1-10= 0 0 0 0 0 0 0
idbug1-10= 0 0 0 0 0 0 0
  uebal= na+          uacion= cl-
  nxmod= 1
  species= pd-oxyannite
  type= 1          option= -1          xlkmod= 0.
                na+          0.001  0
                cat+          0.022  0
                al+++          19    gibbsite
                sio2(aq)       19    quartz
                hco3-          19    calcite
                so4--          0.0005  0
                cl-            0.020  0
                h+              -6.0  16
hco3-          co3--          30
end11.

```

Figure 18. Last page of output, electrical balance crash.

so4--	50000e-03	0	tot conc. total
o2(aq)	0	27	dependent species
h2(aq)	0	27	dependent species
ch4(aq)			not present in the model
hs-	0.	30	eliminated species
co3--	0.	30	eliminated species
clo4-			not present in the model
oh-	0.	30	eliminated species

the ion that defines equiv. stoich. ionic strength is H^+

electrical balance will be achieved by adjusting the concentration of na^+

iter = 0	delmax = 0.	del() = 0.	beta(xi) = -.755e+00	delfnc = 0.
iter = 1	delmax = .538e+01	del(na+) = -.134e+01	beta(xi) = -.709e+00	delfnc = 0.
iter = 2	delmax = .112e+03	del(na+) = -.200e+01	beta(xi) = -.705e+00	delfnc = -.199e+02
iter = 3	delmax = .112e+05	del(na+) = -.200e+01	beta(xi) = -.705e+00	delfnc = -.988e+02
iter = 4	delmax = .112e+07	del(na+) = -.200e+01	beta(xi) = -.705e+00	delfnc = -.990e+02
iter = 5	delmax = .112e+09	del(na+) = -.200e+01	beta(xi) = -.705e+00	delfnc = -.990e+02
iter = 6	delmax = .112e+11	del(na+) = -.200e+01	beta(xi) = -.705e+00	delfnc = -.990e+02
iter = 7	delmax = .112e+13	del(na+) = -.200e+01	beta(xi) = -.705e+00	delfnc = -.990e+02

----- ludolf (l-u decomp.) failed in newton -----

----- iteration has gone sour (iter = 8) -----

the ion adjusted for electrical balance is crashing to zero
 electrical balancing requires an ion of opposite charge

newton-raphson iteration failed after 8 steps

----- reading the input file -----

----- end of input file -----

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 EQ3NR's PICKUP file from the bottom portion 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 EQ3NR's PICKUP file will be discussed in more detail in a subsequent EQ6 manual (Wolery, 1983a).

EQ3NR automatically writes a PICKUP file unless the user specifies otherwise (by setting IOPT3 to -1); however, it is not automatically disposed to an output medium or file storage. On most batch-oriented systems, it will be lost upon job termination unless appropriate disposition instructions are included in the job control file.

Figure 19 illustrates the PICKUP file generated for the sea water example presented in Section 5.2. The following discussion assumes that the reader is familiar with the parameters that appear on the EQ3NR INPUT file (see Section 4). The PICKUP file begins with a repetition of the thirty-line title (UTITL). This is followed by a line identifying the ion used to estimate the activity of water ("UACION= CL-"). The line after that gives the temperature (°C) of the EQ3NR run ("TEMPCI= .25000E+02"). The EQ6 run that uses this input may actually start at a different temperature; the TEMPCI input allows EQ6 to be aware that a temperature jump is being called for by the user.

The alter/suppress options follow in the same format as on the INPUT file. In this example, the option is executed for one species (NXMOD= 1) and the species, PD-oxyannite, a mineral ("TYPE= 1"; "TYPE" is actually the parameter JXMOD) is to be suppressed ("OPTION= -1"; "OPTION" is the parameter KXMOD); therefore, the log K alteration parameter (XLKMOD) is zero.

The next five inputs (KCT, KMT, KXT, KDIM, and KPRS) are key parameters in the scheme by which EQ6 organizes important variables. KCT is equivalent to the number of chemical elements in the system. KDIM is the number of total master species which, in EQ6, includes not only the aqueous master species discussed in this report, but also all mineral species in equilibrium with the water. KMT and KXT mark, respectively, the last pure mineral and last solid-solution end member 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

Figure 19, PICKUP file, seawater example.

input file name= iswmoj created= 07/24/82 creator= l.j. wolery

sea water test case, major components only. This is a recalculation of the classic chemical model of garrels and thompson (1962). The analytical data used here are taken from table iii of nordstrom et al. (1979), who discuss the application of various computer codes to this benchmark problem.

in this run, eq3nr calculates the electrical imbalance of the sea water analysis. such imbalance results from errors in the chemical analysis of individual components and from the fact that any such set of analyses is always more or less incomplete (in principle including trace elements in the model should tend to minimize calculated electrical imbalance). eq3nr could be set to force electrical balance by adjusting the concentration of a selected component, say cl-, by setting "uebal= cl-" below. it is not necessary to do this to initialize eq6 calculations.

the mineral pd-oxyannite (proton-deficient oxyannite) is suppressed. it is a hypothetical biotite end-member and does not exist as a pure phase.

references

nordstrom, d.k., et al. 1979. a comparison of computerized chemical models for equilibrium calculations in aqueous systems. p. 857-892 in jenne, e.a., ed., chemical modeling in aqueous systems, acs symposium series 93, american chemical society, washington, d.c.

garrels, r.m., and thompson, m.e. 1962. a chemical model for sea water at 25 c and one atmosphere total pressure. amer. jour. sci. 260, 57-66.

uacion= cl-
tempci= .25000e+02
nxmod= 1
species= pd-oxyannite
type= 1 option= -1 xlkmod= 0.
kcl= 9 kmt= 12 kxl= 12

Figure 19, PICKUP file, seawater example (continued).

kdim= 12		kprs= 0
o		.556285506665117e+02
na		.468377555458902e+00
k		.102076832574559e-01
ca		.102869261477051e-01
mg		.531495577041772e-01
h		.111020499406332e+03
c		.210409891848798e-02
cl		.545877640820247e+00
s		.282329425971820e-01
electr		.792690165368981e-03
h2o	h2o	.174436573354141e+01
na+	na+	-.346651517028610e+00
k+	k+	-.199845506547392e+01
ca++	ca++	-.204320079190620e+01
mg++	mg++	-.133464463077247e+01
h+	h+	-.812514785281826e+01
hco3-	co3--	-.281517486465616e+01
cl-	cl-	-.272892148365106e+00
so4--	so4--	- 183411753524162e+01
o2(g)	o2(g)	-.164299329903120e+02
xisteq		-.262904694056841e+00
xi		-.193271570969194e+00

having values equal to that of KDIM. KPRS is a flag to indicate whether or not there are any mineral and solid-solution end-member species in the "physically removed subsystem," a concept relating only to the flow-through open system model in EQ6. KPRS must always be zero on EQ3NR's PICKUP file.

The PICKUP file next lists the symbols of the KCT chemical elements and their masses (MTE; relative to a mass of aqueous solution containing one kilogram of solvent), in moles, in the system. The calculated electrical imbalance (ELECTR) is given in the same format.

The last part of the EQ3NR INPUT file gives the names of the "run" master iteration variables (the "run" master aqueous species and the two ionic strength functions), the corresponding "data file" master species, and the values of the corresponding variables. For aqueous master species, these variables are the logarithms of their molal concentrations, and for the ionic strength functions, the logarithms of their respective values. If a run master species is not the same as the corresponding data file master species, it marks the pair of species for a basis switch.

8. SOLVING THE GOVERNING EQUATIONS

8.1. INTRODUCTION

The governing equations that apply to speciation-solubility modeling were introduced in Section 2. The purpose of this section is to derive the mathematics necessary to solve them. Our approach is to set up the problem in terms of n equations in n unknowns (or "iteration variables") and apply the Newton-Raphson method to solve them. We begin this section by introducing this method, and discussing methods to aid convergence. We also describe crash diagnostics. Finally, we organize the governing equations and unknowns into suitable form, and derive the necessary mathematics for applying the Newton-Raphson method to solve them.

8.2. THE NEWTON-RAPHSON METHOD

The Newton-Raphson method is a well-known iterative technique for solving nonlinear systems of algebraic equations (see Van Zeggeren and Storey, 1970;

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 \underline{z} of iteration variables), one may construct a set of residual functions (represented by the vector $\underline{\alpha}$). Each member of these functions has a value of zero when the n equations are satisfied.

A simple one-dimensional example will illustrate this. Suppose we wish to solve the general quadratic trinomial,

$$ax^2 + bx + c = 0 \quad ,$$

where

a , b , and c are given coefficients,
 x is the only unknown.

The residual function can be defined as

$$\alpha = ax^2 + bx + c \quad .$$

Other definitions, however, are possible. The only requirement is that they take the 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 \underline{z}_k and $\underline{\alpha}_k$ are the iteration variable and residual function vectors on the k -th iteration. Let \underline{z}_0 represent the set of starting estimates. An iteration step is made by calculating \underline{z}_{k+1} from \underline{z}_k . The Newton-Raphson method does this by computing a vector of correction terms, $\underline{\delta}$, by solving the matrix equation:

$$\underline{J} \underline{\delta} = -\underline{\alpha} \quad .$$

Here \underline{J} is the so-called Jacobian matrix, defined as

$$\underline{J} = (\partial \alpha_i / \partial z_j) \quad .$$

where i and j are the matrix coordinates. In our example,

$$J = d(ax^2 + bx + c)/dx = 2ax + b .$$

The correction term vector is then applied:

$$\underline{z}_{k+1} = \underline{z}_k + \underline{\delta}_k .$$

If the iteration converges, all elements of both $\underline{\alpha}$ and $\underline{\delta}$ approach zero. It is useful to define another residual function, vector $\underline{\beta}$, which is identical to $\underline{\alpha}$, except that some elements may be normalized to provide a better measure of convergence. It is then convenient to define β_{\max} and δ_{\max} as the largest absolute values of the elements of $\underline{\beta}$ and $\underline{\delta}$, respectively. Both β_{\max} and δ_{\max} may then be used in tests to determine if the iteration has satisfactorily converged.

A useful measure of how well convergence is proceeding may also be constructed. The Newton-Raphson method is a so-called second order method. This means that in a close neighborhood of the solution,

$$\delta_{i,k+1} = \sum_{j=1}^n P_{i,j} \delta_{j,k} ,$$

where the $P_{i,j}$ are constants. In practice, their values are generally ignored. However, this behavior suggests that in the close neighborhood of the solution, $\delta_{\max,k+1}$ should be much less than $\delta_{\max,k}$. The function δ_{func} (the variable DELFNC in EQ3NR) is defined:

$$\delta_{\text{func},k+1} = 1 - (\delta_{\max,k+1}/\delta_{\max,k}) ,$$

may, therefore, be expected to approach (from below) a value of unity if the iteration is converging. Convergence to a lesser value, say ≈ 0.72 instead of ≈ 0.99 , usually implies a minor error in the writing of the Jacobian matrix.

In EQ3NR, subroutine NEWTON executes the Newton-Raphson iteration. Subroutine BETAS computes the residual functions, and subroutine MATRIX writes the Jacobian matrix.

8.3. METHODS TO AID CONVERGENCE

Several techniques are used in EQ3NR to aid convergence. These are:

- Use of logarithmic iteration variables.
- Under-relaxation techniques.
- Automatic generation of good starting estimates.
- Optimization of starting estimates.
- User-specified and automatic basis-switching.

We have not found it necessary to use the so-called "curve-crawler" techniques 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

$$\Delta \log x = (1/2.303) \Delta x/x .$$

Because of this, under-relaxation techniques are especially effective when applied in conjunction with logarithmic iteration variables.

Under-relaxation is the technique of judiciously reducing the magnitude of the correction terms. This involves replacing the correction equation given above by

$$z_{k+1} = z_k + \kappa \delta_k ,$$

where κ is a positive number less than one. There are several methods of applying under-relaxation. EQ3NR uses two relatively simple methods that have been implemented and extensively tested in the EQ6 code (see Wolery, 1979, p. 20). The first of these limits the size of the largest correction term:

$$\kappa = \delta' / \delta_{\max} ,$$

where δ' (SCREW2) is the imposed limit. (It normally has a value of 2.) Imposing this limit not only aids convergence, but is very helpful in inducing iteration to provide helpful information about the nature of the problem when

the iteration diverges. The other method incrementally reduces κ , as necessary, to reduce an absolute measure of divergence defined as $\beta_{\max,k+1} - \beta_{\max,k}$. This method is stopped after a given number of iterations.

EQ3NR usually generates very good starting estimates. This is largely the function of subroutine ARRSET. Subroutine NEWTON may subsequently modify the estimates generated by ARRSET. Several_sub-algorithms are used. A master species constrained by a total concentration will, at least initially, be assigned a concentration equal to the total concentration. If this is a poor assumption, the computed corresponding mass balance residual (element of β) will be a very large positive number. In such a case, ARRSET will either initiate an automatic basis switch to replace the master species by the species that dominates the mass balance, or NEWTON will optimize the starting estimate by decrementing it in successive steps until the mass balance residual is in reasonable range.

Starting values for some master species must be estimated simultaneously by solving a matrix equation. This is the case for $O_{2(g)}$ when an Eh or pe value is input and for all cases in which heterogeneous or homogeneous equilibria must be satisfied. This is done by subroutine ARRSET after values have been selected for other master species and the ionic strength functions. Activity coefficient estimates exist at this time. ARRSET then solves the logarithmic forms of the mass action equations that define the required equilibria. These form a linear set; hence, a matrix equation must be solved.

8.4. 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 the Newton-Raphson iteration, but some cases are not sufficiently obvious to be caught at this stage. When the iteration diverges, the user should examine the iteration summary on the OUTPUT file for clues. Subroutine NEWTON may print some helpful crash diagnostics based on its examination of the iteration.

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 (β), 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. The iteration summary identifies the master species whose residual function is greatest in magnitude, and gives the value of that function, for each iteration (e.g, on each line of the summary, ". . . BETA(Fe++) = . . .").

"Blowing down" is much more likely to be encountered by the user. This describes the process in which an iteration variable becomes sufficiently negative to create an apparently singular matrix and hence to terminate iteration. Usually, the significance of this is that there is not a positive (no physically realistic) value of this variable to satisfy the governing equations. When an iteration variable is blowing down, its correction term (δ) typically has the value $-\delta'$ (usually -2.0) for the last several iterations.

One example of this occurs when a master species is constrained to satisfy electrical balance, but to do so requires a negative total concentration. In this case, a master species of opposite charge should have been selected for this purpose. Another example occurs when bicarbonate (or carbonate) is constrained to satisfy an input value of titration alkalinity, but other constraints (usually equilibrium constraints) on other master species are such that the contribution from noncarbonate species must exceed the total alkalinity. In this case, the carbonate contribution to the total alkalinity must be negative, a physical impossibility.

8.5. ORGANIZATION OF THE GOVERNING EQUATIONS AND ITERATION VARIABLES

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 can be reduced by substitutions and one can then construct the residual functions in any number of ways. Once the residual functions have been chosen, the form of the Jacobian becomes fixed by the requirement that $\underline{J} = (\partial a_i / \partial z_j)$.

In the EQ3NR code, the number of equations and unknowns is reduced by substituting all governing aqueous mass action equations into the mass balance, electrical balance, alkalinity balance, ionic strength, and equivalent

stoichiometric ionic strength equations. The remaining aqueous species giving rise to unknowns then comprise a relatively small master set. As a trade-off, the ionic strength (I) and the equivalent stoichiometric ionic strength (I_E) must be included as master iteration variables. As a whole, however, this approach considerably reduces the size of the Jacobian matrix.

The master iteration variables reside in the vector \underline{z} , which has the following structure:

$$\underline{z} = \begin{bmatrix} t_1 & (\log a_{\text{H}_2\text{O}(l)}) \\ t_2 & (\log m_2) \\ \cdot & \cdot \\ t_2 & (\log m_s) \\ \cdot & \cdot \\ t_{s_B-1} & (\log m_{s_B-1}) \\ t_{s_B} & (\log f_{\text{O}_2}) \\ t_{s_B+1} & (\log m_{s_B+1}) \\ \cdot & \cdot \\ t_2 & (\log m_s) \\ \cdot & \cdot \\ t_{s_Q} & (\log m_{s_Q}) \\ t_{I_E} & (\log m_{I_E}) \\ t_I & (\log I) \end{bmatrix}$$

Auxiliary master aqueous species with JFLAG = 30 are excluded from this set. The structure is further simplified if $s_Q = s_B$. For a problem in which this is the case, it is implied that the aqueous solution is in a state of complete homogeneous equilibrium. If $s_Q = s_B + 1$, homogeneous 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 greater than zero option). In all other cases, only partial homogeneous equilibrium is implied.

We will first look at the aqueous mass action equations that are to be eliminated. Here K_r is the thermodynamic equilibrium constant for the reaction in which the formally associated species, denoted by $s^*(s_r)$, is consumed, s_Q is the number of aqueous master species, and b_{sr} is the stoichiometric reaction coefficient. Here, s denotes a species, r the

reaction, and γ the activity coefficient. The mass action equations take the logarithmic form:

$$\log K_r = b_{1r} i_1 + b_{s_B r} i_{s_B} + b_{s^* r} (i_{s^*} + \log \gamma_{s^*}) + \sum_{\substack{s^*=2 \\ \text{skip } s_B}}^{s_Q} b_{s^* r} (i_{s^*} + \log \gamma_{s^*})$$

Note that s^* denotes the only species in the equation not in the master set. (Here s^* refers to either a nonmaster species or an auxiliary master species with JFLAG - 30.) This can be rearranged to give

$$i_{s^*} = \log K_r / b_{s^* r} - \log \gamma_{s^*} - (b_{1r} / b_{s^* r}) i_1 - (b_{s_B r} / b_{s^* r}) i_{s_B} - \sum_{\substack{s^*=2 \\ \text{skip } s_B}}^{s_Q} (b_{s^* r} / b_{s^* r}) (i_{s^*} + \log \gamma_{s^*})$$

Recall the relation $dx/d \log x = 2.303x$ and that $\log m_{s^*} = i_{s^*}$. We then use the chain rule to derive

$$\begin{aligned} dm_{s^*} / dx &= (dm_{s^*} / di_{s^*}) (di_{s^*} / dx) \\ &= 2.303 m_{s^*} (di_{s^*} / dx) \end{aligned}$$

We use this relation to derive the following:

$$dm_{s^*} / di_1 = 2.303 m_{s^*} (-b_{1r} / b_{s^* r})$$

$$dm_{s^*} / di_{s'} = 2.303 m_{s^*} (-b_{s' r} / b_{s^* r}) \quad , \text{ for } s' = 2, s_Q, \text{ and}$$

$$dm_{s^*} / di_{I_E} = 0 \quad ,$$

$$dm_{s^*}/dI = 2.303m_{s^*} - \Gamma_{s^*} + \sum_{\substack{s=2 \\ \text{skip } s_B}}^{s_Q} (b_{s^*r}/b_{s^*r}) \Gamma_{s^*} .$$

These relations are used below to derive the Jacobian elements corresponding to the mass, charge, and alkalinity balance residual functions and also the residual functions corresponding to the ionic strength and the equivalent stoichiometric ionic strength.

Certain factors will appear repeatedly in some of the derivations below and will be given special symbols. In the EQ3NR code, these parameters are evaluated before the calculation of the Jacobian matrix elements in which they appear. This is done to avoid repetitive arithmetic in the code. Again implying that $s^* = s_r$, we make the following definitions

$$H_{sr} \equiv m_{s^*} u_{s^*} / b_{s^*r} ,$$

$$H_{zr} \equiv m_{s^*} z_{s^*} / b_{s^*r} ,$$

$$H_{\tau r} \equiv m_{s^*} \tau_{s^*} / b_{s^*r} ,$$

$$H_{I_E r} \equiv m_{s^*} u_{s^*} s_E / b_{s^*r} , \text{ and}$$

$$H_{I_r} \equiv m_{s^*} z_{s^*}^2 / 2b_{s^*r} .$$

In the code, these vector parameters are computed in the array STOR1 as they are needed.

We also define:

$$L_r \equiv \sum_{\substack{s=2 \\ \text{skip } s_B}}^{s_Q} b_{sr} \Gamma_s .$$

Here, $\Gamma_s = \partial \log \delta_s / \partial \log I$, which is given by a function described later in this section. The L_r parameters reside in the array STOR2 in EQ3NR.

8.6 DERIVATION OF RESIDUAL FUNCTIONS AND THE JACOBIAN MATRIX

We will now take each remaining governing equation, construct a corresponding pair of residual functions (α and β), and derive the corresponding row of elements in the Jacobian matrix by partial differentiation of the α residuals. The α residuals are the true Newton-Raphson residual functions and are used to define the Jacobian matrix. The β residuals are better measures of satisfactory convergence.

1. The activity of water. The governing equation is

$$\log a_{\text{H}_2\text{O}}(t) = v_{\text{H}_2\text{O}}(I_E) .$$

where $v_{\text{H}_2\text{O}}$ is a function given in Section 2.3.3. The corresponding master iteration variable is $i_1 = \log a_{\text{H}_2\text{O}}(t)$. We define the residual functions

$$\alpha_1 = v_{\text{H}_2\text{O}}(I_E) - i_1 , \text{ and}$$

$$\beta_1 = \alpha_1 .$$

The only nonzero elements of the corresponding row of the Jacobian matrix are

$$J_{11} = -1.0 , \text{ and}$$

$$J_{1I_E} = r_1 .$$

Here $r_1 = \partial \log a_{\text{H}_2\text{O}} / \partial \log I_E$, which is described later in this section.

2. Mass balance. This may be applied to any aqueous species in the master set ($s = 1$ through s_Q) except $\text{H}_2\text{O}(l)$ ($s = 1$), $\text{O}_2(g)$ (s_B), and H^+ . The corresponding master iteration variable is $i_s = \log m_s$. 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_s^T). Alternatively, one may enter total concentration in nonmolal units using other JFLAG values (molar, JFLAG = 1; mg/L, JFLAG = 2; mg/kg, JFLAG = 3),

which EQ3NR will then recompute into molal units and set the JFLAG to zero.

The residual functions are defined

$$a_s = -m_s^T + \sum_{s'=2}^{s_T} u_{s's} m_{s'} \quad , \text{ and}$$

$$j_s = a_s / m_s^T .$$

To calculate the corresponding Jacobian elements with the set of aqueous species unknowns reduced to the master set, we write:

$$\begin{aligned} a_s &= -m_s^T + \sum_{s'=2}^{s_T} u_{s's} m_{s'} + \sum_{s''=s_B+1}^{s_T} u_{s''s} m_{s''} \\ &= -m_s^T + \sum_{s'=2}^{s_T} u_{s's} m_{s'} + \sum_{r=1}^{r_T} u_{s''s} m_{s''} \quad , \end{aligned}$$

where in the last summation it is implied that $s'' = s_r$. From this point, we can use the relations developed above to derive the Jacobian elements:

$$\begin{aligned} J_{s1} &= \partial a_s / \partial t_1 \\ &= \sum_{r=1}^{r_T} u_{s''s} (dm_{s''} / dt_1) \\ &= -2.303 \sum_{r=1}^{r_T} u_{s''s} m_{s''} (b_{1r} / b_{s''r}) \\ &= -2.303 \sum_{r=1}^{r_T} b_{1r} H_{sr} \quad , \end{aligned}$$

$$\begin{aligned}
J_{SS'} &= \partial \alpha_S / \partial l_{S'} \\
&= u_{S'S} (dm_{S'} / dl_{S'}) + \sum_{r=1}^{r_T} u_{S''S} (dm_{S''} / dl_{S''}) \\
&= -2.303 \left[u_{S'S} m_{S'} - \sum_{r=1}^{r_T} u_{S''S} m_{S''} (b_{S'r} / b_{S''r}) \right] \\
&= -2.303 \left(u_{S'S} m_{S'} - \sum_{r=1}^{r_T} b_{S'r} H_{Sr} \right) ,
\end{aligned}$$

$$J_{SI_E} = 0 ,$$

$$\begin{aligned}
J_{SI} &= \partial \alpha_S / \partial l_I \\
&= \sum_{r=1}^{r_T} u_{S''S} (dm_{S''} / dl_I) \\
&= 2.303 \left[\sum_{r=1}^{r_T} u_{S''S} m_{S''} \left(-\Gamma_{S''} + \sum_{\substack{s^*=2 \\ \text{skip } s_B}}^{s_Q} b_{S''r} \Gamma_{S''} / b_{S''r} \right) \right] \\
&= 2.303 \sum_{r=1}^{r_T} \left[-H_{Sr} (b_{S''r} \Gamma_{S''} + L_r) \right] .
\end{aligned}$$

3. Electrical balance. This governing equation may be applied to one of the ions in the aqueous species master set, denoted by s_z . The corresponding master iteration variable is $l_{s_z} = \log m_{s_z}$. Apart from the definition of the β residual, the treatment is exactly analogous to that for mass balance. Note that the electrical charge $z_{s''}$ takes the place of the stoichiometric equivalence factors $u_{S''S}$. The governing equation is

$$\sum_{s'=1}^{s_T} z_{s'} m_{s'} = 0 .$$

The residual functions are defined:

$$\alpha_z = \sum_{s'=1}^{s_T} z_{s'} m_{s'} \quad , \text{ and}$$

$$\beta_z = \alpha_z / I \quad .$$

The Jacobian elements are given by:

$$J_{s_z 1} = -2.303 \sum_{r=1}^{r_T} b_{1r} H_{zr} \quad ,$$

$$J_{s_z s'} = -2.303 \left(z_{s'} m_{s'} - \sum_{r=1}^{r_T} b_{s'r} H_{zr} \right) \quad ,$$

$$J_{s_z I_E} = 0 \quad , \text{ and}$$

$$J_{s_z I} = 2.303 \sum_{r=1}^{r_T} \left[-H_{zr} (b_{s'r} \Gamma_{s'} + L_r) \right] \quad .$$

4. Alkalinity balance. This governing equation may be applied only to HCO_3^- or CO_3^{2-} , denoted by s_A . The corresponding master iteration variable is $t_{s_A} = \log m_{s_A}$. The treatment is exactly analogous to that for mass balance. A_t , the titration alkalinity (JFLAG = 10), or A_c , the carbonate alkalinity (JFLAG = 12), plays the role of total concentration. EQ3NR will accept the titration alkalinity or carbonate alkalinity in molar equivalents, if the JFLAG is set to 11 or 13, respectively. It then recomputes the alkalinity to molal equivalents and resets the JFLAG from 11 to 10, or from 13 to 12. The alkalinity factors, τ_s , are the weighting factors in place of u_{s^*s} . Their values depend on the type of alkalinity balance that is selected. To be completely explicit, we could subscript the alkalinity factors; e.g., $\tau_{s,t}$ or $\tau_{s,c}$. In the derivation below we will use A_x to represent the alkalinity and $\tau_{s,x}$ the

alkalinity factors, where x is either t or c. The governing equation is

$$\sum_{s'=1}^{s_T} \tau_{s',x} m_{s'} = A_x .$$

The residual functions are defined:

$$a_A = -A_x + \sum_{s'=1}^{s_T} \tau_{s',x} m_{s'} , \text{ and}$$

$$\beta_x = a_x / A_x .$$

The Jacobian elements are given by:

$$J_{s_I} = -2.303 \sum_{r=1}^{r_T} b_{lr} H_{\tau r} ,$$

$$J_{s_s'} = -2.303 \left(\tau_{s',x} m_{s'} - \sum_{r=1}^{r_T} b_{s'r} H_{\tau r} \right) ,$$

$$J_{s_I E} = 0 , \text{ and}$$

$$J_{s_I} = 2.303 \sum_{r=1}^{r_T} \left| -H_{\tau r} (b_{s'r} \Gamma_{s''} + L_r) \right| .$$

5. Specified thermodynamic activity. This represents the JFLAG = 16 option for $s = 2$ through s_Q , skipping s_B . The corresponding master iteration variable is $i_s = \log m_s$. This option is most frequently employed with the hydrogen ion in order to specify a pH value ($\text{pH} = -\log a_{\text{H}^+}$). The governing equation is

$$i_s + \log \gamma_s = \log a_s .$$

The residual functions are

$$\alpha_s = -\log a_s + i_s + \log \gamma_s, \text{ and}$$

$$\beta_s = \alpha_s.$$

The only non-zero Jacobian elements are

$$J_{ss} = 1.0, \text{ and}$$

$$J_{sI} = \Gamma_s.$$

This option can be applied to a nonbasis species by using basis switching (see Section 3.1 for details).

6. Specified free concentration. This represents the JFLAG = 4 option for $s = 2$ through s_Q , skipping s_B . The free concentration is entered in molal units. If it is entered in molar units (JFLAG = 5), the EQ3NR code will convert it to molal units and reset JFLAG to 4 before beginning Newton-Raphson iteration. The governing equation is

$$\log m_s = \log m_s.$$

The "unknown" here is really a known; hence,

$$\alpha_s = 0, \text{ and}$$

$$\beta_s = 0.$$

In order to prevent singularity in the Jacobian, we set

$$J_{ss} = 1.0.$$

This option can also be applied to a nonbasis species by using basis switching (see Section 3.1).

7. Equilibrium with a stoichiometric mineral. This option (JFLAG = 19) may be specified for any aqueous species denoted by $s = 2$ through s_Q , including s_B ($O_2(g)$). Let φ denote the mineral in question and s_φ denote the aqueous species required to satisfy the corresponding solubility equilibrium. If s_φ is not s_B , the governing equation is

$$\log K_\varphi = b_{s_\varphi} (l_{s_\varphi} + \log \gamma_{s_\varphi}) + b_{l\varphi} l_1 + b_{s_B\varphi} l_{s_B} + \sum_{\substack{s'=2 \\ \text{skip } s_\varphi \\ \text{skip } s_B}}^{s_Q} b_{s'\varphi} (l_{s'} + \log \gamma_{s'})$$

If $s_\varphi = s_B$, the governing equation is

$$\log K_\varphi = b_{l\varphi} l_1 + b_{s_B\varphi} l_{s_B} + \sum_{\substack{s'=2 \\ \text{skip } s_B}}^{s_Q} b_{s'\varphi} (l_{s'} + \log \gamma_{s'})$$

In the first case, the residual function is defined:

$$\alpha_{s_\varphi} = \left[1/b_{s_\varphi} \right] \left[\log K_\varphi - b_{s_\varphi} \log \gamma_{s_\varphi} - b_{l\varphi} l_1 - b_{s_B\varphi} l_{s_B} - \sum_{\substack{s'=2 \\ \text{skip } s_\varphi \\ \text{skip } s_B}}^{s_Q} b_{s'\varphi} (l_{s'} + \log \gamma_{s'}) \right] - l_{s_\varphi}$$

In the case where $s_\varphi = s_B$, it is defined:

$$\alpha_{s_\varphi} = \left[1/b_{s_\varphi} \right] \left[\log K_\varphi - b_{l\varphi} l_1 - \sum_{\substack{s'=2 \\ \text{skip } s}}^{s_Q} b_{s'\varphi} (l_{s'} + \log \gamma_{s'}) \right] - l_{s_\varphi}$$

In either case, we define:

$$\beta_{s_{\psi}} = \alpha_{s_{\psi}} .$$

The Jacobian elements are then

$$J_{s_{\psi} 1} = -b_{1\psi} / b_{s_{\psi}\psi} ,$$

$$J_{s_{\psi} s'} = -b_{s'\psi} / b_{s_{\psi}\psi} \quad \text{for } s' = 2 \text{ through } s_Q \text{ except } s_{\psi} ,$$

$$J_{s_{\psi} s_{\psi}} = -1.0 ,$$

$$J_{s_{\psi} I_E} = 0 ,$$

For s_{ψ} not s_B ,

$$J_{s_{\psi} I} = -\Gamma_{s_{\psi}} - \sum_{s'=2}^{s_Q} \underset{\substack{\text{skip } s \\ \text{skip } s_B}}{b_{s'\psi} \Gamma_{s'} / b_{s_{\psi}\psi}} .$$

For $s_{\psi} = s_B$,

$$J_{s_{\psi} I} = - \sum_{s'=2}^{s_Q} \underset{\substack{\text{skip } s \\ \text{skip } s_B}}{b_{s'\psi} \Gamma_{s'} / b_{s_{\psi}\psi}} .$$

8. Equilibrium with an end member of a solid solution mineral. This option (JFLAG = 20) can be specified for any aqueous species denoted by $s = 2$ through s_Q , including $s_B(O_2(g))$. The treatment is closely analogous to that for equilibrium with a mineral of fixed composition. Let σ and ψ denote the end member and solid solution phase. Rather than subscripting σ with ψ (e.g., denoting the constrained aqueous species by $s_{\sigma\psi}$, we will merely imply this in the

derivations below (e.g., denote the same aqueous species by s_σ). The mole fraction of the end member (x_σ) is entered as part of the specification for this option. The activity coefficient of the end member is symbolized by λ_σ . If s_σ is not s_B , the governing equation is

$$\log K_\sigma = b_{s_\sigma\sigma} (t_{s_\sigma} + \log \gamma_{s_\sigma}) + b_{l_\sigma} t_1 + b_{\sigma\sigma} (\log x_\sigma + \log \lambda_\sigma) + b_{s_B\sigma} t_{s_B} + \sum_{\substack{s'=2 \\ \text{skip } s_\sigma \\ \text{skip } s_B}}^{s_Q} b_{s'\sigma} (t_{s'} + \log \gamma_{s'})$$

If $s_\sigma = s_B$, the governing equation is

$$\log K_\sigma = b_{l_\sigma} t_1 + b_{s_B\sigma} t_{s_B} + \sum_{\substack{s'=2 \\ \text{skip } s_B}}^{s_Q} b_{s'\sigma} (t_{s'} + \log \gamma_{s'})$$

In the first case, the residual function is defined:

$$a_{s_\sigma} = \left[1/b_{s_\sigma\sigma} \right] \left[\log K_\sigma - b_{s_\sigma\sigma} \log \gamma_{s_\sigma} - b_{l_\sigma} t_1 - b_{s_B\sigma} t_{s_B} - \sum_{\substack{s'=2 \\ \text{skip } s_\sigma \\ \text{skip } s_B}}^{s_Q} b_{s'\sigma} (t_{s'} + \log \gamma_{s'}) \right] - t_{s_\sigma}$$

In the case where $s_\sigma = s_B$, it is defined:

$$a_{s_\sigma} = \left[1/b_{s_\sigma\sigma} \right] \left[\log K_\sigma - b_{l_\sigma} t_1 - \sum_{\substack{s'=2 \\ \text{skip } s_\sigma}}^{s_Q} b_{s'\sigma} (t_{s'} + \log \gamma_{s'}) \right] - t_{s_\sigma}$$

In either case, we define:

$$b_{s_{\sigma}} = a_{s_{\sigma}} .$$

The Jacobian elements are then

$$J_{s_{\sigma} I} = -b_{I\sigma} / b_{s_{\sigma}\sigma} ,$$

$$J_{s_{\sigma} s'} = -b_{s'\sigma} / b_{s_{\sigma}\sigma} \quad \text{for } s' = 2 \text{ through } s_Q, \text{ except } s_{\sigma} ,$$

$$J_{s_{\sigma} s_{\sigma}} = -1.0 , \text{ and}$$

$$J_{s_{\sigma} I E} = 0 .$$

For s_{σ} not s_B ,

$$J_{s_{\sigma} I} = -\Gamma_{s_{\sigma}} - \sum_{s'=2}^{s_Q} \underset{\substack{\text{skip } s_{\sigma} \\ \text{skip } s_B}}{b_{s'\sigma} \Gamma_{s'} / b_{s_{\sigma}\sigma}} .$$

For $s_{\sigma} = s_B$,

$$J_{s_{\sigma} I} = - \sum_{s'=2}^{s_Q} \underset{\substack{\text{skip } s_{\sigma} \\ \text{skip } s_B}}{b_{s'\sigma} \Gamma_{s'} / b_{s_{\sigma}\sigma}} .$$

9. Equilibrium with a gas. This option (JFLAG = 21) can be specified for any aqueous species denoted by $s = 2$ through s_Q , including $s_B(O_2(g))$. The treatment is closely analogous to that for equilibrium with a mineral of fixed composition. Let g denote the gas in question and s_g denote the aqueous species that is required to satisfy the corresponding solubility equilibrium. The fugacity

of the gas, f_g , is entered as part of the specification for this option. If s_g is not s_B , the governing equation is

$$\log K_g = b_{s_g g} (t_{s_g} + \log \gamma_{s_g}) + b_{lg} t_1 + b_{gg} \log f_g \\ + b_{s_B g} t_{s_B} + \sum_{\substack{s'=2 \\ \text{skip } s_B}}^{s_Q} b_{s'g} (t_{s'} + \log \gamma_{s'}) .$$

If $s_g = s_B$, the governing equation is

$$\log K_g = b_{lg} t_1 + b_{s_B g} t_{s_B} + \sum_{\substack{s'=2 \\ \text{skip } s_B}}^{s_Q} b_{s'g} (t_{s'} + \log \gamma_{s'}) .$$

In the first case, the residual function is defined:

$$a_{s_g} = \left[\frac{1}{b_{s_g g}} \right] \left[\log K_g - b_{s_g} \log \gamma_{s_g} - b_{lg} t_1 - b_{s_B g} t_{s_B} \right. \\ \left. - \sum_{\substack{s'=2 \\ \text{skip } s_B}}^{s_Q} b_{s'g} (t_{s'} + \log \gamma_{s'}) \right] - t_{s_g} .$$

In the case where $s_g = s_B$, it is defined:

$$a_{s_g} = \left[\frac{1}{b_{s_g g}} \right] \left[\log K_g - b_{lg} t_1 - \sum_{\substack{s'=2 \\ \text{skip } s_B}}^{s_Q} b_{s'g} (t_{s'} + \log \gamma_{s'}) \right] - t_{s_g} .$$

Note that the latter does not have much practical value because we can directly specify $\log f_{O_2(g)}$ as shown later in this section.

In either case, we define:

$$b_{s_g} = a_{s_g} .$$

The Jacobian elements are then

$$J_{s_g 1} = -b_{1g}/b_{s_g g} ,$$

$$J_{s_g s'} = -b_{s'g}/b_{s_g g} \text{ for } s' = 2 \text{ through } s_Q, \text{ except } s_g ,$$

$$J_{s_g s_g} = -1.0 ,$$

$$J_{s_g I_E} = 0 .$$

For s_g not s_B ,

$$J_{s_g I} = -\Gamma_{s_g} - \sum_{s'=2}^{s_Q} b_{s'g} \Gamma_{s'} / b_{s_g g} .$$

skip s_g
skip s_B

For $s_g = s_B$,

$$J_{s_g I} = - \sum_{s'=2}^{s_Q} b_{s'g} \Gamma_{s'} / b_{s_g g} .$$

skip s_g
skip s_B

10. Aqueous homogeneous equilibrium. This option (JFLAG = 27) excludes the species to which it is applied (this species must be in the

auxiliary basis set) and its ion-pairs and complexes from the mass balance of the corresponding master species in the strict basis set (i.e., the master species that formally corresponds to a chemical element). This is a good choice for dissolved gas species such as $O_2(aq)$ and $H_2(aq)$. If bisulfide is an auxiliary master species with $JFLAG = 27$, and sulfate is in the strict master species set, then bisulfide and its "complexes" are not included in calculating the sulfate mass balance that must satisfy an input total concentration of sulfate. If $JFLAG = 30$ for bisulfide, then bisulfide and its complexes are included.

Let s^* be the auxiliary master species constrained by $JFLAG = 27$, and let r denote its formally associated reaction. Then the governing equation is

$$\log K_r = b_{s^*r} (l_{s^*} + \log \gamma_{s^*}) + b_{lr} l_l + b_{s_B r} l_{s_B} + \sum_{s'=2}^{s_Q} b_{s'r} (l_{s'} + \log \gamma_{s'}) \quad .$$

skip s^*
skip s_B

The residual function is then defined:

$$\alpha_{s^*} = \left[1/b_{s^*r} \right] \left[\log K_r - b_{s^*r} \log \gamma_{s^*r} - b_{lr} l_l - b_{s_B r} l_{s_B} - \sum_{s'=2}^{s_Q} b_{s'r} (l_{s'} + \log \gamma_{s'}) \right] - l_{s^*} \quad .$$

skip s^*
skip s_B

We also define:

$$B_{s^*} = \alpha_{s^*} \quad .$$

The Jacobian elements are then

$$J_{s'1} = -b_{1r}/b_{s'r} ,$$

$$J_{s*s'} = -b_{s'r}/b_{s'r} \text{ for } s' = 2 \text{ through } s_Q, \text{ except } s^* ,$$

$$J_{s*s^*} = -1.0 ,$$

$$J_{s*I_E} = 0 , \text{ and}$$

$$J_{s*I} = -\Gamma_{s^*} - \sum_{s'=2}^{s_Q} b_{s'r} \Gamma_{s'} / b_{s'r} .$$

skip s^*
skip s_B

11. Specified $\log f_{O_2}$. This option (IOPT1 = 0) allows direct specification of the logarithm of oxygen fugacity (l_{s_B}). The governing equation is

$$l_{s_B} = l_{s_B} .$$

The residuals are

$$\alpha_{s_B} = 0 , \text{ and}$$

$$\beta_{s_B} = 0 .$$

The only nonzero Jacobian element in the corresponding row is

$$J_{s_B s_B} = 1.0 .$$

12. Specified Eh. This option (IOPT1 = -1) allows indirect specification of $\log f_{O_2}$. If pe^- is specified (IOPT1 = -2), EQ3NR

converts it to Eh before it performs the Newton-Raphson iteration. Letting F be the Faraday constant, R the gas constant, and T the absolute temperature, the governing equation is

$$l_{s_B} = 4EhF/(2.303RT) + \log K_{Eh} + 2l_1 - 4(l_{H^+} + \log \gamma_{H^+}) .$$

The residual functions are

$$\alpha_{s_B} = 4EhF/(2.303RT) + \log K_{Eh} + 2l_1 - 4(l_{H^+} + \log \gamma_{H^+}) - l_{s_i} , \text{ and}$$

$$\beta_{s_B} = \alpha_{s_B} .$$

The nonzero Jacobian elements in the corresponding row are

$$J_{s_B 1} = 2.0 ,$$

$$J_{s_B H^+} = -4.0 ,$$

$$J_{s_B s_B} = -1.0 , \text{ and}$$

$$J_{s_B I} = -4\Gamma_{H^+} .$$

13. An aqueous redox couple determines $\log f_{0_2}$. This represents the IOPT1 = 1 option. This is the method of estimating the redox state of aqueous solutions that has the greatest degree of real meaning. The couple is specified by the UREDOX input, which defines the corresponding redox reaction r. The governing equation is

$$\log K_r = b_{1r} l_1 + b_{s_B} l_{s_B} + \sum_{\substack{s'=2 \\ \text{skip } s_B}}^{s_0} b_{s'r} (l_{s'} + \log \gamma_{s'}) .$$

The residual functions are

$$a_{s_B} = \left[1/b_{s_B r} \right]$$

$$\cdot \left[\log K_r - b_{1r} i_1 - \sum_{\substack{s'=2 \\ \text{skip } s_B}}^{s_Q} b_{s'r} (i_{s'} + \log \gamma_{s'}) \right] - i_{s_B} \quad , \text{ and}$$

$$i_{s_B} = \varepsilon_{s_B} .$$

The nonzero Jacobian elements in the corresponding row are

$$J_{s_B 1} = -b_{1r}/b_{s_B r} ,$$

$$J_{s_B s'} = -b_{s'r}/b_{s_B r} \quad \text{for } s' = 2 \text{ through } s_Q, \text{ except } s_B ,$$

$$J_{s_B s_B} = -1.0 \quad , \text{ and}$$

$$J_{s_B I} = - \sum_{\substack{s'=2 \\ \text{skip } s_B}}^{s_Q} b_{s'r} \bar{r}_{s'} / b_{s_B r} .$$

14. Equivalent stoichiometric ionic strength. The corresponding master iteration variable is $i_{I_E} = \log I_E$. The treatment is closely analogous to that for mass balance. The factor $u_{s's_E}$, where s_E denotes the defining ion (either Na^+ or Cl^-), is just a special case of the general stoichiometric equivalence factor $u_{s's}$.

The governing equation is

$$\sum_{s'=1}^{s_T} u_{s's_E} m_{s'} = I_E .$$

The residual functions are defined:

$$a_{I_E} = -I_E + \sum_{s'=1}^{s_T} U_{s'} s_E, \text{ and}$$

$$b_{I_E} = a_{I_E} / I_E.$$

The Jacobian elements are given by:

$$J_{I_E I} = -2.303 \sum_{r=1}^{r_T} b_{I_E r} H_{I_E r},$$

$$J_{I_E s'} = -2.303 \left(U_{s'} m_{s'} - \sum_{r=1}^{r_T} b_{s' r} H_{I_E r} \right),$$

$$J_{I_E I_E} = -2.303 I_E, \text{ and}$$

$$J_{I_E I} = 2.303 \sum_{r=1}^{r_T} \left[-H_{I_E r} (b_{s^* r} r_{s^*} + L_r) \right].$$

15. Ionic strength. The corresponding master iteration variable is $i_I = \log I$. The treatment is closely analogous to that for mass balance. The factor $z_{s^*}^2/2$ takes the role of the stoichiometric reaction coefficient $u_{s^* s^*}$.

The governing equation is

$$0.5 \sum_{s'=1}^{s_T} z_{s'}^2 m_{s'} = I.$$

The residual functions are defined:

$$a_I = -I + 0.5 \sum_{s'=1}^{s_T} z_{s'}^2 m_{s'}, \text{ and}$$

$$b_I = a_I / I.$$

The Jacobian elements are given by:

$$J_{I1} = -2.303 \sum_{r=1}^{r_T} b_{1r} H_{Ir}$$

$$J_{Is} = -2.303 \left(z_s^2 m_s / 2 - \sum_{r=1}^{r_T} b_{s,r} H_{Ir} \right),$$

$$J_{II_E} = 0, \text{ and}$$

$$J_{II} = 2.303 - 1 - \left[\sum_{r=1}^{r_T} H_{Ir} (b_{s,r} \Gamma_{s,r} + L_r) \right].$$

16. The Γ_s factors that appear in many of the above equations are derivative functions of the activity coefficient equations discussed in Section 2. They have the following definitions:

$$\Gamma_1 \equiv \partial \log a_{H_2O}(l) / \partial \log I_E, \text{ and}$$

$$\Gamma_s \equiv \gamma \log \gamma_s / \partial \log I, \text{ for } s \text{ greater than } 1.$$

When the activity of water is described by the equation of Helgeson (1969), then:

$$\Gamma_1 = (2/2.303\omega) \left(\varphi' + J'D' - D'v_{H_2O,1} I_E^{3/2} / 2B'^2 + v_{H_2O,2} I_E^{1/2} + 4v_{H_2O,3} I_E^{2/3} + 9v_{H_2O,4} I_E^{3/4} \right).$$

For electrically charged aqueous species whose activity coefficients are approximated by Helgeson's (1969) B equation,

$$\Gamma_s = -Az_s^2 I^{-1/2} \left[2 \left(1 + a_{sB}^0 I \right)^2 \right] + B.$$

For neutral, but polar, aqueous species such as $CaSO_4^0$,

$$\Gamma_s = 0.$$

For neutral, relatively nonpolar species, which are assigned the activity coefficient of $\text{CO}_2(\text{aq})'$

$$\Gamma = v_{\text{CO}_2,1} + 2v_{\text{CO}_2,2}^{\text{I}} + 3v_{\text{CO}_2,3}^{\text{I}^2} + 4v_{\text{CO}_2,4}^{\text{I}^3} .$$

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APPENDIX A

GLOSSARY OF MAJOR VARIABLES IN EQ3NR

This glossary covers the major variables in the EQ3NR code. Variable names may be preceded by the corresponding algebraic symbols used in this report. Variables beginning with I, J, K or N are integer, beginning with Q are logical, and beginning with U contain alphanumeric strings. Variables that begin with other letters, including L and M, should be type real on machines with 60 to 64 bits per word and type double (or equivalent) on hardware with 32 bits per word.

<u>J</u>	AA	The Jacobian matrix.
a_s	ACT	Activity of an aqueous species.
$\log a_s$	ACTLG	Log of the activity of an aqueous species.
A	ADH	Debye-Huckel A constant.
A	AFF	Affinity of a fixed composition mineral to precipitate, kcal.
	AFFLCX	Affinity of a solid-solution phase to precipitate.
	AFFX	Affinity of an end-member component of a solid solution.
	ALK	Alkalinity; titration alkalinity, A_t , if JFLAG = 10 or 11 for bicarbonate or carbonate ion; carbonate alkalinity, A_c , if JFLAG = 12 or 13.
α	ALPHA	Residual function vector.
2.303	AL10	$\ln 10$.
	APX	Solid-solution thermodynamics parameters.
	ATWT	Atomic weight of a chemical element.
\bar{a}	AZERO	Debye-Huckel ion size parameter.
B	BDH	Debye-Huckel B constant.
<u>β</u>	BETA	Residual function vector, with normalized mass balance elements.
β_{\max}	BETAMAX	Largest absolute value of any element of BETA.
B'	BTERM	The B' factor used to compute the activity of water as a function of equivalent stoichiometric ionic strength.
\bar{B}	BDOT	Extended Debye-Huckel \bar{B} constant.

v_{CO_2}	CCO2	Coefficient for computing $\log \gamma_{\text{CO}_2(\text{aq})}$ as a function of ionic strength (I).
$v_{\text{H}_2\text{O}}$	CH2O	Coefficient for computing $\log a_{\text{H}_2\text{O}}$ as a function of equivalent stoichiometric ionic strength (I_E).
b_{sr}	CDRS	Stoichiometric reaction coefficient for aqueous redox and dissociation reactions. CDRS(NS,NRS) is the coefficient for the NS-th aqueous species in the NRS-th reaction. CDRS(NSQ1,NRS) is the coefficient of the species that is formally associated with the reaction. If the NS-th species is an auxiliary master species and NRS is its own formally associated reaction, CDRS(NS,NRS) = 0 and CDRS(NSQ1,NRS) is its coefficient.
b_{sp}	CDRM	Stoichiometric reaction coefficient for dissolution reactions of minerals of fixed composition. CDRM(NS,NM) is the coefficient of the NS-th aqueous master species appearing in the dissolution reaction of the NM-th mineral. CDRM(NSQ1,NM) is the coefficient of the NM-th mineral.
b_{sg}	CDRG	Stoichiometric reaction coefficient for dissolution reactions of gas species. CDRM(NS,NG) is the coefficient of the NS-th aqueous master species appearing in the dissolution reaction of the NG-th gas. CDRG(NSQ1,NG) is the coefficient of the NG-th gas.
c_{cs}	CESS	Stoichiometric mass coefficient of an aqueous species. CESS(NC,NS) is the number of moles of the NC-th chemical element in one mole of the NS-th aqueous species.
m	CONC	Molal concentration of an aqueous species.
log m	CONCLG	Log of molal concentration.
	CSGRT	Molal concentrations of the aqueous species, sorted in order of increasing value.
	CSTOR	Stoichiometric mass balance factors of aqueous species for oxygen in the O^{2-} valence form and hydrogen in the H^+ valence form; compare with STORE.
	CSP	Constraining solution parameter array; the meaning of each member of this array is determined by the corresponding member of the JFLAG array.

	CSPB	Array into which the CSP values are read from the INPUT file.
	CTE	Equivalent total mass of a chemical element in a given valence form or combination of valence forms in mutual equilibrium per kilogram of water.
δ	DEL	Vector of Newton-Raphson correction terms.
δ_{func}	DELFNC	Convergence function that measures the improvement in DELMAX, defined as $[1.0 - (\text{DELMAX}_i / \text{DELMAX}_{i-1})]$.
δ_{max}	DELMAX	Largest absolute value of any element of DEL.
D'	DTERM	The D' factor used to compute the activity of water as a function of equivalent stoichiometric ionic strength (I_E).
	E	Work array used in solving matrix equations.
Eh	EH	Default theoretical redox potential, in volts.
F	FARAD	The Faraday constant, 23062.3 cal/equiv-volt.
f_{O_2}	FO2	Default hypothetical equilibrium oxygen fugacity.
	FO2LG	Log of default hypothetical equilibrium oxygen fugacity.
f	FUG	Fugacity of a gas species.
log f	FUGLG	Log fugacity of a gas species.
	GG	Work array that has the same dimensions as AA, the Jacobian matrix, and is used in solving matrix equations.
log γ	GLG	Log of activity coefficient of an aqueous species.
Γ	GM	Derivative function for activity coefficients of aqueous species.
s_E	IACION	Index of the aqueous species (Na^+ or Cl^-) that defines the equivalent stoichiometric ionic strength (I_E).
	IBASIS	Array that contains a record of basis switching.
	IDBUG1, etc.	Debugging print option switches (see Section 4).
s_2	IEBAL	Index of the charged aqueous species chosen for electrical balancing.
	IER	Error flag parameter; appears in the argument list of many subroutines.
σ_T	IKT	Number of end-member components in a given solid solution.
	IKTMAX	Maximum allowed number of end members in any solid solution.
	IINDEX	Array containing the indices of the master aqueous species for which the starting iteration values must be simultaneously estimated.

INDEX Array that contains the indices of the master iteration variables that appear for a given problem.

IOPT1, Program option switches (see Section 4).
etc.

IPRNT1, Print option switches (see Section 4).
etc.

IR Work array used in solving matrix equations.

ISTACK Work array used in sorting aqueous species in increasing order of concentration.

ITERMX Limit on the number of Newton-Raphson iterations.

JCFLAG Status switch array for chemical elements:
 = 0 means an element does not appear in the current model,
 = 1 means an element appears in the current model.

JFLAG Switch array that defines the type of constraint (governing equation) applied to each master aqueous species (see Section 4).

JFLAGB Array used to read in JFLAG values from the INPUT file.

JGFLAG Status switch array for gas species:
 = 0 means the gas appears in the current model,
 = 2 means the gas is thermodynamically suppressed.

JKFLAG Status switch array for solid solution end-member components:
 = 0 means the component appears in the current model,
 = 2 means the component is thermodynamically suppressed,
 = 4 means the component could not be found among the minerals of fixed composition.

JMFLAG Status switch array for minerals of fixed composition:
 = 0 means the mineral appears in the current model,
 = 2 means the mineral is thermodynamically suppressed.

JSFLAG Status switch array for aqueous species:
 = 0 means the species appears in the current model,
 = 2 means the species is thermodynamically suppressed,
 = 3 means the species does not appear in the model.

JSOL Array whose values define chosen treatments of solid-solution thermodynamics.

JSORT Indices of the aqueous species, sorted in increasing order of concentration.

JSTACK Work array used in sorting aqueous species in increasing order of concentration.

JXFLAG Status switch array for solid solutions:

- = 0 means the mineral appears in the current model,
- = 4 means the mineral has no active end-member components.

JXMOD Flag specifying the type of a species/reaction affected by an alter/suppress option (see KXMOD; read from the INPUT file):

- = 0 aqueous species/reaction,
- = 1 mineral,
- = 2 gas,
- = 3 solid solution.

KCARB Variable denoting the position of HCO_3^- (or CO_3^{2-}) in the set of master iteration variables.

KCT Number of chemical elements present in the aqueous system currently being modeled.

KDIM Dimension of the Jacobian matrix; $\text{KDIM} = \text{KXI}$ in EQ3NR.

KHYDR Variable denoting the position of H^+ in the set of master iteration variables.

KKINDEX Array identifying ($\text{KKINDEX} = 1$) aqueous master species for which starting iteration values must be simultaneously estimated.

KMAX Maximum allowed number of master variables readable by EQ6.

KSB Variable denoting the position of the hypothetical aqueous species $\text{O}_2(\text{g})$ in the set of master iteration variables; $\text{KSB} = \text{KCT} + 1$.

KSQ Number of aqueous species in the set of master iteration variables.

KXISTQ Variable denoting the position of equivalent stoichiometric ionic strength in the set of master iteration variables; $\text{KXISTQ} = \text{KSQ} + 1$.

KXI Variable denoting the position of ionic strength in the set of master iteration variables; $\text{KXI} = \text{KSQ} + 2$.

KXMOD Flag defining the type of alter/suppress option (see Section 4; read from the INPUT file):

- = -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 λ LAMLG log of the activity coefficient of a solid solution end-member component.

MTE Total mass of an element per 1000 g of H₂O (solvent).

M MWTSS Molecular weight of an aqueous species.

NCARB Index of C or the aqueous master species (usually HCO₃⁻ or CO₃²⁻); that is formally associated with carbonate mass balance.

NCHLOR Index of Cl or the master aqueous species (usually Cl⁻) that formally corresponds to Cl⁻ mass balance.

σ τ NCOMP Number of end-member components in a given solid solution.

NCOMPB Number of solid solution end-member mole fraction values for a given solid solution read from the INPUT file.

ϵ τ NCT Total number of chemical elements.

NCTMAX Maximum allowed number of chemical elements.

NEND Array that stores the indices of fixed composition minerals that correspond to end-member components of solid solutions.

N;T Total number of gas species read from the data file.

NGTMAX Maximum allowed number of gas species.

NHYDR Index of H or H⁺.

NMAX Array containing the indices of aqueous species that would make good basis switches with aqueous master species.

NMT Total number of minerals of fixed composition read from the data file.

NMTMAX Maximum allowed number of minerals of fixed composition.

NRSQ Number of reactions associated with auxiliary master species; same as the number of auxiliary aqueous master species.

ϵ τ NRSQ Total number of aqueous ion-pairing, complexing, and redox reactions read into memory.

	NRSTMX	Maximum allowed number of aqueous reactions.
s_B	NSB	Index denoting the hypothetical aqueous species $O_{2(g)}$; NSB = NCT + 1.
	NSODIU	Index of Na or the aqueous master species (usually Na^+) that formally corresponds to Na^+ mass balance.
	NSP	Array containing the indices of the mineral, solid -solution, or gas species that define phase equilibrium (solubility) constraints on the INPUT file.
	NSPEC	Array that contains the indices of aqueous master species for which constraining data were read from the INPUT file.
s_Q	NSQ	Total number of aqueous master species.
	NSQB	Total number of aqueous master species for which constraints are read from the INPUT file.
	NSQMAX	Maximum allowed number of aqueous master species.
	NSQ1	Argument in a stoichiometric reaction coefficient array (CDRS, CDRM, CDRG) denoting the formally associated species (aqueous, mineral, or gas) that is destroyed in a given reaction; NSQ1 = NSQ + 1.
s_T	NST	Total number of aqueous species read from the data file; includes all master species but other species are included only as needed for a given input problem.
	NSTMAX	Maximum allowed number of aqueous species.
	NXMOD	Number of species/reactions affected by alter/suppress options (see KXMOD); read from the INPUT file.
ψ_T	NXT	Total number of solid solution phases read into memory.
	NXTB	Number of solid solution compositions read from the INPUT file.
	NXTMAX	Maximum allowed number of solid solutions.
w	OM	Water constant, 1000 ÷ the molecular weight of H_2O .
$\log w$	OMLG	Log of the water constant.
ψ'	OSCOFF	Osmotic coefficient of water.
pe^-	PE	Log of activity of the hypothetical electron species.
P	PRESS	Pressure, in bars.
	QBASSW	Logical switch indicating whether basis switching has occurred.
R	RCONST	The gas constant, 1.98726 cal/mol-°K.

	RES	Work array used in solving matrix equations.
-a	RHS	Negative copy of the ALPHA array.
o	RHO	Density of aqueous solution, g/mL.
	SCREW2	Under-relaxation parameter that bounds the magnitude of DELMAX.
S	SX	Solid-solution derivative function.
u	STORE	Stoichiometric mass balance factor.
H	STOR1	The H factors defined in Section 8.
L _r	STOR2	The L _r factor defined Section 8.
C _{T5}	TDSPKG	Total dissolved salts, mg/kg.
	TDSPL	Total dissolved salts, mg/L.
	TEMPC	Temperature, °C.
T	TEMPK	Temperature, °K
	TITR	Titration factor of an aqueous species; the number of equivalents of alkalinity per mole of the species.
	TOLBT	Convergence bound on BETAMX.
	TOLDL	Convergence bound on DELMAX.
	TOLSAT	Limit on the absolute value of the affinity of a mineral of fixed composition for the mineral to be listed as "saturated".
	TOLXAT	Limit on the absolute value of the affinity of a solid solution for the phase to be listed as "saturated".
	UACION	Name of the aqueous species (Na ⁺ or Cl ⁻) that defines the equivalent stoichiometric ionic strength (I _E).
	UBASIS	Name of an aqueous species that is to be switched with a master aqueous species.
	UEBAL	Name of the aqueous species chosen for electrical balancing.
	UELEM	Name of a chemical element (chemical symbol).
	UGAS	Name of a gas species (usually, a chemical formula).
	UJTYPE	Alpha character string that describes a JFLAG option.
	ULG1	Array containing the names of the master iteration variables.
	UMEMB	Name of a solid solution end-member component read from the INPUT file.
	USOLB	Name of a solid-solution phase read from the INPUT file.
	USPEC	Name of an aqueous species (usually, a chemical formula).

	USPECB	Name of an aqueous species read from the INPUT file.
	UMIN	Name of a mineral (usually, an alphabetic name; more rarely, a chemical formula).
	UPHASE	Name of a mineral, gas, or solid-solution species that defines a phase equilibrium (solubility) constraint on the INPUT file.
	UREDOR	Name of an auxiliary master species corresponding to an aqueous redox couple used to calculate the default hypothetical equilibrium oxygen fugacity in aqueous solution.
	USOLX	Name of a solid solution (alphabetic name).
	UTITL	Textual title from the INPUT file.
	UTITLD	Title from the thermodynamic data file.
	UXTYPE	Alpha character string that describes a solid-solution thermodynamics treatment.
	VOLG	Volume of a perfect gas at 298.15°K and 1 bar pressure, 22413.6 cm ³ .
W	W	Solid solution excess Gibbs energy parameter.
X _{H₂O}	WFS	Mass fraction of H ₂ O in aqueous solution.
x	XBAR	Mole fraction of a solid-solution end member.
	XBARB	Mole fraction of a solid-solution end member as read from the INPUT file.
	XBARLG	Log of the mole fraction of a solid-solution end member.
	XBARLM	Upper limit on the mole fraction of a solid-solution end member, usually 1.0.
J'	XJTERM	The J' factor used to compute the activity of water as a function of equivalent stoichiometric ionic strength (I _E).
I	XI	True ionic strength.
	XILG	Log of true ionic strength.
I _E	XISTEQ	Equivalent stoichiometric ionic strength.
	XISTLG	Log of equivalent stoichiometric ionic strength.
log K _{Eh}	XLKEH	Log of equilibrium constant of the half-reaction relating the hypothetical electron and O ₂ (g).
log K _g	XLKG	Log of the equilibrium constant of the dissolution reaction of a gas species.

	XLKMOD	Log K alter option parameter (see KXMOD). Read from the INPUT file.
log K_r	XLKS	Log of the equilibrium constant of an aqueous redox or dissociation reaction.
log K_φ	XLKM	Log of the equilibrium constant of a dissolution reaction of a mineral of fixed composition.
log Q/K	XLQK	Saturation index of a mineral.
z	z	Electrical charge of an aqueous species.
\underline{z}	ZLG1	Array of master iteration variables.

APPENDIX B

GLOSSARY OF MAJOR VARIABLES IN EQTL

This glossary covers the major variables in the EQTL data base preprocessor. Most of these variables are duplicates of those occurring in EQ3NR; however, the user is advised that in EQTL:

- CDRS encompasses CDRM and CDRG.
- CESS encompasses minerals and gases besides aqueous species.
- XLKS encompasses XLKM and XLKG.
- USPEC encompasses UMIN and UGAS.
- MWTSS encompasses minerals, gases, and aqueous species.

As in EQ3NR, variable names may be preceded by the corresponding algebraic symbols used in this report. Variables beginning with I, J, K, or N are integer, with Q are logical, and with U contain alphanumeric strings. Variables beginning with any other letters, including L and M, should be type real on machines with 60 to 64 bits per word and type double on hardware with 32 bits per word.

A	ADH	Debye-Huckel A constant.
	APX	Solid-solution thermodynamics parameters.
	ARS	Polynomial coefficients for describing the temperature dependence of log K values.
	ATWT	Atomic weight of a chemical element.
\dot{a}	AZERO	Debye-Huckel ion-size parameter.
B	BDH	Debye-Huckel B constant.
\dot{B}	BDOT	Extended Debye-Huckel \dot{B} constant.
ν_{CO_2}	CCO2	Coefficient for computing $\log \gamma_{\text{CO}_2(\text{aq})}$ as a function of ionic strength (I).
$\nu_{\text{H}_2\text{O}}$	CH2O	Coefficient for computing $\log a_{\text{H}_2\text{O}}$ as a function of equivalent stoichiometric ionic strength (I_E).
b	CDRS	Stoichiometric reaction coefficient for any type of reaction on the data file. CDRS(NS,NRS) is the coefficient for the NS-th aqueous species in the NRS-th reaction. CDRS(NSQ1,NRS) is the coefficient of the species formally

associated with the reaction. If the NS-th species is an auxiliary master species, and NRS is its own formally associated reaction, $CDRS(NS,NRS) = 0$ and $CDRS(NSQ1,NRS)$ is its coefficient.

c	CESS	Stoichiometric mass coefficient of any type of species. $CESS(NC,NS)$ is the number of moles of the NC-th chemical element in one mole of the NS-th species.
σ_T	IKT	Number of end-member components in a given solid solution.
	IKTMAX	Maximum allowed number of end-members in any solid solution.
	JRFLAG	$JRFLAG(I,NRS)$ is a status switch for the log K data in the I-th temperature range (1 = 0-100°C, 2 = 100-300°C) for the NRS-th reaction: = 0 data exists, = 1 no data exists.
	JSOL	Array whose values define chosen treatments of solid-solution thermodynamics.
M	MWTSS	Molecular weight of any kind of species.
σ_{TV}	NCOMP	Number of end-member components in a given solid solution.
c_T	NCT	Number of chemical elements on the data file.
	NCTS	Number of chemical elements in a given species.
	NCTMAX	Maximum allowed number of chemical elements.
	NDRS	Number of species appearing in the reaction associated with a given species.
	NEND	Array that stores the indices of fixed composition minerals corresponding to end-member components of solid solutions.
s_B	NSB	Index denoting the hypothetical aqueous species $O_2(g)$; $NSB = NCT + 1$.
s_Q	NSQ	Total number of aqueous master species on the data file.
	NSQMAX	Maximum allowed number of aqueous master species.
	NSQ1	Argument in a stoichiometric reaction coefficient array (CDRS) denoting the formally associated species (aqueous, mineral, or gas) that is destroyed in a given reaction; $NSQ1 = NSQ + 1$.
	OXFAC	Stoichiometric factors for selected oxides in the chemical elements.
P	PRESS	Pressure, in bars.

	TEMPC	Temperature, °C.
T	TEMPK	Temperature, °K.
τ	TITR	Titration factor of an aqueous species; the number of equivalents of alkalinity per mole of the species.
	TOL	Tolerance parameter on the rms error in polynomial fitting that triggers writing the affected grid data onto the computer terminal screen in order to alert the user to a potentially serious problem with the data.
	UELEM	Name of a chemical element (chemical symbol).
	UOXIDE	Names of selected oxides in the chemical elements.
	USPEC	Name of a species (chemical formula or proper name).
	UTITLD	Title lines of the thermodynamic data file.
	VOL	Volume of a species at 298°K and 1.013 bars pressure.
	XBARLM	Upper limit on the mole fraction of a solid-solution end member, usually 1.0.
log K_{Eh}	XLKEH	Log of equilibrium constant of the half-reaction relating the hypothetical electron and $O_2(g)$.
log K	XLKS	Log of the equilibrium constant of any type of reaction.
z	Z	Electrical charge for an aqueous species.

APPENDIX C

GLOSSARY OF EQ3NR SUBROUTINES

EQ3NR is a moderately large code. "MAIN." refers to the main program. EQ3NR uses several routines from the EQLIB library (see Appendix E).

- MAIN.** Supervises the speciation-solubility calculation. It connects the (INPUT, DATA1, OUTPUT, PICKUP, and RLIST) files, initializes key arrays, and sets default values for important run parameters. It also performs the "idiot-proofing" checks on the input constraints and writes the PICKUP file (interfacing output for input to EQ6) at the end of the run.
- ARRSET** Sets up the matrix structure for Newton-Raphson iteration and estimates starting values for the iteration variables.
- RXNLST** Writes all the aqueous redox and complex dissociation reactions on the file RLIST (a debugging mode activity).
- READX** Reads the INPUT file and writes an "instant echo" of the INPUT data on EQ3NR's OUTPUT file (primarily to aid in debugging format errors on the INPUT file). READX contains full internal documentation for the INPUT file.
- ECHOX** Writes an echo of the INPUT data on the OUTPUT file. Unlike the "instant echo" written by READX, this echo is retained as part of a permanent record of the run. It includes some data file statistics, default values chosen by EQ3NR, and changes in the INPUT constraint options made by the code to resolve inconsistencies.
- SCRIPX** Writes the results of the speciation-solubility calculation on the OUTPUT file.
- SWITCH** Executes a basis switch of a master aqueous species with another aqueous species, which may or may not be another master species.
- PREAC** Writes a display of a reaction on the OUTPUT file.
- GCOEFF** Calculates the activity of water and the activity coefficients of the solute aqueous species.
- ELIM** Effectively removes an auxiliary master species with JFLAG = 30 from the master set. The set of reactions is rewritten so that this species no longer appears in any reaction except its own formally associated reaction. User-controlled basis switching takes place

before ELIM is called, so it is possible to switch a master species in the strict set into the auxiliary set and set its JFLAG switch to 30.

SETUP Converts input concentration data not on the molal scale to that scale.

WTERM Computes the coefficients (W) for the excess Gibbs energy functions of solid solutions from the related coefficients (APX) read from the data file.

LAMDAX Calculates the activity coefficients of end-member components of solid solution minerals.

ECHOLK Writes the species that were loaded from the data file, and the log K values of their associated reactions, on the OUTPUT file.

SXTERM Computes the SX (Λ) solid solution functions that are required to evaluate the saturation states of hypothetical (not specified on the INPUT file) compositions of solid solution minerals.

HPSATX Calculates the saturation states of hypothetical solid solution minerals.

NEWTON Executes the Newton-Raphson iteration to solve the speciation-solubility problem. It may optimize the set of starting values for the iteration variables that were estimated by ARRSET. NEWTON also writes informative crash diagnostics.

MATRIX Writes the Jacobian matrix (J).

FLAGST Sets up the status switch arrays JSFLAG, JMFLAG, JKFLAG, JXFLAG, and JGFLAG.

NCMPX Computes all parameters that derive from the iteration variables and are necessary to write the Jacobian matrix (e.g., all aqueous species concentrations and activities).

GASES Computes the equilibrium fugacities of gas species.

BETAS Computes the residual functions ($\underline{\alpha}$: ALPHA; $\underline{\beta}$: BETA; β_{\max} : BETAMX).

GMCALC Computes the r function for water and the aqueous solute species.

INDATX Reads the data file DATA1, calculates the values of all temperature-dependent parameters, and decodes species data from the INPUT file by matching species names.

STOICH Calculates the stoichiometric factors u from the reaction coefficients b , the JFLAG options, and the basis switches that have been executed.

APPENDIX D

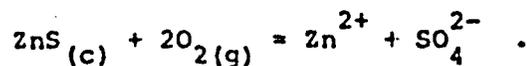
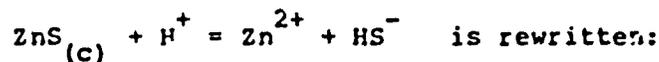
GLOSSARY OF EQTL SUBROUTINES

EQTL, the EQ3/6 data base preprocessor, is a relatively small code. It reads the primary data file DATA0, processes the data, and writes the three secondary data files DATA1, DATA2, and DATA3. "MAIN." refers to the main program. EQTL uses several routines from the EQLIB library (see Appendix E).

- MAIN. Sets up the job.
- PCRAQ Processes data for aqueous species and their associated reactions.
- PCKSG Processes data for minerals and gases and their associated reactions.
- GRIDPY Writes a comparison of an original set of data on a temperature grid with the corresponding values calculated from interpolating polynomial fits. The rms errors are flagged if they exceed a set tolerance.
- INTRPY Fits two interpolating polynomials to a set of data on the temperature grid. The first covers the range 0-100°C, the second, 100-300°C. The 100°C is heavily weighted to minimize the difference in the two fits at this temperature.
- FUNC A function subroutine that evaluates the interpolating polynomials, which have the form:

$$f(x) = a_1 + a_2x + a_3x^2 + a_4x^3 + a_5x^4 .$$

- RXNCHK Checks each reaction for mass and charge balance. If a calculated imbalance is detected, a warning message is printed.
- ELIMY Rewrites the reactions by removing a master species in the auxiliary basis from the master species set. For example, if HS^- is in the auxiliary set and SO_4^{2-} is in the strict set, then the reaction:



- PREACY Writes a display of a reaction on either the EQTL OUTPUT file or on the terminal screen.

APPENDIX E

GLOSSARY OF EQLIB SUBROUTINES

EQLIB is a library of subroutines that is used to support EQ3NR, EQ6, EQTL, and MCRT.

QSORT	Sorts an array of real numbers.
QNEOF	Tests for the end-of-file condition.
STRIPS	Copies a file, and deletes comment lines that are marked by an asterisk in column one.
TEXP	Function 10^x with an argument test to avoid overflow. TEXP returns a pseudo-infinite value if overflow would otherwise occur.
LOG	Function $\log_{10} x$ with an argument test. LOG returns -500. when the argument is zero.
SGECO	Calls SGEFA to perform an L-U decomposition of a real matrix, then estimates the condition of the matrix.
SGEFA	Performs an L-U decomposition of a real matrix.
SGESL	Solves a matrix equation of the form $AX = B$, given right-hand-side vector B and an L-U decomposition of matrix A.
SASUM	Sums the magnitudes of the components of an array.
SAXPY	Computes the sum of $Y + sX$, where Y and X are vectors, and s is a scalar.
SDOT	Computes a vector dot product.
SSCAL	Computes the product sX , where X is a vector, and s is a scalar.
ISAMAX	Finds the index of the largest component of a vector.
ITREF	Iteratively refines the X vector calculated by SGESL.
LSQP	Writes a least-squares polynomial fit to an array of (x,y) points.
SCAL	Scales the x arguments for LSQP.
RSCAL	Unscaled the polynomial coefficients for LSQP after a fit has been made with scaled arguments.
POLX	Finds the coefficients of a polynomial that exactly fits an array of (x,y) points.

APPENDIX F

RUNNING EQ3NR AND RELATED CODES AT LLNL

The EQ3/6 software package is a set of geochemical modeling codes and supporting data files. The codes include the EQTL data base preprocessor, the EQ3 speciation-solubility modeling code, and the EQ6 reaction path/kinetic code for predicting the consequences of reactions in aqueous geochemical systems (Wolery, 1978, 1979, 1983a). The MCRT package (Wolery, 1983b) consists of various input data files and one code, MCRT, whose main purpose is to process thermodynamic data into a form suitable for inclusion in the EQ3/6 thermodynamic data base. MCRT also performs temperature extrapolations of 25°C data.

The EQ3/6 (in XPORT directory .977823:EQ3/6:3230:7600) and MCRT (in .977823:MCRT:3230:7600) software packages are available in 7600 format at the LLNL. The "3230" denotes the release number (see Appendix H). Cray versions (in .977823:EQ3/6:3230:CRAY and .977823:MCRT:3230:CRAY) are also available. Sample inputs and outputs are included in the package directories along with source codes, executable files, and data files.

Cray files differ in format from 7600 files. To convert a 7600 file, say DATA0, to Cray format, execute:

```
TRANS I=(DATA0,7600),O=(DATA0,CRAY) / t v
```

To convert a Cray file to 7600 format, execute:

```
TRANS I=(DATA0,CRAY),O=(DATA0,7600) / t v
```

Only files consisting of text (i.e., source codes data files, inputs, and outputs) are translatable. Binaries, executable files, libraries of relocatable code, etc., are not translatable in this fashion.

The program source codes are almost identical for the 7600 and the Cray. There are, however, some minor differences, and in any case, one must use different sets of compilers, loaders, and supporting system libraries. Executable files for the 7600 are generated by FTN, which both compiles and loads. CFT (the standard Cray compiler) and LDR (a loader) are used to make

executable files that will run on the Cray. The CFT compiler neither requires nor likes the LEVEL 2 specifications needed to run most of the codes on the 7600, and all lines bearing such specifications must be deleted or commented out. The other differences pertain to opening/closing files and testing for the end-of-file condition. In the 7600 source code, corresponding Cray lines are written just below lines for the 7600. These Cray lines are commented out by "CCRAY" beginning in column one.

To make a new executable file for the 7600, say for the EQ3NR code, (designated here as the file EQ3NR50) the "50" denotes a stage number, (see Appendix H). Use FTN to compile and load:

```
FTN (I=EQ3NR50,NALL,OPT=1,R=2,GLIB=EQLIB01B,PM,SET) / t v
```

The required input files are

- o EQ3NR50 EQ3NR source code
- o EQLIB01B binary version of the EQLIB library

To create the binary version of the EQLIB library on the 7600, simply compile the source code (EQLIB01) via FTN:

```
FTN (I=EQLIB01,B=EQLIB01B,OPT=1,R=2) / t v
```

The output files are

- o EQ3NR50B binary file
- o EQ3NR50L compilation listing
- o EQ3NR50M load map
- o EQ3NR50X executable file

The executable file is the only file listed above that is required to run the code. Executable files are included in the .977823 directories.

To make a new executable file on the Cray, first compile with CFT, again using the example EQ3NR50:

```
CFT I=EQ3NR50,B=EQ3NR50B,L=EQ3NR50L / t v
```

Then input EQ3NR50B and EQLIB01Q* to the loader LDR:

```
LDR I=EQ3NR50B,X=EQ3NR50X,ML=EQ3NR50M,LIB=EQLIB01Q,LIB=FORLIB / t v
```

To execute a code, you need the corresponding executable file and the requisite data and input files. To execute MCRT, where MCRT01X is the controllee file, type

```
MCRT01X / t v
```

You must provide the five data files REAC, MDELEM, MDAQS0, MDAQS, and MDSOL. The file named REAC plays the role of defining the problem input. There is not a file named INPUT. The output files are OUTPUT and DFILE.

To execute EQ3NR, provide an input file, IRWTC, and the data file DATA1 and type

```
EQ3NR50X INPUT=IRWTC / t v
```

The output files are OUTPUT and PICKUP.

IRWTC is specified at the input file on the execute line. If one wants, for instance, to use the output file named ORWTC and the pickup file named PRWTC, type

```
EQ3NR50X INPUT=IRWTC,OUTPUT=ORWTC,PICKUP=PRWTC / t v
```

To execute EQ6, provide an input file, I5RCTS, and the data files DATA2 and DATA3, and type

```
EQ6U01X INPUT=I5RCTS / t v
```

The output files are OUTPUT, PICKUP, and a set of summary output tables called TABA, TABB, TABC, etc.

* The binary file EQLIB01B can not be directly used as a library on the Cray. To create EQLIB01Q, first compile the source code (EQLIB01) with CFT:

```
CFT I=EQLIB01,B=EQLIB01B / t v
```

Then input EQLIB01B to the Cray library-making routine BUILD:

```
BUILD NL=EQLIB01Q,B=EQLIB01B / t v
```

To execute EQTL, provide DATA0 and type

EQTL01X / t v

The output consists of DATA1, DATA2, DATA3, and a file called SLIST, which lists the species on the data file. Additions, deletions, and revisions of these data files first be made in DATA0, using a text editor. For instance, one could merge the DFILE output of an MCRT run into DATA0. When this is done, it is possible to run EQTL to make new versions of DATA1, DATA2, DATA3, and SLIST. We strongly recommend that users not attempt to make direct modifications to the contents of DATA1, DATA2, and DATA3.

APPENDIX G

METHODS USED TO VERIFY THE OPERATION OF EQ3NR

Two principal methods were used to verify proper calculations by EQ3NR. First, EQ3NR.3175BU37 has been tested against EQ3.3015U19, a version of the old EQ3 code which uses a different numerical algorithm. This was done using three test cases (sea water, major constituents only-see the example in Section 5.2; sea water with trace elements; and river water) based on the code comparison study of Nordstrom et al. (1979b). Subsequent versions of EQ3NR were periodically verified in a version-to-version manner with these and other test cases.

The second approach was to check for consistency in the input and output of EQ3NR runs. EQ3NR is a code with many options; what is an input in one run may be an output in another. For example, Eh may be input and oxygen fugacity calculated. The run may be repeated with the oxygen fugacity value that was obtained as an input. The original Eh value should be reproduced. Some input constraints are automatically double-checked. For example, if a master aqueous species is constrained to satisfy a given mineral solubility equilibrium (see example in Section 5.3), the saturation index for that mineral should be zero in the mineral saturation listing on the OUTPUT file.

It has not been possible to check every possible combination of input constraint options during the development of this code. We recommend that users periodically check the input/output of their runs for consistency, especially when trying out a new combination of input options. Problems should be reported to Thomas J. Wolery at Lawrence Livermore National Laboratory.

APPENDIX H

IDENTIFICATION OF CODE AND DATA BASE VERSIONS

The activities of revising, extending, and maintaining computer programs and their data bases require a system for identifying the versions that are produced on both long-term and day-to-day time scales. This appendix documents the system that has been devised for use in developing the EQ3/6 and MCRT aqueous geochemical modeling code packages and their package elements.

Package elements, as defined here, are codes or data files. Sample inputs and outputs that are included in software package versions that are externally released (i.e., distributed outside LLNL), are not treated by the identification scheme used for codes and data files.

The complete identification of a code or data file consists of: (1) an alphanumeric name, (2) an external release number of four digits, and (3) a two digit developmental stage number. In short, these will be referred to as the "name," "release," and "stage." In simple terms, the "release" number identifies a product produced on time scales of six months to a year and the "stage" number identifies a product on a day-to-day basis.

The external release number identifies software packages distributed outside the LLNL. New versions of the EQ3/6 and MCRT packages are periodically released. These are made available to the National Energy Software Center, Argonne National Laboratory (NESC), 9700 South Cass Ave., Argonne, IL 60439 (Telephone 312-972-7250), which will process requests for these materials. The material can also be requested from the LLNL.

The version numbers increase sequentially and are primarily chosen so that they will not be easily confused in telephone conversations. Otherwise, they are chosen arbitrarily. An external release of the EQ3/6 package is identified by the package name and the version number, separated by a period. For example, the December 1981 release of EQ3/6 was EQ3/6.3175. Similarly, the concurrent MCRT release was MCRT.3175.

To date, there have been five external releases of EQ3/6 and two of MCRT (minor updates are now designated by suffixing "B", "C", etc. to the release number), and the the following versions now exist.

<u>Code Package</u>	<u>Version No.</u>	<u>Date</u>
EQ3/6	2020	Feb. 1979
	2055	Nov. 1979
	3015	Dec. 1980
		Revised April 1981
	3175	Dec. 1981
	3175B	Sept. 1982
	3230	Aug. 1983
MCRT	3175	Dec. 1981
	3175B	Sept. 1982
	3230	Aug. 1983

To date, releases of MCRT have been concurrent with releases of EQ3/6; however, this is not likely to be true of future MCRT releases.

The full name of a code or data file is its name, a period, the release number, a letter "U", and the stage number. For EQ6 this is illustrated by: EQ6.3175U50. This name is always given on the first line of a code or data file, and includes the date. A short name eliminates the release number, taking it to be understood, e.g., EQ6U50. The letter U in the release number is retained in the short name only if the code or data file name ends in a number. For the MCRT code, an element of the MCRT package, the full name, MCRT.3175U31, shortens to MCRT31. Short names are used to identify files on the LLNL computer system, including file storage. In the file storage, the release number is an explicit part of the directory chain name.

Stage names identify day-to-day versions created during code or data base revision, development, etc. They are primarily meaningful only within the LLNL. Substage names can be added to the short versions during daily development (such as EQ6U50-1, EQ6U50-2, etc.) to minimize the effects of a system failure or an extremely bad editing error. External release of a code package version usually terminates further use of the associated release number. Exceptions to this rule generally are made only to correct subsequently discovered errors. Otherwise, a higher version number is selected (e.g., 3230 succeeds 3175) and the stage numbering returns to 01.

Copies of day-to-day versions, identified by stage numbers, are usually not saved for more than a few weeks after being superseded. In the case of source codes, revisions can extend for several stage-level versions before any attempt is made to test the code.

APPENDIX I

FORTRAN CONVENTIONS, CODE PORTABILITY, FIELD LENGTHS, AND REDIMENSIONING

The ease of portability of a FORTRAN code can be greatly improved by specific restrictions and conventions. This section lists those that have been adopted in developing the codes in the EQ3/6 and MCRT software packages. These conventions were adopted in light of the experience obtained while transferring the codes to Cray, UNIVAC, IBM, and VAX computer systems.

1. All common blocks appear in the main program.
2. Variable and subroutine names are restricted to six characters.
3. The following conventions apply to the first letter of a variable name (exceptions not permitted):
 - (a) I, J, and K: INTEGER
 - (b) L and M: REAL on 60 and 64 bit machines, REAL*8 on 32 bit computers.
 - (c) Q: LOGICAL.
 - (d) U: All character string variables, typed INTEGER on 60 and 64 bit machines, REAL*8 on 32 bit machines (REAL may suffice on some UNIVAC computers).
 - (e) All others: REAL on 60 and 64 bit machines, REAL*8 on 32 bit computers.
4. One statement per line.
5. All labels are numeric; none are alphabetic or alphanumeric.
6. No IF-THEN-ELSE constructions.
7. No arithmetic IF statements.
8. No constants in subroutine argument lists. This prevents specific types of conflicts for converting to double precision (REAL*8); i.e.,

```
VAR1=1.0  
VAR2=1.E-7  
CALL SUBR(VAR1,VAR2) ,
```

not

```
CALL SUBR(1.0,1.E-7) .
```

In the first example, VAR1 and VAR2 are REAL*8, the assigned values will be converted to REAL*8, and the subroutine call will be correct. In the second case, an execution error will result because of a REAL-REAL*8 mismatch.

9. Character string variables are initialized only by either reading from a file or by DATA statements. Use:

```
DATA UVAR/"ENDIT. "/
```

```
.  
. .  
. . .
```

```
IF (UDUM.NE.UVAR) GO TO 235 ,
```

not

```
IF (UDUM.NE."ENDIT. ") GO TO 235 .
```

10. No PRINT or "simple" READ statements. Use:

```
WRITE (5,120) A,B,C  
READ (60,125) D,E,F ,
```

not

```
PRINT 120, A,B,C  
READ 125, D,E,F .
```

EQ3NR.3230U48 is dimensioned to handle a maximum of:

```
NCTMAX: 40 chemical elements.  
NSQMAX: 80 aqueous master species (strict plus auxiliary basis  
species).  
NSTMAX: 300 total aqueous species.  
NRSTMX: 259 aqueous reactions (aqueous redox reactions and ion-pair  
and aqueous complex dissociation reactions;  
NRSTMX = NSTMAX-NCTMAX-1).  
NMTMAX: 275 minerals of fixed composition.  
NGTMAX: 15 gases.  
NXTMAX: 10 solid solutions.  
IKTMAX: 6 end-member components per solid solution.
```

NXMDMX: 20 species affected by the alter/suppress option.
KMAX: 82 iteration master species (KMAX = NSQMAX+2).

The required total field length at these dimensions is about 331,000B words. Each word is equal to 8 bytes (64 bits) on the Cray, and roughly 8 bytes (60 bits) on the CDC 7600. On the 7600, the SCM (small core memory) field length is about 152,000B words.

EQTL.3230U01 is dimensioned to handle a maximum of:

NCTMAX: 50 chemical elements.
NSQMAX: 75 aqueous master species (strict plus auxiliary basis species).
IKTMAX: 6 end-member components per solid solution.

EQTL is indifferent to the total number of aqueous species, minerals, gases, and solid solutions on the data file. It never has them all in memory at the same time. The required total field length at these dimensions is about 75,000B words. Each word is equal to 8 bytes (64 bits) on the Cray, and approximately 8 bytes (60 bits) on the CDC 7600. On the 7600, the total field length is essentially all SCM.

To aid in redimensioning any of the EQ3/6 codes, as well as MCRT, the source codes include commented out copies of symbolic common and dimension statements. Each main program includes a copy of all common blocks and the corresponding set of symbolic common blocks is located just above them. Symbolic dimension statements are located just above the corresponding dimension statements in the main program and its subroutines. For example, the commented-out symbolic common block

```
C   COMMON CDRS(NSQMAX+1,NRSTMX),CESS(NCTMAX,NSTMX),  
C   $ CDRM(NSQMAX+1,NMTMAX),CDRS(NSQMAX+1,NGTMAX)
```

is given in the main program of EQ3NR.3230U48, to indicate the proper dimensions corresponding to

```
COMMON CDRS(81,259),CESS(40,300),CDRM(81,275),CDRG(81,15) .
```

Users are strongly advised to use global pattern replacement techniques as the exclusive means of code redimensioning, because the slightest mismatch

in array dimensions is usually disastrous. A highly recommended technique is to double-check the results of redimensioning by using text editor features that permit the display of changed lines in a one-after-the-other format. At LLNL, the TRIX AC commands "TP" and "DOP" can be very effectively used for this purpose.